Silikáty *XXIV*, s. 17—22 (1980)

THE EFFECT OF DIRECT CURRENT ON THE CORROSION OF TIN OXIDE ELECTRODES IN LEAD GLASS MELT

Jiří Matěj, Jaroslav Kutzendörfer+, Manfred Friedrich+

Joint Laboratory for the Chemistry and Technology of Silicates, Czechoslovak Academy of Sciences and Institute of Chemical Technology, 166 28 Prague 6, Suchbátarova 5

+Institute of Chemical Technology, Department of the Technology of Silicates, 166 28 Prague 6, Suchbátarova 5

Received 28. 7. 1978

Direct current of a density of up to 50 mAmp/cm² accelerates corrosion of tin oxide electrodes of both polarities. Corrosion of the cathode increases roughly linearly with current density. Components of the melt penetrate into the cathode material. Corrosion of the anode is substantially less extensive. Its dependence on current density shows an insignificant peak at about 10 mAmp/cm². The increased corrosion is probably due to mixing of the melt by bubbles of the liberated oxygen. The observed cation depletion in the anodic region takes place at higher current densities and acts in the opposite direction.

INTRODUCTION

Owing to their relatively good electrical conductivity, materials based on SnO_2 are suitable as electrodes, in particular for application in melts. The possiblity of industrial utilization arises above all in the glass industry. Beside their application as heating electrodes in the melting of lead glasses where the use of otherwise convenient molybdenum electrodes brings about certain difficulties, tin oxide electrodes may also be used as auxiliary ones in the introduction of various methods of protecting electrodes as well as furnace lining with direct current. For both theoretical and practical reasons knowledge of the behaviour of tin oxide electrodes under the effects of direct current is therefore desirable.

A theoretical analysis of the effect of direct current on the dissolution of a solid in a melt has been worked out by Hrma [1], [2]. The effect of one of the consequences of direct current passage is considered, namely the electric field gradient in the melt, and a further possible result is an electrochemical reaction which takes place if the current passage through the electrode material is mediated by other charge carriers than the melt. The findings on anodic and cathodic behaviour of Al_2O_3 and ZrO_2 as summarized by Godron [3] are essentially in agreement with this general rule.

Having introduced certain simplifying assumptions Hrma reaches the conclusion that the electric field gradient at a cathodic polarity of the electrode accelerates its corrosion, while a gradient of the opposite sign corresponding to anodic polarity slows down the electrode corrosion.

Experimental data on the effect of electric current on corrosion of tin oxide electrodes in a lead glass melt are given in the study by Pavlovský et al. [4]. At cathodic polarity of the material an actually considerable increase in corrosion was found; however, a comparable increase in the rate of corrosion was also found at anodic polarity. Moreover, from the behaviour under the effect of alternating current it is possible to presume that some non-specified electrochemical reaction has also taken place. The study was not concerned with investigation of the reaction products on the electrodes and with changes in their material. The single relatively considerable direct current density of 0.5 Amp/cm^2 was dealt with.

The present study had the aim of investigating the behaviour of tin oxide material at current densities lower by 1 or 2 orders of magnitude.

EXPERIMENTAL

The experiments were carried out in a glass melt having the composition of 14% K_2O, 21% PbO and 65% SiO_2 (% by weight). The material of the electrodes was of local manufacture. It contained at least 99% SnO_2, the rest being CuO and Sb_2O_3. The apparent density was 6.8 kg/cm^3, the total porosity was 2.9% [5]. The material was cut into electrodes having the form of bars $7 \times 7 \times 70$ mm in size.

All the experiments were carried out at 1400 ± 3 °C, their duration was 40 hours, the current density was 0—50 mAmp/cm^2 ± 5%. The electrodes were arranged vertically and symmetrically, both electrodes were of SnO_2. The temperature was measured by a thermocouple placed in a protective corundum tube immersed in the melt between the electrodes. The experiments were carried out in a corundum Oxal crucible situated in a vertical tubular furnace with platinum-rhodium heating wire. The crucible contained 80 g of glass melt. In the melt there were two vertical parallel electrodes at a distance of 10 mm, immersed 40 mm into the melt. The eletrodes were fed from a stabilised low voltage source at a constant current. The leads were carried out by winding the Pt wire into the electrode slot at a point above the melt level (in spite of this the melt tended to climb up to this point).

After concluding the experiments the electrodes were withdrawn from the crucible and allowed to coll freely in the switched off furnace at a point having an initial temperature of about 500—600 °C. The cooled electrodes were cast into a resin and their corrosion was evaluated microscopically on sections as a loss in thickness in both horizontal axes of the bar. The extensive corrosion of edges has thus affected the results to a minimum degree. The mean value for all the sections divided by two, that is the loss in wall thickness, was taken as a measure of the corrosion. Polished sections for the electron microprobe were also prepared from these sections.

THE RESULTS AND DISCUSSION

In the diagram in Fig. 1 the loss of electrodes is plotted vs. current density. With the cathode the loss increases considerably with current density while up to 12 mAmp/cm^2 the course is linear and its slope is indicative of a low initial value. The loss of anode material is much smaller and exhibits a peak at a current density of about 10 mAmp/cm^2. At a 50 mAmp/cm^2 the loss is equally minute as in the current-free state.

The characteristic features of the corrosion of the anode and of the cathode showed significant differences. The anodes were coated with a glass layer containing numerous bubbles. At current densities of up to 12 mAmp/cm^2 this layer was crystallized to a very small degree only. At 50 mAmp/cm^2 the strongly crystallized layer was 3 mm in thickness. This layer showed considerable potassium and lead depletion (Figs. 2-5). The depletion is indicated by a comparison of the corresponding regions in Figs. 4 and 5 (anode) and Figs. 9, 10 (cathode). The layer contained fine SnO_2 particles which imples that even at anodic polarity and at a density of 50 mAmp/cm^2 the electrode is subject to certain dissolution (Fig. 6).

Close to the cathode-melt interface one can observe penetration of all the melt components into the electrode (Figs. 7—10). Their distribution in the electrode material is non-uniform and corresponds obviously to pore distribution. No crystalline particles were found close to the electrode with the exception of a thin layer of tin oxide particles which was probably formed by crystallization of the boundary diffusion layer in the course of cooling (Figs. 7 and 11). However, considerable amounts of substantially larger SnO_2 particles were established at the crucible bottom in the region below the cathode. In the neighburhood of the cathode there were found individual metallic beads several tens of μm in size. Simultaneous presence of Sn and Pt was determined by the electron microprobe. The beads are therefore reaction products arising at the point of contact between the platinum supply leads and the electrode.

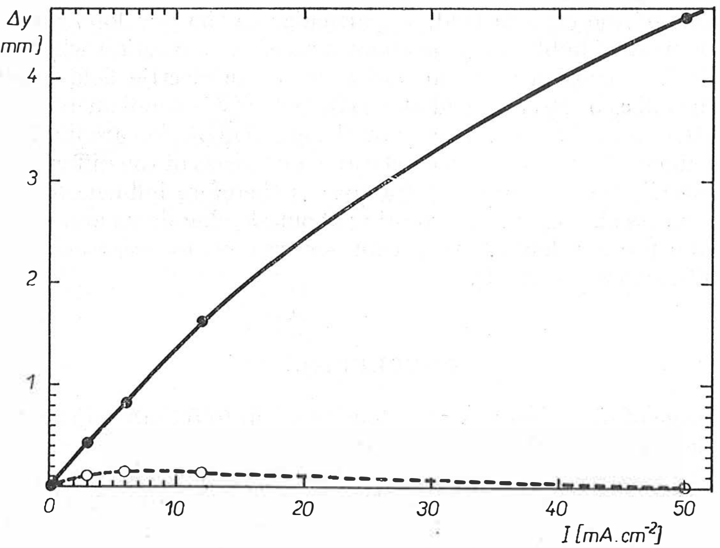


Fig. 1. Corrosion of tin oxide electrode vs. current density at: a) cathodic polarity—full line, b) anodic polarity—dashed line.

The behaviour of tin oxide material described is in agreement with the character of its conductivity. With the electron character of conductivity of the tin oxide material [6] and at anodic polarity the conditions are complied with for an electrochemical reaction taking place at the electrode surface since the character of the charge carrier is changed. The development of bubbles most probably results from the reaction

$$SiO_3^{2-} = SiO_2 + 1/2O_2 + 2e^-.$$

In the case of the cathode, on the other hand, there is the possibility that cations are conducted by its material. Such a conduction would obviously be facilitated by the melt-filled pores observed. It is probable that the mobile potassium cations gradually penetrate into greater depth and that their reduction takes place on the platinum lead, where the potassium immedietely reduces SnO_2 to Sn which forms the metal beads mentioned above. The penetration of potassium ions, probably due to surface diffussion, possibly contributes (by forming a liquid phase at the crystal boundaries) to melt penetration into the material and possibly also to liberation of SnO_2 particles which were found at the crucible bottom; however, this assumption could not so far be verified.

The findings described above are also in agreement with the results presented recently in the REEL research report [7]. It was found that at cathodic polarity of the tin oxide electrode in a lead glass melt its corrosion is significantly accelerated and that no crystalline interlayer is formed between the electrode and the melt.

At anodic polarity the behaviour is more complex. No suppression of the corrosion by the electric field predicted by the studies by Hrma [1], [2] was established; on the contrary, more extensive corrosion took place at lower current density values similarly to the results of study [4] and the corrosion is again reduced at a current density of 50 mAmp/cm². This behaviour is probably due to further effectes arising apart from that of the electric field, in particular to the development of bubbles.

The development of bubbles brings about extensive convection which may significantly accelerate corrosion and thus act against the electric field effect. On the other hand, the effect of electric field at anodic polarity is supplemented by another one acting in the same direction, namely by the alkali depletion around the electrode which brings about an increase in viscosity and a decrease of the diffusion coeficient. Corrosion at anodic polarity of the refractory is therefore influenced by a sum of at least three effects among which two bring about slowing down and one acceleration, so that the process depends in a complex way on the respective conditions. These were different in study [4].

CONCLUSION

During passage of direct current at a density of up to 50 mAmp/cm² through tin oxide electrodes in a lead glass melt the corrosion of the cathode is significantly acce-le-rated in agreement with the theory of the effect of electric field on dissolution. Glass components penetrate to a considerable degree into the cathode material. With the exception of reduction to Sn in the zone of platinum supply leads no other cathodic reaction was determined. The behaviour at the anode is a more complex one: Apart from the assumed effect of electric field the development of oxygen bubbles may accelerate corrosion and the cation depletion of the anodic region may have the opposite effect.

References

[1] Hrma P.: Silikáty *17*, 303 (1973).
[2] Hrma P.: Silikáty *18*, 217 (1974).
[3] Godron Y.: *Review of the Literature on Electrochemical Phenomena in Relation to the Mechanism of the Corrosion of Oxides and Refractory Materials by Molten Glasses.* Institut National du Verre, Charleroi 1975.
[4] Pavlovskij V. K., Romeykova S. P., Shashkin V. S.: Fyzika i chimija stekla *2*, 157 (1976).
[5] Vrbacký I.: Proc. *1st Seminary Technical Ceramics* (in Czech), p. 7/1, VÚEK, Hradec Králové 1975.
[6] Kofstad P.: *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides,* p. 355. J. Wiley, New York 1972.
[7] Bedroš P.: Unpublished Research Report REEL, p. 43, State Glass Research Institute Hradec Králové 1977.

VLIV STEJNOSMĚRNÉHO PROUDU NA KOROZI CÍNIČITÝCH ELEKTROD V OLOVNATÉ SKLOVINĚ

Jiří Matěj, Jaroslav Kutzendörfer+, Manfred Friedrich+

Společná laboratoř pro chemii a technologii silikátů ČSAV a VŠCHT, Praha

+*Vysoká škola chemicko-technologická, katedra technologie silikátů, Praha*

Byla studována koroze elektrod z kysličníku cíničitého v olovnaté sklovině o složení (hmot. %) 14 % K_2O, 21 % PbO, 65 % SiO_2 při průchodu stejnosměrného proudu o hustotě 0—50 mA/cm^2 a teplotě 1400 °C po dobu 40 h.

Působením proudu byla koroze elektrod obojí polarity zpravidla urychlována. Koroze katody byla větší a vzrůstala s proudovou hustotou zhruba lineárně. Elektronovou mikrosondou byla ve sklovině v těsné blízkosti katody zjištěna pouze tenká vrstvička drobných částic SnO_2. Značný výskyt mnohem větších částic SnO_2 byl zjištěn u dna kelímku v oblasti pod katodou. V pórech elektrody byly zjištěny součásti skloviny. S výjimkou redukce Sn v oblasti platinových přívodů nebyla pozorována jiná katodická reakce. Je navržen výklad tohoto chování založený na možnosti transportu náboje materiálem katody draselnými kationty.

Koroze anody byla podstatně nižší. Její závislost na proudové hustotě vykazovala nevýrazné maximum kolem 10 mA/cm^2. Příčinou zvýšené koroze je zde pravděpodobně míchání taveniny bublinkami vylučujícího se kyslíku. Protichůdně působí pozorované značné ochuzení anodické oblasti na kationty, které se uplatňuje při vyšších proudových hustotách.

Obr. 1. *Závislost koroze cíničitých elektrod na proudové hustotě při: a) katodické polaritě — plně, b) anodické polaritě — čárkovaně.*
Obr. 2. *Rozhraní cíničitá elektroda (anoda) — sklovina, proudová hustota 50 mA/cm². Snímek z elektronové mikrosondy, kompozice.*
Obr. 3. *— jako obr. 2, plošné rozložení* Si.
Obr. 4. *— jako obr. 2, plošné rozložení* K.
Obr. 5. *— jako obr. 2, plošné rozložení* Pb.
Obr. 6. *— jako obr. 2, plošné rozložení* Sn.
Obr. 7. *Rozhraní cíničité elektrody (katoda)—sklovina, proudová hustota 50 mA/cm². Snímek z elektronové mikrosondy, kompozice.*
Obr. 8. *jako obr. 7, plošné rozložení* Si.
Obr. 9. *jako obr. 7, plošné rozložení* K.
Obr. 10. *jako obr. 7, plošné rozložení* Pb.
Obr. 11. *jako obr. 7, plošné rozložení* Sn.

ВЛИЯНИЕ ПОСТОЯННОГО ТОКА НА КОРРОЗИЮ ОЛОВЯННО-ОКИСНЫХ ЭЛЕКТРОДОВ В СВИНЦОВО-СИЛИКАТНОЙ СТЕКЛОМАССЕ

Иржи Матей, Ярослав Куцендерфер+, Манфред Фридрих+

Общая лаборатория химии и технологии силикатов ЧСАН и ХТИ, Прага

+*кафедра технологии силикатов ХТИ, Прага*

Исследовали коррозию электродов из двуокиси олова в свинцово-силикатной стекломассе составом (% по весу) 14 % K_2O, 21 % PbO, 65 % SiO_2 при ходе постоянного тока плотностью 0—50 мА/см^2, при температуре 1400 °C во время 40 часов.

Под действием тока коррозия электродов обеих полярностей, как правило, ускорялась. Коррозия катода оказывалась большей и росла в зависимости от плотности тока приблизительно линейно. С помощью электронного микрозонда в стекломассе вблизи катода установили тонкую пленку мелких частиц SnO_2. Значительное количество гораздо больших частиц SnO_2 было установлено при дне тигля в области под катодом.

В порах электрода установили компоненты стекломассы. За исключением восстановления Sn в области платиновых подводов не заметили другой катодной реакции. Авторами предлагается объяснение рассматриваемого поведения, основывающегося на возможности транспорта заряда веществом катода с помощью калиевых катионов.

Коррозия анода существенно ниже. Ее зависимость от плотности тока достигает нерезкого максимума около 10 мА/см². Причиной повышенной коррозии является вероятно перемешивание расплава пузырьками выделяющегося кислорода. Противоположно действует наблюдаемое значительное обеднение анодной области на катионы, которое принимает участие при более высоких плотностях тока.

Рис. 1. Зависимость коррозии оловянно-окисных электродов от плотности тока при: а) катодной полярности — сплошная линия, б) анодной полярности — штриховая линия.

Рис. 2. Граница раздела электрод (анод) — стекломасса, плотность тока 50 мА/см². Съемка из электронного микрозонда, композиция.

Рис. 3. Граница раздела электрод (анод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение Si. *Съемка из электронного микрозонда.*

Рис. 4. Граница раздела электрод (анод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение K. *Съемка из электронного микрозонда.*

Рис. 5. Граница раздела электрод (анод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение Pb. *Съемка из электронного микрозонда.*

Рис. 6. Граница раздела электрод (анод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение Sn. *Съемка из электронного микрозонда.*

Рис. 7. Граница раздела электрод (катод) — стекломасса, плотность тока 50 мА/см². Съемка из электронного микрозонда, композиция.

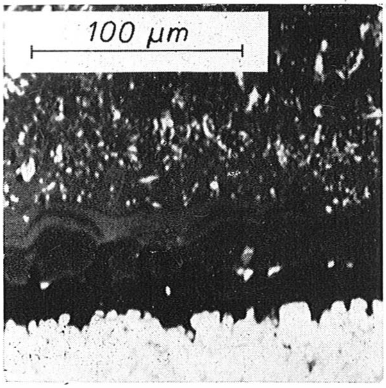
Рис. 8. Граница раздела электрод (катод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение Si. *Съемка из электронного микрозонда.*

Рис. 9. Граница раздела электрод (катод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение K. *Съемка из электронного микрозонда.*

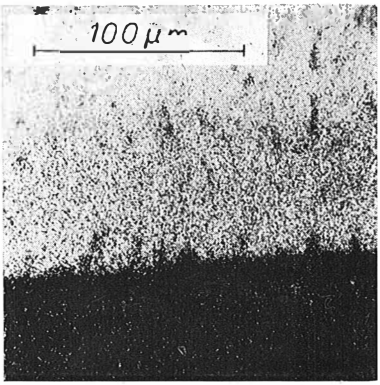
Рис. 10. Граница раздела электрод (катод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение Pb. *Съемка из электронного микрозонда.*

Рис. 11. Граница раздела электрод (катод) — стекломасса, плотность тока 50 мА/см². Плоскостное расположение Sn. *Съемка из электронного микрозонда.*

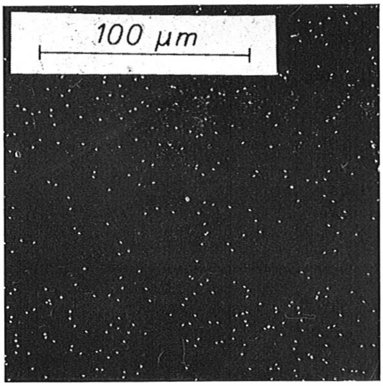
2



3



4



5

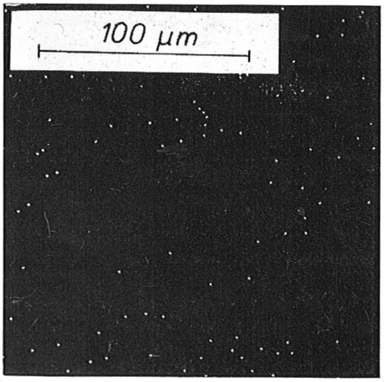


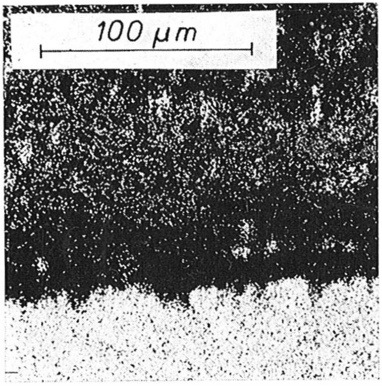
Fig. 2. Electrode (anode)—melt interphase, current density 50 mAmp/cm^2. Microprobe micrograph, composition.

Fig. 3. Electrode (anode)—melt interphase, current density 50 mAmp/cm^2. Microprobe micrograph. Planar distribution of Si.

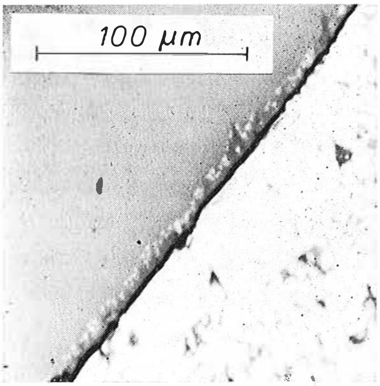
Fig. 4. Electrode (anode)—melt interphase, current density 50 mAmp/cm^2. Microprobe micrograph. Planar distribution of K.

Fig. 5. Electrode (anode)—melt interphase, current density 50 m/Amp/cm^2. Microprobe micrograph. Planar distribution of Pb.

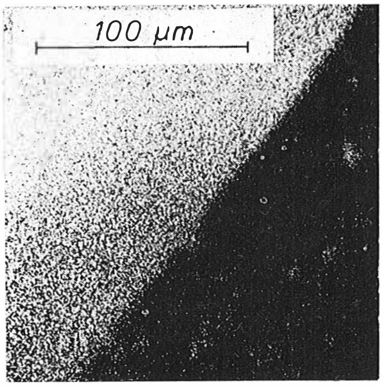
6



7



8



9

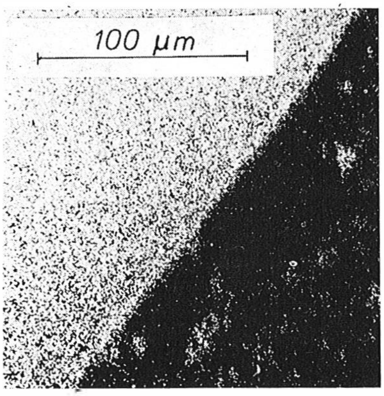


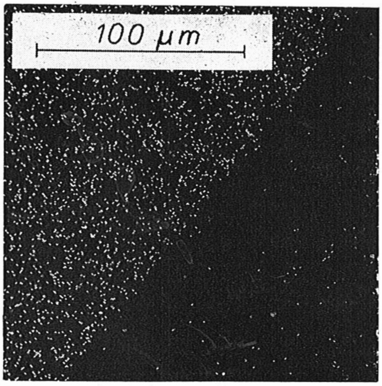
Fig. 6. Electrode (anode)—melt interphase, current density 50 m/Amp/cm^2. Microprobe micrograph. Planar distribution of Sn.

Fig. 7. Electrode (cathode)—melt interphase, current density 50 mAmp/cm^2. Electron microprobe micrograph, composition.

Fig. 8. Electrode (cathode)—melt interphase, current density 50 mAmp/cm^2. Electron microprobe micrograph. Planar distribution of Si.

Fig. 9. Electrode (cathode)—melt interphase, current density 50 mAmp/cm^2. Electron microprobe micrograph. Planar distribution of K.

10



11

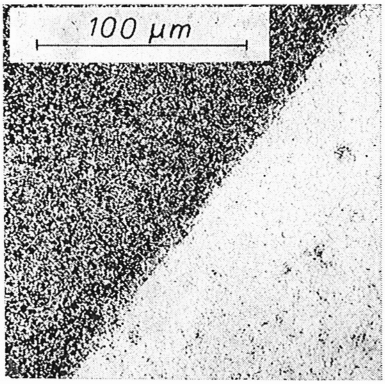


Fig. 10. Electrode (cathode)—melt interphase, current density 50 mAmp/cm². *Electron microprobe micrograph. Planar distribution of* Pb.

Fig. 11. Electrode (cathode)—melt interphase, current density 50 mAmp/cm². *Electron microprobe micrograph. Planar distribution of* Sn.