Original Paper

Electric melting of glass: Influence of cathodic currents on the formation of protective layers on molybdenum electrodes

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Dedicated to Prof. Dr. Helmut A. Schaeffer on the occasion of his 60th birthday

The influence of cathodic currents on the corrosion of molybdenum electrodes during electrical melting of glass was studied with the aid of laboratory experiments. It is shown that cathodic currents lead to the formation of molybdenum silicide layers on the electrode. Best results were obtained using a DC current density of $3.75 \, \text{mA/cm}^2$ at a heating current density of $1 \, \text{A/cm}^2$. Higher DC current densities resulted in molybdenum silicide layers, which dissolve in the melt as silicide particles. Simultaneous to the molybdenum silicide layers, at the counter electrodes MoO_2 layers are formed, which also dissolve as particles in the melt.

Elektrisches Glasschmelzen: Einfluß von kathodischen Strömen auf die Bildung von Schutzschichten auf Molybdän-elektroden

Der Einfluß kathodischer Schutzströme auf die Korrosion von Molybdänelektroden bei der Elektroschmelze von Glas wurde mit Hilfe von Laborexperimenten untersucht. Es zeigte sich, daß kathodische Ströme zur Ausbildung einer Molybdänsilicidschicht auf der Elektrode führen. Hierbei erwiesen sich Gleichstromdichten von $3{,}75 \, \text{mA/cm}^2$ bei einer Heizstromdichte von $1 \, \text{A/cm}^2$ als optimal. Höhere Gleichstromdichten führten zu Molybdänsilicidschichten, die sich als Silicidpartikel wieder in der Schmelze auflösten. Gleichzeitig mit den Molybdänsilicidschichten bilden sich an der Gegenelektrode MoO_2-Schichten, die sich ebenfalls als Partikel in der Schmelze auflösen.

1. Introduction

Electric melting of glass is a technique of increasing industrial importance [1 and 2]. It is economically advantageous for relatively small glass furnaces and a production of less than $40 \, \text{t/d}$. Another advantage is that the evaporation of hazardous compounds such as NO_x, SO_2 or lead-containing ones is minimized without further technical expenditure. This is caused by the cold top, in which evaporated compounds are recovered. Today, the electrode material predominantly used is metallic molybdenum [1 to 13]. It is mechanically stable even at temperatures of $1600 \, °\text{C}$, and possesses a high extent of chemical stability against the corrosive effect of some glass melts, such as borosilicate melts. In other glass melts, such as lead glass melts or melts containing relatively large quantities of antimony, arsenic or nickel, the corrosion rates are fairly high (see e.g. [3 to 6]). Molybdenum is a less noble metal and can be oxidized by many compounds. According to the electrochemical series of elements [7] which, however, slightly depends on the glass composition, many polyvalent cations can be reduced by molybdenum. Among these, Sb^{5+}, As^{5+}, Fe^{3+}, Ce^{4+}, Sn^{4+} and Mn^{3+} should be mentioned. Some of them, such as antimony, arsenic and tin, as well as other elements, such as Ni^{2+} or Co^{2+}, which usually are not seen as polyvalent, are reduced to the metallic state.

Hereby, alloys may be formed, which further enhances the corrosion process. These redox processes lead to a loss of the electrode material and also to a contamination of the melt with molybdenum compounds [2 to 8]. Therefore, techniques have been developed to minimize the corrosion of the molybdenum. Altogether, three techniques are worth mentioning: the anodic [5], the cathodic [2] and the low-frequency passivation [9]. During the anodic passivation, a DC potential is superimposed on the heating currents in such a manner, that the molybdenum electrodes are polarized anodically. By analogy, during cathodic passivation, molybdenum is polarized cathodically versus a counter electrode additionally inserted into the glass melt. In both cases, it is assumed that protective layers are formed which decrease the corrosion rate. In the past few years, mainly two types of investigations concerning molybdenum corrosion have been carried out: first, fundamental laboratory experiments, some of them using electrochemical methods to clarify the mechanisms of the corrosion process [5 to 7 and 10 to 13] and secondly, studies carried out in industrial glass tanks [2, 3 and 9]. The first are on a time scale of some minutes to a few hours. By contrast, in industrial tanks electrochemical methods can hardly be carried out: here the main method is to study the molybdenum content of the final glass and the corrosion of electrodes drawn from the furnace. Since the latter requires some months, the data obtained, e.g. concerning the influence of parameters, such as the DC

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current density on the corrosion rate, are not as numerous as desired. Therefore, laboratory experiments which are closer to the technical system than those described above are helpful and possibly enable one to close the gap between the fundamental and the industrial studies. Besides, longer times than in previous laboratory studies are required especially to study the formation of protective layers and the influence of experimental parameters thereon.

2. Experimental procedure

Figure 1 shows the equipment used for the laboratory experiments. Inside of a furnace with SiC heating elements, a container fabricated from refractory based on zirconium silicate (ZAC 1681) was located. The inside of the container was 11.5 cm in length, 7 cm in width and 8 cm in height. It contained approximately 800 g of the glass melt. At the front, an overflow made from a platinum plate was located. Overflow melt was collected in a platinum crucible. The glass melt was prepared by inserting cullet or batch into the container, preheated to 1450 °C. After the melt was soaked for 1 to 3 h, molybdenum electrodes were inserted. Here, a silica tube flushed with argon was inserted in the furnace from the top and slightly dipped into the melt. Then the molybdenum electrode was introduced into the melt. This procedure was repeated twice, until all three electrodes required were inserted. The electrodes consisted of molybdenum rods (diameter: 5 mm, length: 7 cm) contacted with a tungsten wire (diameter: 1 mm) at the top (figure 2). The molybdenum electrodes were embedded in an alumina tube (inner diameter: 5, outer diameter: 8 mm) in such a manner that 5 cm in length were not covered by alumina. To avoid alumina corrosion, additionally a sleeve prepared from refractory (outer diameter: 20, inner diameter: 8 mm) was slipped on the lower part of the alumina tube. The electrodes were located in such a way that the refractory tube dipped into the melt by around 1 cm. Between the two rear electrodes, the alternating voltage was supplied. The resulting current densities were adjusted to certain values in the range of 0.5 to 2 A/cm^2 of the electrode surface. In the most experiments, a value of 1 A/cm^2 was used. Between these two "heating" electrodes and the third electrode, a direct potential was superimposed. The resulting current densities (related to the area of the working electrodes) were in the range of 0 to 20 mA/cm^2 at the temperature of 1450 °C used.

In a series of experiments, the potentials were varied and the resulting currents recorded, or the DC potential was kept constant and the current measured as a function of time. During the most experiments, however, both DC and AC currents were kept constant and the corrosion behavior was studied by examining the layers formed at the electrode surface. For this purpose, the electrodes were drawn from the melt, then embedded in resin and cross cut. Here, special care has to be taken
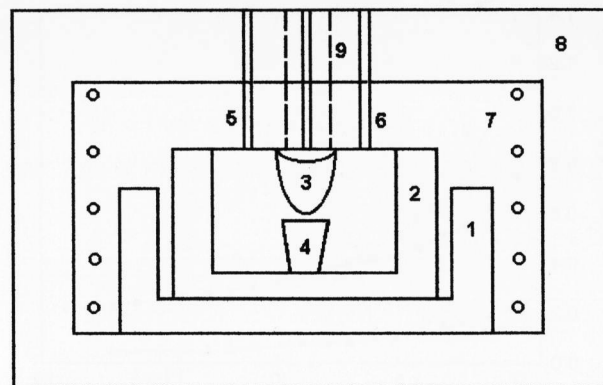

Figure 1. Schematic drawing of the furnace used. 1: protective tub, 2: container made from refractory, 3: platinum overflow, 4: platinum crucible for the overflowing glass, 5: heating electrodes, 6: counter electrode, 7: SiC heating elements; 8: furnace, 9: inlet for cullet or batch.
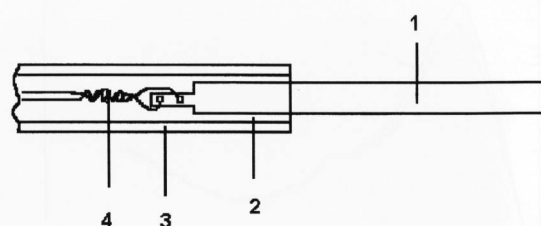

Figure 2. Schematic drawing of the electrodes used. 1: molybdenum rod, 2: alumina tube, 3: refractory sleeve, 4: tungsten wire.

Table 1. Chemical composition of the glass melt

	content in wt%
SiO$_2$	72.11
Na$_2$O	13.27
CaO	6.34
MgO	3.47
Al$_2$O$_3$	1.12
B$_2$O$_3$	1.83
K$_2$O	1.7
Sb$_2$O$_3$	0.15

that the adjacent glass is not crumbled away. Then the cut is ground and polished and subsequently 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)).

For all experiments, a soda−lime−silica glass melt was used, whose composition is given in table 1.

3. Results and discussion

The AC potential between the heating electrodes was increased with time and the AC current was measured.

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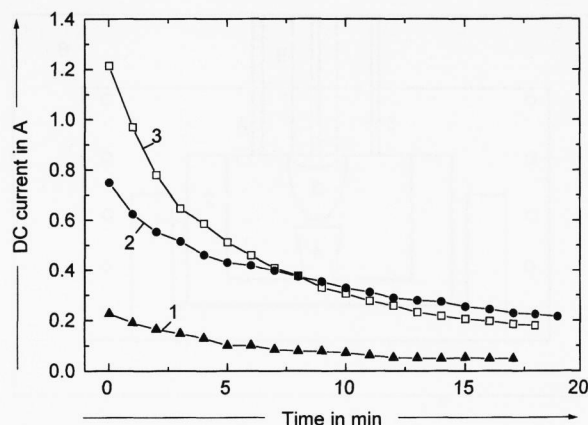
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Figure 3. Direct current as a function of time (AC current density: 1 A/cm^2). DC potentials applied: curve 1: 1 V, curve 2: 2.4 V, curve 3: 4 V.
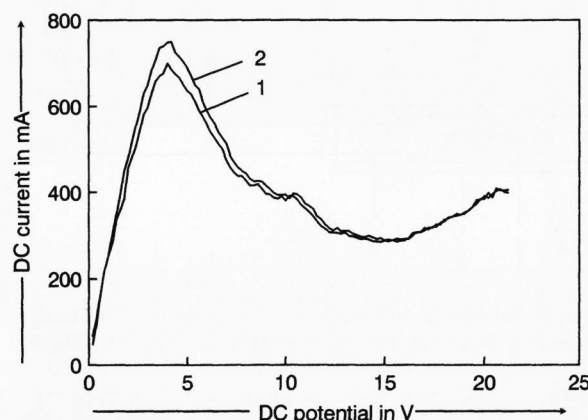

Figure 4. Direct current as a function of the DC potential (AC current density: 1 A/cm^2). Curve 1: current after 2 min, curve 2: initial values.
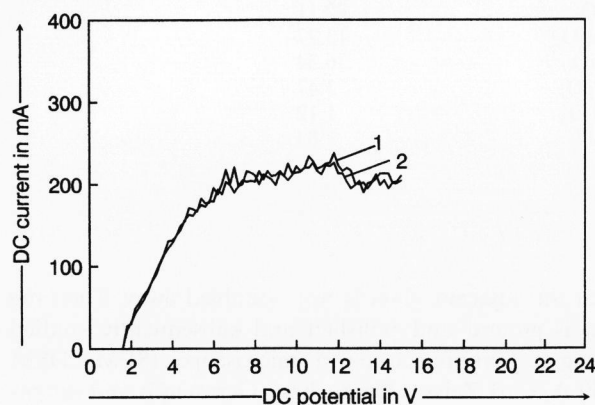

Figure 5. Direct current as a function of the DC potential (AC current density: 1 A/cm^2). Before the measurement, a DC current density of 5 mA/cm^2 was applied. Curve 1: current after 2 min, curve 2: initial values.

The values obtained did not depend on the scan rate and increased linearly with the potential. To obtain a current density of 1 A/cm^2, an AC potential of 20.3 V was neces-

sary. The strict proportionality between the AC current and the AC potential is evidence of a purely ohmic behavior. Any influence of electrochemical reactions or the electrochemical double layer cannot be seen. By contrast, the dependence of the DC current on the DC potential is not at all ohmic. This is illustrated by figure 3. Here, an AC current density of 1 A/cm^2 was attached between the two heating electrodes and a certain DC potential was superimposed between these two electrodes on the one hand and the counter electrode on the other hand. The DC potentials were switched on and the DC current recorded as a function of time. At a potential of 1 V (curve 1), at the beginning, a current of around 210 mA was observed. The current decreases with time, after 5 min, a current of around 110 mA and after 15 min of around 50 mA was observed. Curve 2 was recorded using a DC potential of 2.4 V. Here, the current decreases in approximately the same manner. Within 15 min, it decreases from an initial value of 780 to 250 mA, i.e. by more than the factor of 3. Curve 3 is attributed to a DC potential of 4 V. At the beginning, this results in a DC current of 1.2 A. By comparison to curves 1 and 2, the current decreases much faster and at 8 min, the current is equal to that observed at a potential of 2.4 V. After that, the observed currents are even lower than those of curve 2 and after 15 min, a current of around 200 mA is reached. Figure 4 shows a current-potential curve. By analogy to figure 3, also here, an AC current density of 1 A/cm^2 was superimposed. The curve was recorded after soaking the electrodes in the glass melt for 6 d. The heating electrodes acted as cathodes and the counter electrode as anode. The potentials were increased in steps of 200 mV. The current was measured immediately after increasing the potentials and again after 2 min; then the potential was increased again. Within these 2 min, the current decreases slightly. The upper curve in figure 4 is attributed to the initial values, while the lower curve is related to the values after 2 min. First, a nearly linear increase in current was observed, then the slope decreases and at around 4 V, a maximum was reached. Then the current decreases again, reaches a minimum at 15 V and finally a slight increase was observed. The current maximum and minimum are attributed to currents of 750 and 290 mA, respectively. In figure 5, another current-potential curve is shown which was recorded using a similar procedure as in figure 4. The pretreatment of the electrodes was different, however. Previous to the measurement, a cathodic DC current density of 5 mA/cm^2 was attached to the heating electrodes. By contrast to figure 4, a maximum in the current-potential curve is not observed. The current increases from 0 at 1.5 V up to a value of around 200 mA which is reached at 7 V. Then the current remains constant.
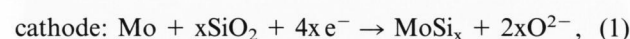
The maximum in the current-potential curve shown in figure 4 is due to a passivation of the electrodes. An electrochemical reaction takes place at the electrodes and the product of this reaction hinders the further reaction. In the case of an electrochemical reaction with-

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out any kinetic hindrance, the current should increase linearly or exponentially for reactions controlled by the ohmic resistance of the electron transfer reaction, respectively. The occurrence of passivation effects can also be observed in figure 3. First, the current decreases with time, due to an increasing quantity of reaction products which hinders further current flow. Secondly, the decrease depends on the potential. At the end of the measurement, the current at a potential of 4 V is even lower than at 2.4 V. Obviously, the barrier formed by the larger quantity of reaction products at 4 V is higher. The nonoccurrence of a maximum in the current-potential curve shown in figure 5 is caused by the current density of 5 mA/cm^2 supplied before the measurement was carried out. This current flow already led to the formation of the passivation layer and hence, it need not to be formed during the measurement. Current-potential curves of molybdenum electrodes in soda−lime−silica glass melts have previously been reported in [5 and 6]. They were recorded using a three-electrode equipment. The curves shown there for anodic potentials were fairly similar to those shown in figure 4. While at potentials lower than −700 mV, a steep increase of the cathodic currents with decreasing potential was reported and no hint at a kinetic hindrance was visible at lower potentials. In figures 3 to 5, however, curves are shown recorded between molybdenum electrodes. That means, while the heating electrodes are polarized negatively, the counter electrode possesses a positive potential. Since potentials more negative than −700 mV lead to increasing currents, the current flow shown in figures 3 to 5 is not controlled by the cathodic processes, i.e., the behavior of the negatively polarized heating electrodes. It is controlled by reaction products formed at the anodes, i.e. the counter electrode.
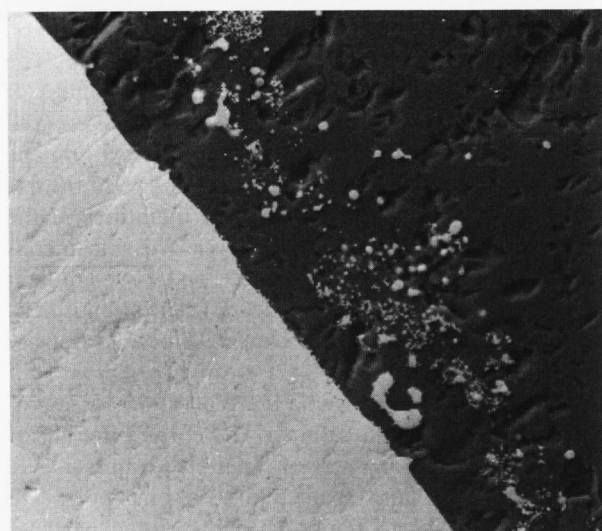
Figures 6a to f show SEM micrographs of heating electrodes after a corrosion time of 50 h. An AC current of 1 A/cm^2 and different DC current densities in the range of 0 to 20 mA/cm^2 were supplied. Figure 6a shows a micrograph attributed to a DC current density of 0 mA/cm^2. The light region represents the metallic molybdenum and the dark region the adherent glass. In the vicinity of the electrode, a layer possessing a thickness of around 50 μm occurs, in which numerous inclusions of light appearance are seen. As proved by EDX, these particles consist of metallic molybdenum; other elements could not be detected. WDX spectra gave evidence that oxygen does not occur in these particles. Obviously, metallic molybdenum is dissolved from the electrode and spread into the glass melt. Figure 6b shows a micrograph of an electrode after supplying a DC current density of 1.25 mA/cm^2. Here, a layer whose appearance is slightly darker than the electrode is seen. This layer has a thickness of around 20 μm, is porous and also here some light particles can be seen in the glassy phase. As proved by EDX, this layer consists of molybdenum silicide. Also at higher cathodic potentials, such layers are observed. An increase of the current density to 2.5 mA/cm^2 led to an increase of the layer thick-

ness to around 35 μm. Figure 6c shows a micrograph attributed to a DC current density of 3.75 mA/cm^2. The layer observed possesses a nearly constant thickness of around 50 μm. By contrast to figure 6b, light-colored particles cannot be seen in the adherent glass. EDX line scans of molybdenum, silicon and oxygen proved the following: oxygen occurs solely in trace quantities in the molybdenum electrode and in the layer. The silicon concentration in the layer is constant, i.e. no silicon gradient is observed. Also the molybdenum concentration is constant over the whole layer thickness. A current density of 5 mA/cm^2 resulted also in a strongly adherent, but slightly thicker MoSi$_x$ layer. Figure 6d shows a micrograph after supplying a cathodic DC current density of 6.25 mA/cm^2. The thickness of the molybdenum silicide layer is now around 100 μm and still some pores are visible. By analogy to figure 6c, light-colored particles are not observed. The micrograph shown in figure 6e is attributed to a DC current density of 10 mA/cm^2. The layer thickness is around 20 to 30 μm and hence notably thinner than at potentials of 3.75 and 6.25 mV. Numerous particles consisting of molybdenum silicide and possessing sizes of up to 10 μm in length can be seen in the glass. Obviously, the silicide layer formed dissolves again in the glass melt. At further increasing cathodic current densities, this dissolution process is further enhanced. At a cathodic current density of 20 mA/cm^2 (see figure 6f), the layer thickness increases to around 100 μm, i.e. approximately the same value as at 6.25 mA/cm^2, but the quantity of molybdenum silicide particles in the glass increases by comparison with figure 6e. It can be summarized: without the superposition of a cathodic potential, particles of metallic molybdenum are dissolved in the glass melt. If a cathodic current is applied, molybdenum silicide layers are formed. With increasing current, also the layer thickness increases up to a current density of 6.25 mA/cm^2, which is attributed to a thickness of 100 μm. Further increasing potentials led to a dissolution of the layer and particles of molybdenum silicide dissolve into the glass melt.

Figure 7 shows a micrograph of a counter electrode attributed to a cathodic current density of 5 mA/cm^2. Since two cathodically polarized heating electrodes and only one counter electrode were used, the anodic current density supplied to this electrode was 10 mA/cm^2. Also here an adherent layer can be observed. By contrast to figures 6b to f, this layer consists of molybdenum oxide, MoO$_2$, as proved by EDX and XRD. Here, some oxidic particles can be seen in the glass, which gives evidence that also this layer dissolves in the melt. The electrochemical reactions occurring at the cathode and the anode are as follows:
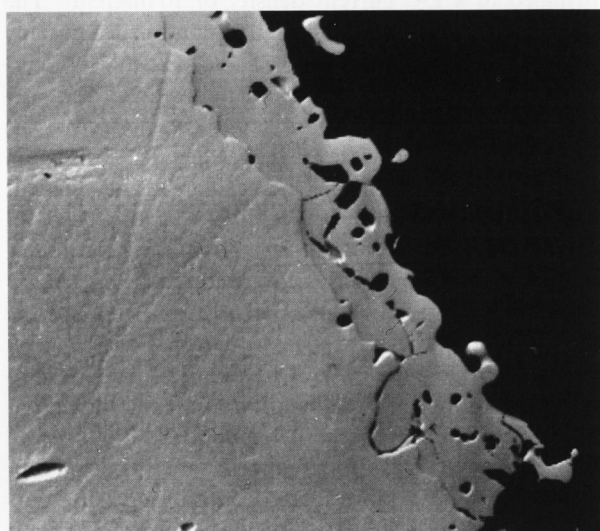
$$\text{cathode: } Mo + xSiO_2 + 4x\,e^- \rightarrow MoSi_x + 2xO^{2-}, \quad (1)$$

$$\text{anode: } \quad Mo + 2O^{2-} \rightarrow MoO_2 + 4e^-. \quad (2)$$

In previous studies, carried out with a three-electrode equipment [5], also the formation of an MoSi$_x$ layer at

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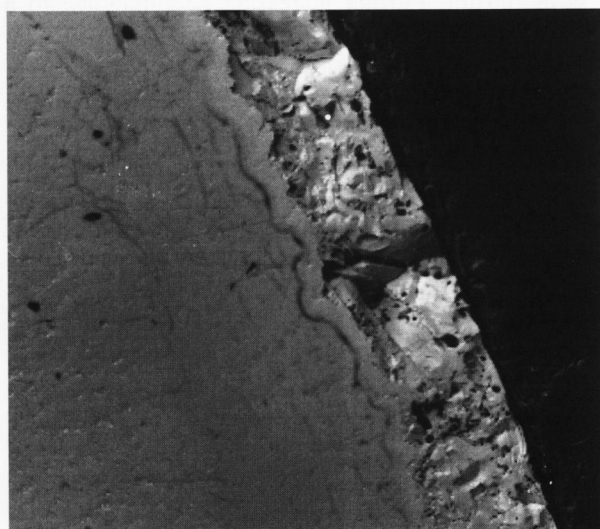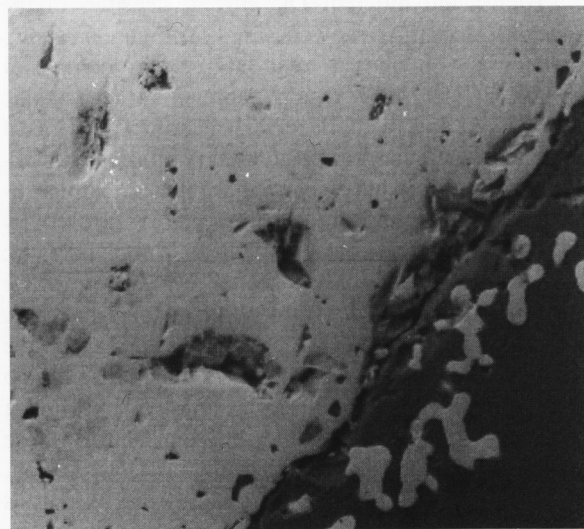
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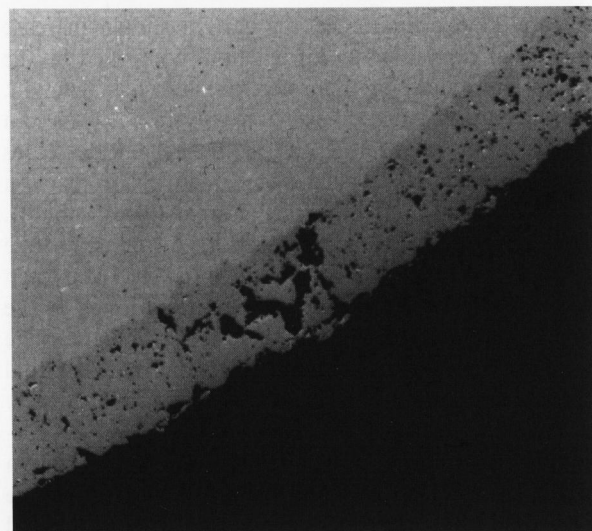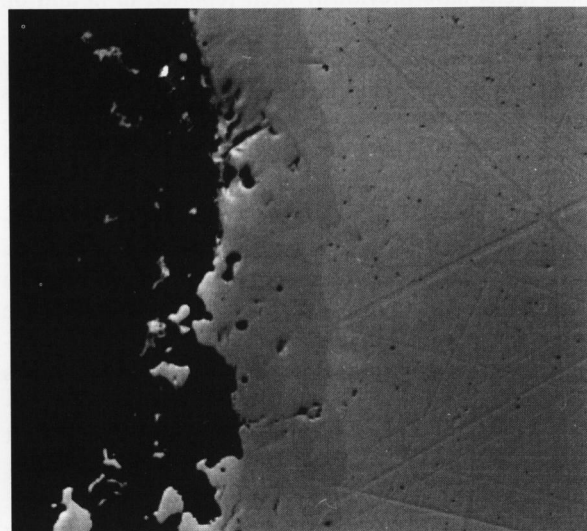
Figures 6a to f. SEM micrographs of heating electrodes after 50 h corrosion time (heating current density: 1 A/cm^2) at different superimposed cathodic DC current densities. a) 0 mA/cm^2, b) 1.25 mA/cm^2, c) 3.75 mA/cm^2, d) 6.25 mA/cm^2, e) 10 mA/cm^2, f) 20 mA/cm^2.

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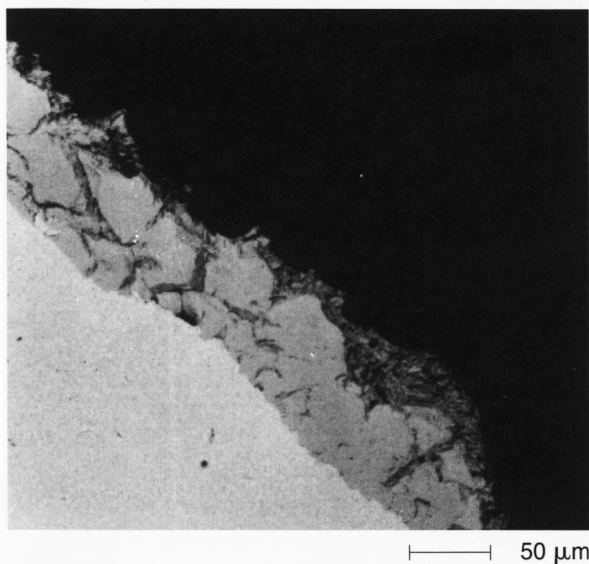
├────────┤ 50 µm

Figure 7. SEM micrograph of a counter electrode (corrosion time: 50 h, heating current density: 1 mA/cm², cathodic DC current density: 3.75 mA/cm²).

cathodic potentials was observed. By contrast, the formation of an MoO₂ layer was not observed before. This is assumed to be due to the relatively low current densities supplied for relatively short times in those studies.

In an industrial glass tank, the superposition of a cathodic potential on the heating electrodes may minimize corrosion. The DC current density most suitable at a heating current of 1 mA/cm² is around 3.75 mA/cm². DC current densities of 2.5 and 5 mA/cm² gave almost as good results. If the current densities are too low, protective MoSi$_x$ layers are not formed and, if they are too high, the layers are dissolved into the melt. The superposition should be current-controlled, because otherwise, the current density decreases with time and is solely limited by the electrochemical process occurring at the counter electrode, the formation of the MoO₂ layer. In an industrial glass furnace, usually starter electrodes located deeply inside the glass tank are used as counter electrodes. By comparison to the heating electrodes used, they possess a relatively small size and hence, the anodic current densities are much higher than the cathodic ones. This should result in an extensive formation of the MoO₂ layer. The problem associated is that also MoO₂ is dissolved and particles of MoO₂ are spread into the

glass. A good prerequisite should be that the temperature at the counter electrodes is as low as possible, because then the layer is assumed to be more stable.

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