OXYGEN BUBBLE DEVELOPMENT ON A PLATINUM ELECTRODE IN BOROSILICATE GLASS MELT BY THE EFFECT OF ALTERNATING CURRENT

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A high-temperature observation of bubble evolution by the effect of mains alternating current (50 Hz) in borosilicate glass melt at temperatures of 1100 and 1225°C was completed by measurement of the polarization curves and measurement of the mean electrode potential and potential course at electrodes fed by rectangular alternating current. The development of oxygen bubbles already starts at a current density of about 30 mA·cm⁻². Above 100 mA·cm⁻², fluctuations in bubble development occur and bubbles start to release from the electrode. Above 220 - 250 mA·cm⁻², massive bubble evolution starts. Bubble development at 1100°C is considerably higher than at 1225°C and limits in their evolution are more noticeable. The limits in bubble development correspond to changes of potential course and of mean electrode potential. An explanation of the changes in electrode behaviour, based on an alternating transition between two mechanisms of oxygen development and/ or on alternating reduction and re-forming of oxidic layer on the electrode in the transition range, has been suggested. Start of bubble evolution at low alternating current density has also been observed in simple sodium-calcium-silicate glass melt. A relation between bubble release and platinum corrosion caused by reduced silicon has been suggested.

INTRODUCTION

Electrochemical bubble development on electrically conductive materials can cause a deterioration of the produced glass melt. Moreover, the development of oxygen may be associated with increasing corrosion caused by alternating current. In this connection, Higgins [1] investigated the development of oxygen on a platinum electrode in a glass melt containing Na_2O, K_2O, CaO, and SiO_2 as major components and no refining agents. By direct observation, it was found that the development of bubbles largely containing oxygen starts between 0.3 and 0.6 A·cm⁻² at 50 Hz, higher current densities being necessary at higher frequencies. The beginning of the oxygen development correlates with increased electrode corrosion. The oxidation of platinum by the developed oxygen is assumed to be the cause of the increased corrosion. The constant ratio of current density to frequency of 2.4×10^{-3} A·sec·cm⁻² arising from the results is in accord with the limiting values found by other authors [2-3] for platinum dissipation into glass melt. The higher oxygen development found at 1050°C than at 1300°C is a remarkable fact. This is also in accordance with the observed corrosion behaviour and can be explained by a more rapid diffusion of oxygen from the electrode at a higher temperature. Higgins confirmed the foregoing conclusions including the charge density necessary for oxygen development on the basis of electrochemical measurements in the same glass melt [4]. The author used the arrangement with the pulses of constant anodic current followed by the rapid passing of the same charge in the opposite direction. The course of anodic potential showed two waves under the described conditions. The first wave was ascribed to the formation of an electrode double-layer and the formation of a PtO_2 film. This is followed by a potential increase and oxygen development. The potential increase at the end of the first wave starts at 1200°C within a range of $0.25 - 500$ mA·cm⁻² at $0.42 - 0.80$ V, respectively. The values of $1.16 - 1.40$ V are given for the oxygen development in the same current density range. Somewhat higher values apply for 1100°C and a current density of 0.25 mA·cm⁻², 0.58 and 1.32 V, respectively. These results were completed by an investigation in several simple melts including a melt of $Na_2O \cdot 2B_2O_3$ [5]. Except for the $Na_2O \cdot 2P_2O_5$ melt, no substantial differences in this behaviour were found. The following paper [6] summarizes the obtained results. The multiples of the electrochemically found times for the beginning of the oxygen development and the current densities amount to 1.9×10^{-3} to 4.7×10^{-3} A·sec·cm⁻² and show no significant dependence on a current density within 0.025 to 1.00 A·cm⁻².

Maric et al. [7] found contradictions between the conclusions of the paper [4] and other published data.

Based on cyclic voltammetry and chronopotentiometry measurements, the authors concluded that oxygen development on platinum electrode in $Na_2O \cdot 2SiO_2$ melt involves two steps. In the first step, oxidation of oxygen anions resulting in the formation of a thin adsorbed oxygen layer: $Pt + O^{2-} = Pt–O + 2e^-$ followed by the decomposition of $2\ Pt–O = 2\ Pt + O_2$ (g) takes place. Above approximately 0.4 V, reactions $Pt–O + O^{2-} = PtO_2 + 2\ e^-$ and/or $Pt–O + O^{2-} = Pt + O_2 + 2\ e^-$ take place as the second step. Di Martino et al. [8] found oxidation of the silica network above +200 mV. The formation of the layer of adsorbed oxygen as the first step is assumed also in that work.

As for the behaviour in the cathodic region, the anodic oxide layer is completely removed during the backward cathodic run in the multicomponent glass melt according to Higgins. This is valid only partially in sodium-disilicate melt [5]. Maric et al. [7] found using cyclic voltammetry that the layer of platinum oxides is decomposed even at a positive potential of +0.18 V. The distinct potential fluctuations attributed to unspecified oxidation products were observed at more negative potentials of −0.4 to −0.9 V. A smooth cathodic course was observed if there was not a previous anodic course and the glass melt did not contain iron oxides, with a more expressed silicate reduction starting below −0.8 V. Di Martino et al. [8] summarized the results of the measurement of redox potentials in several papers. Values higher than +0.15 V are given for the redox pair O(0)/O(-II) in sodium-calcium-silicate glass melt and +0.2 V for borosilicate glass melt, respectively. Values lower than −1.02 V (sodium-calcium-silicate glass melt) and −1.20 and −1.18 V (two borosilicate glass melts) are given for the Si(IV)/Si(0) redox pair. Potentials of −0.53 and −0.59 V (sodium-calcium-silicate glass melt) and −0.39 and −0.41 V (borosilicate glass melt) are given for the Fe(III)/Fe(II) pair and −0.81 V (sodium-calcium-silicate glass melt) and −0.90 to −1.05 V (borosilicate glass melt) for the Fe (II)/Fe(0) pair.

The formation of gas bubbles was directly investigated only by Higgins [1] using a heating microscope. The observation time at the lowest current density of 0.3 A·cm^{-2} (50 Hz) was only 5 minutes. The goal of the present paper is especially a more detailed investigation of gas development at low densities of alternating current.

EXPERIMENTAL

The experiments were carried out mostly in commercial borosilicate glass melt of Pyrex type with a composition of 80.4 SiO_2, 13.0 B_2O_3, 2.3 Al_2O_3, 3.4 Na_2O and 0.9 K_2O (in wt. %). A part of experiments was also carried out in simple model glass melt containing 74 SiO_2, 10 CaO and 16 Na_2O (in wt. %). Working electrodes made of platinum wire with a diameter of 1.0 mm were used in all cases. The wire was insulated by a silica glass capillary except the free bottom part below the glass surface that represented the electrode proper. The reference platinum electrode used almost in all instances was created in a similar way by a platinum wire 1 mm in diameter. The unprotected part of the wire passed through the glass surface in this case and the submerged part was only 5 − 8 mm long. The reference electrode was placed between the working electrodes with its bottom end above the upper part of the working electrodes. Molybdenum wire, 1.2 mm in diameter protected similarly to the working electrodes was used as an auxiliary electrode when direct current was introduced or as an alternative reference electrode. The electrodes were immersed vertically into the glass melt in a crucible or in an observation cell placed in an electrically heated laboratory furnace. After installing all the electrodes, the rest potential of the working electrodes was monitored until a steady value of −30 to −50 mV against reference platinum electrode was attained, which took about 1.5 hours.

The dynamic polarization curves in the borosilicate glass melt were measured in three- electrode-arrangement using a reference electrode, a working electrode and an auxiliary electrode. The free area of the platinum working electrode was 0.322 cm^2 (10 mm). The amount of glass in the crucible was 70 g. The potential was controlled by a potentiostat with a potential scanning rate of 50 mV·min^{-1}.

In direct observation of bubble development, the electrodes were introduced into the observation cell made of silica glass with an inner thickness of 8 mm placed in a special furnace and observed by means of a camera with a picture record [9]. A pair of platinum working electrodes 2 cm long (0.622 cm^2) was used along with a platinum reference electrode. The working electrodes were fed by mains alternating current via regulation and separation transformers and a resistor. The mean electrode potential was measured against the reference electrode after the separation of the AC component by RC filter. In combined AC/DC experiments, a molybdenum auxiliary electrode was also introduced symmetrically to the working electrodes. An adjustable DC source was connected between the auxiliary electrode and the electrical central point between the working electrodes realized by two identical resistors. A more detailed description of the wiring can be found e.g. in the paper [10]. Only one working electrode was connected to a potentiostate in a three-electrode arrangement in experiments at a constant potential. The observation time at every condition setting was 30 min.

To prepare the bubbles for the gas analysis, a pair of platinum electrodes with a horizontal working part 1.5 cm long (0.479 cm^2) was introduced into the ceramic crucible (99.5 % Al_2O_3) containing 70 g of molten borosilicate glass. The electrodes were fed by alternating current for 30 min in the same way as described above. After rapid cooling, the working part of the electrodes

with the adjacent glass and bubbles was separated and analysed by mass spectrometry in a laboratory of Glass Service, Vsetín.

In the investigation of the potential course, vertical electrodes with a working area of 0.636 cm² (2.0 cm) were placed in a ceramic crucible and fed by rectangular and symmetrical alternating current of the frequency of 47.5 Hz of the galvanostate controlled by a function generator. The course of the potential of a selected electrode against the reference electrode was observed by means of a storage oscilloscope. As in the direct observation experiments, the mean electrode potential was also measured.

All the results given in next part refer to the effective values of alternating current.

RESULTS AND DISCUSSION

Effect of direct current

Figure 1 shows the polarization curves of a platinum electrode in borosilicate glass melt at 1100°C. The anodic current starts to increase moderately already at a slightly raised potential. A more expressed current increase starts at about 60 mV. The current increase somewhat slows above about 150 mV·A more extensive stagnation associated with certain current fluctuations occurs above 300 mV. The course of the cathodic polarization curves depends on the state of electrode surface. The cathodic polarization curve for the original surface shows only a slight current increase from the beginning. The maximum current density reaches only −0.6 mA·cm⁻² at −1000 mV. The cathodic polarization curve, measured after the foregoing measurement of the anodic branch, shows a completely different course. The cathodic current rapidly increases from the very beginning, distinct current fluctuations start at −300 mV and the current decreases steeply at −600 mV, attaining a value comparable with that measured on the original surface. This is in principal agreement with the observation in paper [7], despite another method and glass melt used there. In accordance with the quoted paper, the high cathodic current is without any doubt associated with a reduction of anodic products. At a higher temperature of 1225°C (Figure 2), the anodic current is somewhat higher with a steep increase above 100 mV followed by a stagnation at about 250 mV. The effect on the cathodic course after the previous anodic run is less distinct here and finishes at a less negative potential. That effect is even less distinct when the electrode is stirred after finishing the anodic run. This behaviour implies that the high cathodic current is associated above all with the reduction of bubbles on the electrode, which are partially removed by the stirring, and also that the original number of bubbles is less at the higher temperature. Below −800 mV, the cathodic current increases rather extensively in all instances, especially at 1225°C. This corresponds to the starting
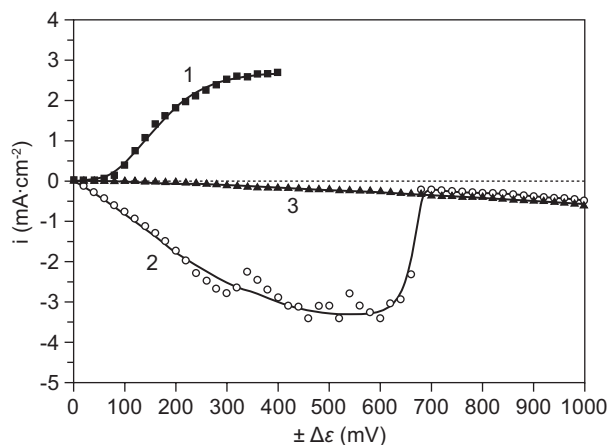

Figure 1. Polarization curve of the platinum electrode in borosilicate glass melt. 50 mV·min⁻¹, 1100°C (1 – anodic branch, 2 – cathodic branch after the measurement of the anodic branch, 3 – cathodic branch for the original surface).

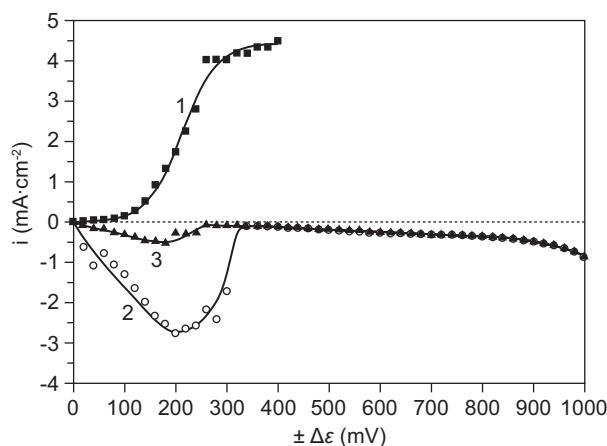Figure 2. Polarization curve of the platinum electrode in borosilicate glass melt. 50 mV·min⁻¹, 1225°C (1 – anodic branch, 2 – cathodic branch after the measurement of the anodic branch, 3 – cathodic branch after the measurement of the anodic branch and stirring of the electrode.
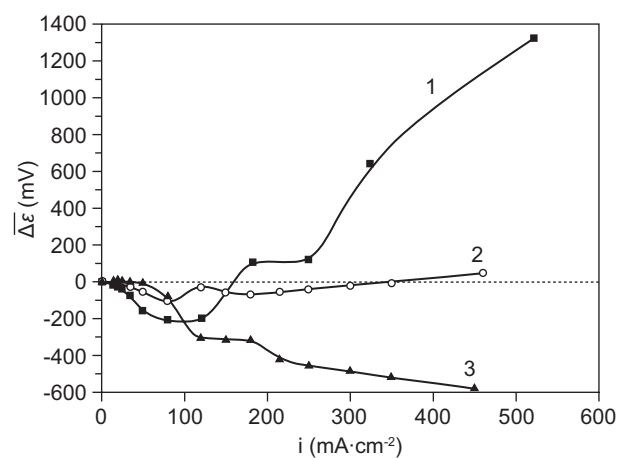

Figure 3. Dependence of the shift of the mean electrode potential $\overline{\Delta \varepsilon}$ of electrodes fed by mains current on current density i. 1 – borosilicate glass melt, 1100°C, 2 – borosilicate glass melt, 1225°C, 3 – soda-lime-silica glass melt, 1225°C.

reduction of Si(IV).

Direct observation of bubble development on the electrodes showed that the visible bubble development by the effect of direct current starts at as a slight potential increase as +20 mV; the time necessary for the onset of the bubble development depends on the history of the electrode surface. At a slightly reduced potential, a visible reduction of the diameter of the previously produced anodic bubbles starts already when the potential decreases to −50 mV as compared with the rest state. This fact again supports the presumption that the rapid current increase in the cathodic branch of the polarization curves after the anodic run mentioned above is associated with the reduction of oxygen bubbles. The following current fluctuations are likely associated with the disappearance of some bubbles which affects the electrode potential and

true electrode area. Cathodic current decreases abruptly after the reduction of all bubbles.

Effect of alternating current and combined effect of direct and alternating current

Development of minute bubbles (Figures 8 and 11) was already observed at very low current densities. Table 1 summarises the limiting current densities for bubble development. Relatively big steps in adjustment of current density were necessary in some cases. So the average values of the current density, where a change in bubble development was observed and of the nearest lower current density, are given as the most probable limits in bubble development. It can be seen from Table 1 that bubble development in borosilicate glass melt at 1225°C, where four independent measurements were carried out, starts in a comparatively large range between 17.5 to 42.5 mA·cm^{-2} with an average value
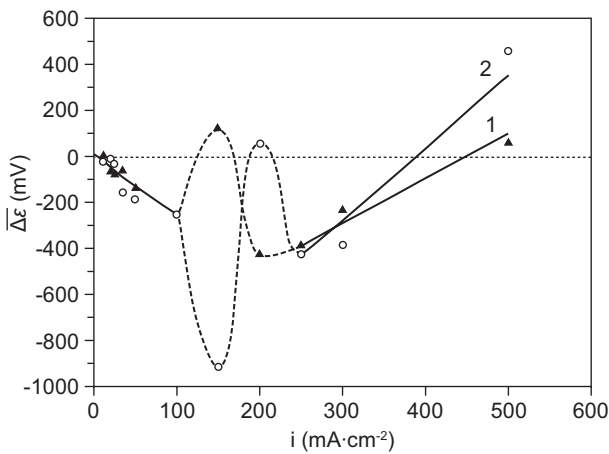

Figure 4. Dependence of the shift of the mean electrode potential $\overline{\Delta\varepsilon}$ of electrodes fed by rectangular current in borosilicate glass melt on current density at 1225°C (1 – electrode 1, 2 – electrode 2). Average limits of the non-stability region found in the bubble development are indicated by vertical lines.
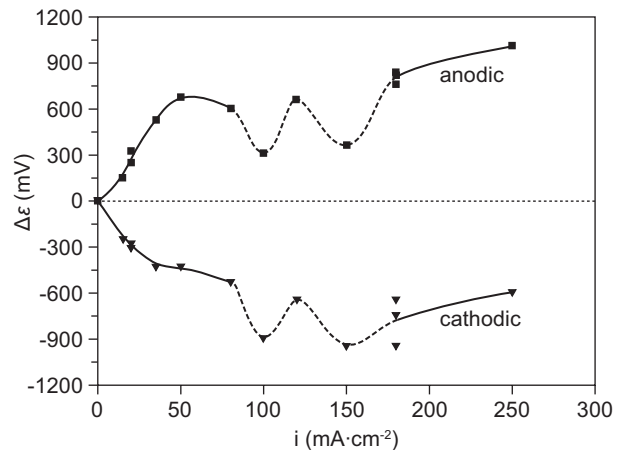

Figure 6. Dependence of the potential elevation on the end of the anodic and cathodic half-periods on the current density of the rectangular current (Borosilicate glass melt, 1100°C).
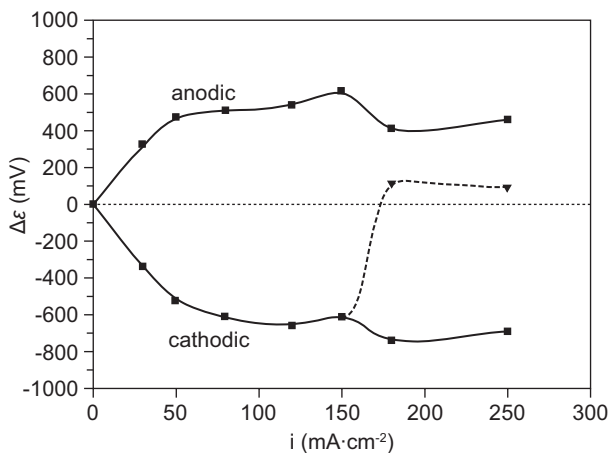

Figure 5. Dependence of the potential elevation De on the end of the anodic and cathodic half-periods on the current density of the rectangular current (Borosilicate glass melt, 1225°C; (▼ – positive values of the potential held during most of the cathodic half-period).
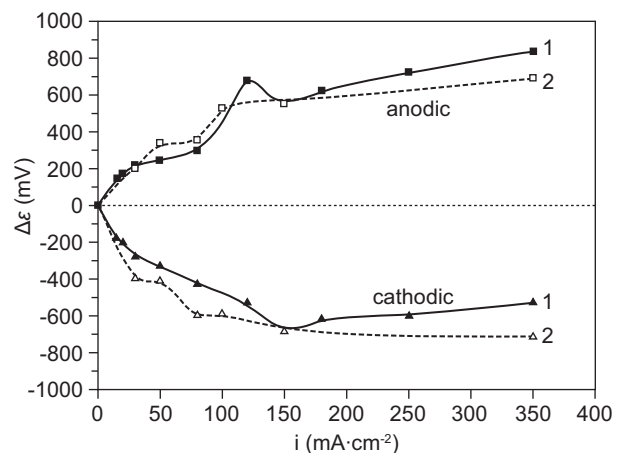

Figure 7. Dependence of the potential elevation on the end of the anodic and cathodic half-periods on the current density of the rectangular current (Soda-lime-silica glass melt, 1225°C; 1 – measurement 1, 2 – measurement 2).

of 27 mA·cm^{-2}. Neither the values for 1100°C in the borosilicate glass melt nor those for the sodium-calcium-silicate glass melt exceed that range. The bubble development increases at increasing current density and bubbles grow. At current densities above
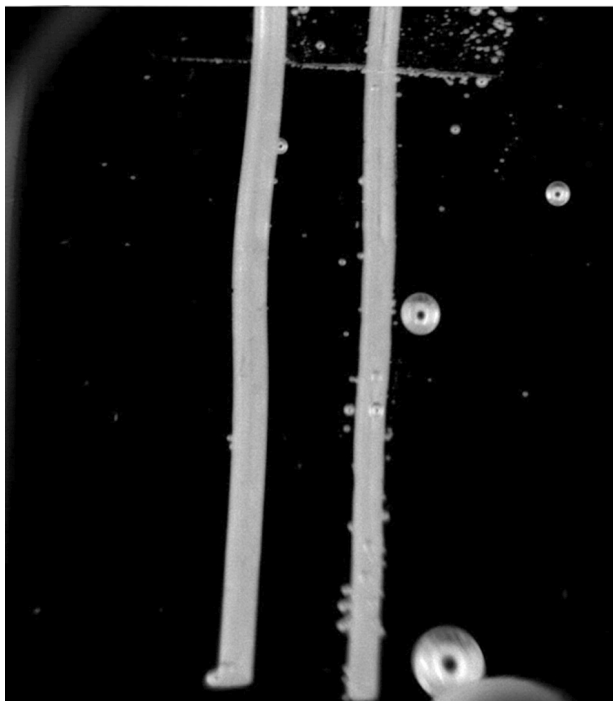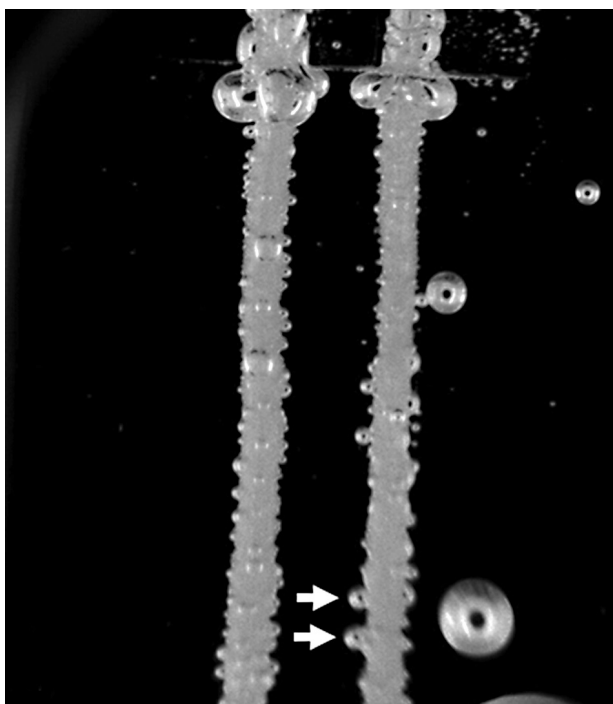

Figure 8. Bubble development on the platinum electrodes at low alternating current density. 1100°C, 55.5 mA·cm^{-2}.

100 mA·cm^{-2}, irregular bubble development starts; some bubbles appear and other disappear (Figure 9, Table 1). At approximately the same current density, bubbles start to release from the electrode surface. At the same time, the mean electrode potential fluctuates as will be shown later. At the highest current densities, on average above 220 mA·cm^{-2}, massive development of large bubbles starts, especially at 1100°C (Figure 10). Certain fluctuations in bubble development above 80 mA·cm^{-2} were also observed in the sodium-calcium-silicate glass melt. A more accurate limit could not be determined with respect to the too large step in the current density adjustment. The bubble development increased again with increasing current density. Another limit in bubble development could not be confirmed in that glass melt.

A comparison of bubble development at higher current densities (cf. Figure 10 vs. Figure 12) shows that the bubble development at 1100°C is considerably higher than that at 1225°C. This corresponds to the analogical difference observed at DC conditions (cf. Figures 1 and 2) and is in accordance with what Higgins [1] found for temperatures of 1050 and 1300°C, respectively. The suggested explanation based on a more rapid diffusion of oxygen from the electrode at higher temperatures seems to be the most probable one.

The mean electrode potential changes with increasing current load. This potential decreases fluently in borosilicate glass melt from the very beginning in all instances attaining a minimum value at about 100 mA·cm^{-2}. Figure 3 shows the results of

a)
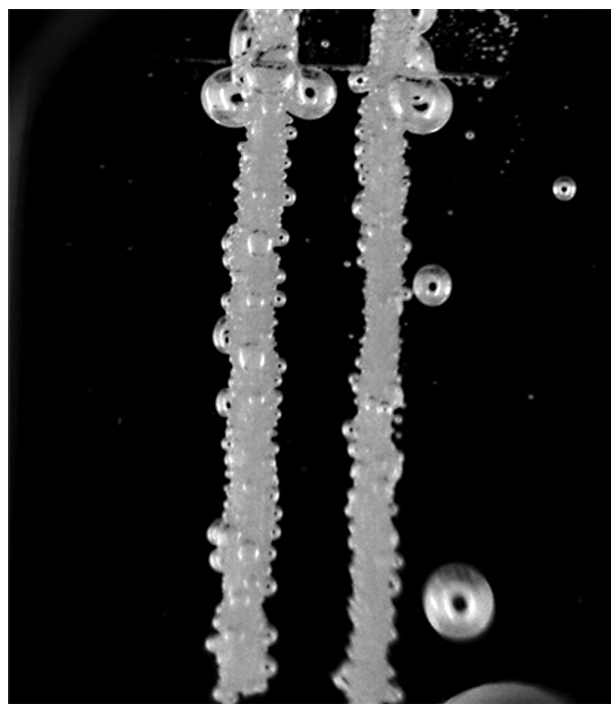
b)

Figure 9. Transition in bubble development on the platinum electrodes. 1100°C, 222 mA·cm^{-2}; a) time τ – the bubbles indicated by arrows are absent in the following picture, b) time τ + 5 min.

independent measurements of the mean electrode potential as a function of current density. The initial decrease of the mean electrode potential in borosilicate glass melt showing a minimum at 100 mA·cm^{-2} for a temperature of 1100°C and at about 80 mA·cm^{-2} for 1225°C, respectively, was confirmed. These limiting current densities are in principal agreement with the beginning of irregular bubble development in Table 1. The subsequent course shows a potential increase towards more positive values followed by a decrease or by a stagnation. The mean electrode potential steadily increases at the highest current densities. The start of the steady potential increase approximately corresponds to the limit of high bubble development in Table 1. In the sodium-calcium-silicate glass melt, the mean electrode potential also decreases to more negative values up

to about 120 mA·cm^{-2} and a stagnation and another potential decrease follow beginning at 180 mA·cm^{-2}. The described potential courses were not appreciably affected by inserting a relatively high resistor of 500 W in the feeding circuit.

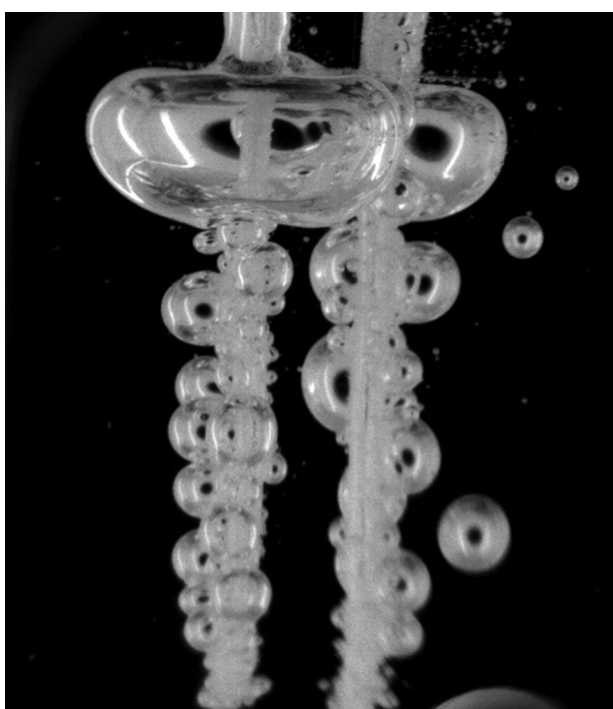When the DC of negative polarity was superposed
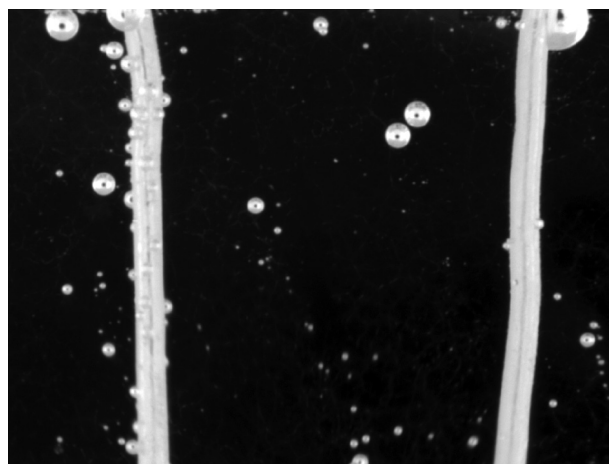

Figure 11. Bubble development on the platinum electrodes at low alternating current density. 1225°C, 80 mA·cm^{-2}.

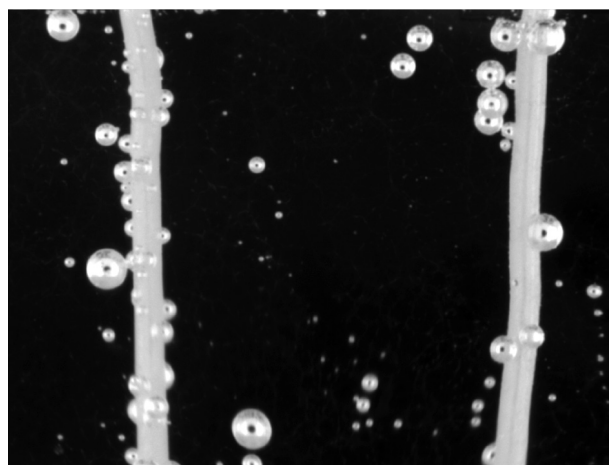Figure 12. Bubble development on the platinum electrodes at high alternating current density. 1225°C, 350 mA·cm^{-2}.

Figure 10. Massive bubble development at the platinum electrodes at high alternating current density. 1100°C, 388 mA·cm^{-2}.

Table 1. Limiting current densities for bubble development calculated as an average of the value at which the respective changes were observed and the nearest lower value (in brackets); BS – borosilicate glass melt, NCS – sodium-calcium-silicate glass melt.

No.	Glass temperature (°C)	Limiting current densities (mA·cm^{-2})		
		Start of bubble development	Start of transition	Start of high bubble development
1	BS, 1100	27 (23-31)	166 (111-222)	250 (222-277)
2	BS, 1225	25 (20-30)	150 (100-200)	225 (200-250)
3	BS, 1225	22.5 (20-25)	100 (80-120)	215 (180-250)
4	BS, 1225	17.5 (15-20)	100 (80-120)	300 (250-350)
5	BS, 1225	42.5 (35-50)	100 (80-120)	150 (120-180)
6	NCS, 1225	40 (30-50)	>80 (80-200)	no expressed transition
Average for No. 2 to 5		27	112.5	222.5

to the alternating current in the borosilicate glass melt at 1225°C and at an AC current density of 209 mA·cm⁻², i.e. in the region of alternating bubble appearance and disappearance, all bubbles disappeared as soon as the mean potential decreased to −570 mV. This indicates that all the bubbles were oxygen ones. At an AC current density of 50 mA·cm⁻², i.e. in the range of the development of small bubbles, the bubbles alternatively appeared and disappeared when the potential became negative, with all the bubbles disappearing at −500 mV. This effect was reversible. Similar behaviour was found at 1100°C. The described behaviour indicates that all the bubbles are oxygen ones, the mechanism of their formation changes, however.

An analysis of minute bubbles confirmed that the bubbles consist of pure oxygen. The bubbles for the analysis were prepared at 1100°C and at current density of 50 mA·cm⁻², i.e. in the region of minute bubble formation. To exclude any doubt about their origin, the bubbles adjacent to the electrode were analysed.

Course of electrode potential under the effect of rectangular alternating current

Figure 4 shows the dependence of the mean electrode potential in the borosilicate glass melt at 1225°C on a current density of rectangular alternating current at a frequency of 47.5 Hz. The dependence corresponds to that found for a sinusoidal alternating current (cf. Figure 3b) except that the effect on the mean electrode potential is far more distinct here. This particularly concerns the very extensive fluctuations of the mean potential of both electrodes in the transition range between 100 and 250 mA·cm⁻². This transition area corresponds to the limits in the bubble development in Table 1. It can be shown that there is no substantial difference between the mean value (and hence also between the charge transferred) of sinusoidal and rectangular current $\bar{\imath}$ at the same effective value i. As Tulloch has shown in [11] and it can be easily derived, $\bar{\imath} = (2\sqrt{2}/\pi)i = 0.9i$ applies for the sinusoidal course while $\bar{\imath} = i = i_{max}$ for the rectangular course.

Figures 13a, b, c show the courses of the instantaneous potential of a platinum electrode in borosilicate glass melt at low current densities of 15 to 50 mA·cm⁻² at 1225°C. It is seen that a delay on the anodic course starts to appear with 30 mA·cm⁻². The lower limit in bubble development corresponds to the onset of that delay. The courses in the cathodic half-period show a hint of delay at the beginning starting at 30 mA·cm⁻² and another
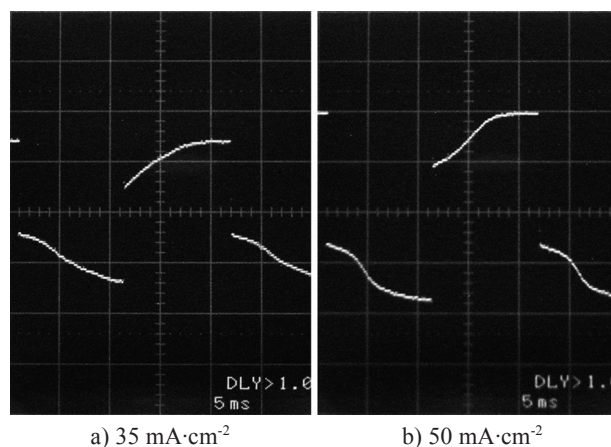

a) 35 mA·cm⁻²   b) 50 mA·cm⁻²

Figure 14. Potential courses in borosilicate glass melt at low current densities (1100°C, 47.5 Hz, 1.0 V/d).

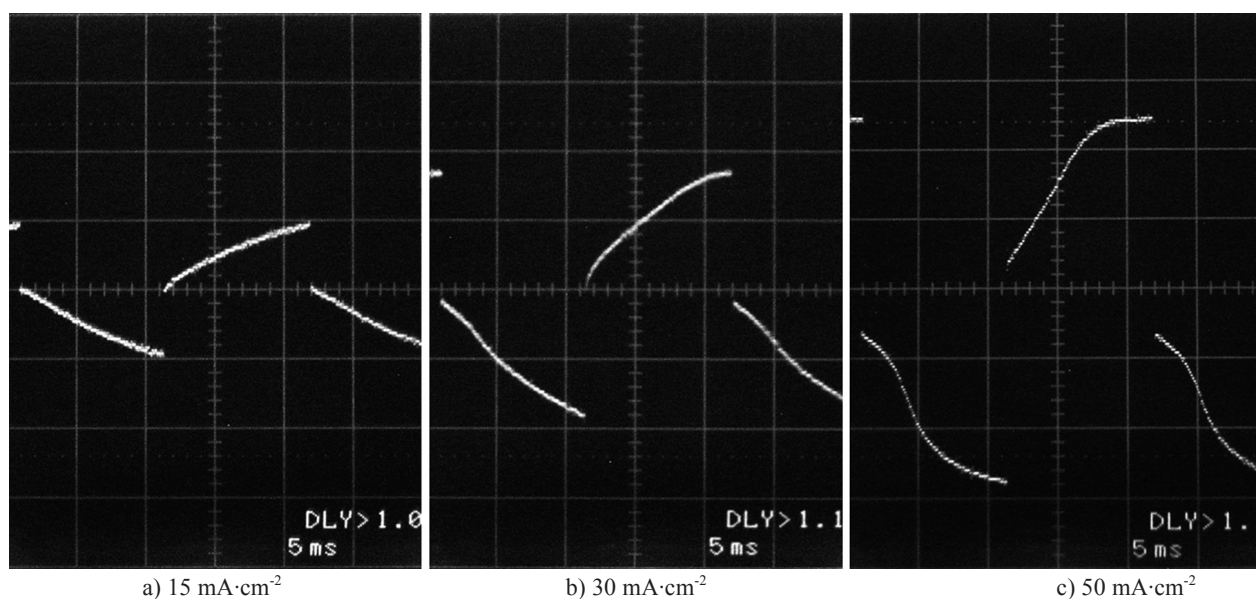a) 15 mA·cm⁻²   b) 30 mA·cm⁻²   c) 50 mA·cm⁻²

Figure 13. Potential courses in borosilicate glass melt at low current densities (1225°C, 47.5 Hz, 0.5 V/d).

delay at the end starting at 50 mA·cm⁻². The behaviour at the temperature of 1100°C at low current densities is similar (Figures 14a, b). The potential elevation in both half periods increases with the current density at both temperatures. Above 100 mA·cm⁻², the non-stability of the course at a constant current density (Figures 15a, b, c) corresponding to the non-stability of the mean electrode potential in Figure 4 and to the non-stability in the bubble development starts. Above 250 mA·cm⁻², courses with a relatively low potential increase in the anodic half-period and two delays in the cathodic one settle at 1225°C (Figure 16a). At 1100°C, an additional potential increase on the end of the anodic half-period starts by 250 mA·cm⁻² (Figure 16b). This explains the distinct increase of the mean electrode potential in Figure 3a. Such an increase was not found at 1225°C up to 500 mA·cm⁻². In some instances, including high current densities (e.g. in Figures 15a, c, and 16b), an inexpressive S – shaped anodic course can be seen. This indicates the possibility of two anodic reactions.

The potentials courses in the soda-lime-silica glass melt differ from the previous ones by a substantially lower ohmic drop as might be expected. The proper potential courses at low current densities (Figures 17a, b) are similar to those for the borosilicate glass melt. At about 100 mA·cm⁻², a rather distinct break in the anodic course appears indicating the possibility of two anodic reactions (Figure 17c). The courses at higher current densities (Figures 17d, e) show one distinct anodic wave and one cathodic one, the anodic wave shortening and the cathodic one extending at the highest current density of 500 mA·cm⁻².

Figures 5 to 7 summarize the potential changes with respect to the rest value (which is not always identical with a zero position in the oscillograms) attained on the end of the anodic and cathodic half-periods, in some instances also during their course, as a function of current density. A comparatively high dissipation of the values in Figures 5 to 7 is caused, in addition to the fluctuations of the courses above 100 mA·cm⁻², also by a relatively high ohmic drop in the borosilicate glass melt exceeding the potential changes in many cases. The reproducibility of these results can be assessed by a comparison of the two independently obtained dependences involved in Figure 7. Figure 5 summarizes the potential changes in the borosilicate glass melt at 1225°C. The potential at the end of the anodic half-period, which is identical with that at the beginning of the cathodic half-period, increases with a current density up to about 80 mA·cm⁻² where it stagnates at about 0.5 V. Above 100 mA·cm⁻², the anodic potential again increases up to 150 mA·cm⁻² and then decreases to 0.4 − 0.45 V. The potential at the end of the
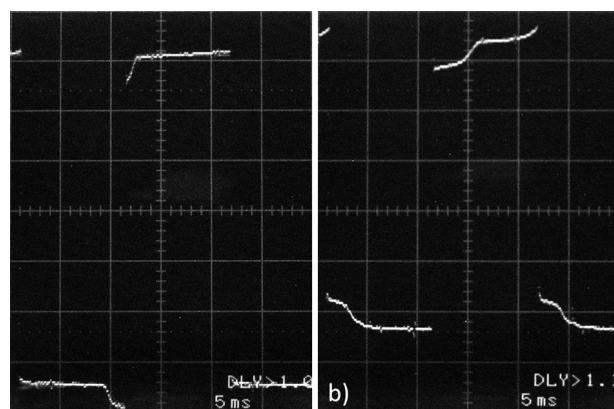
a) 1225°C, 500 mA·cm⁻²   b) 1100°C, 250 mA·cm⁻²

Figure 16. Potential courses in borosilicate glass melt at high current densities (47.5 Hz, 2.0 V/d, 2.0 V/d).
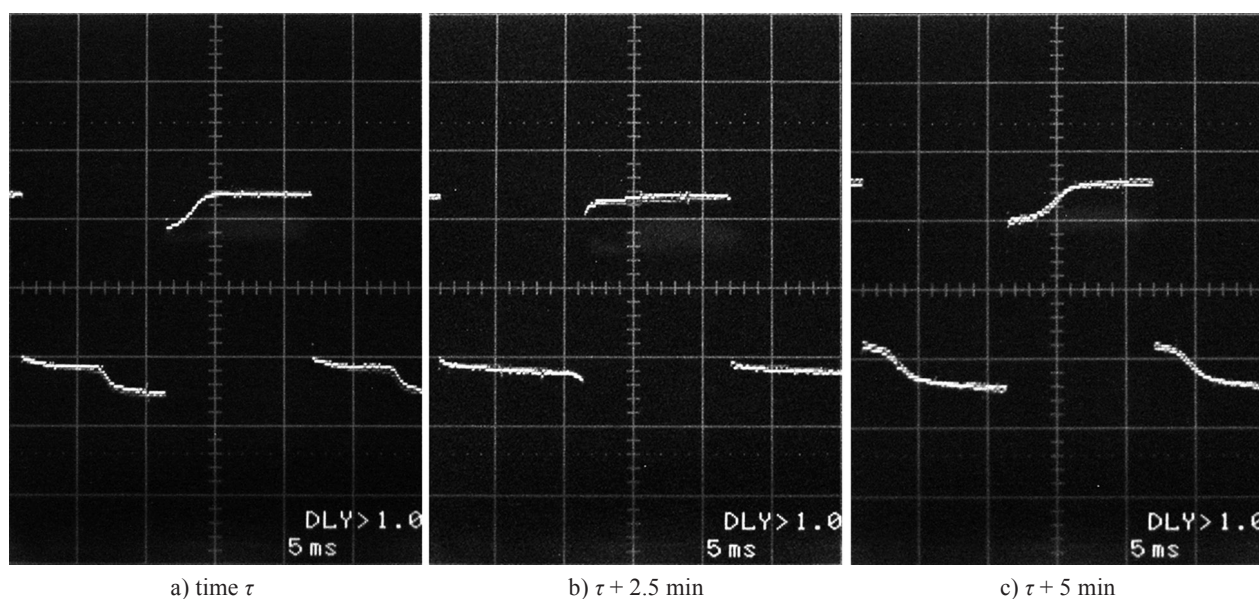

a) time τ   b) τ + 2.5 min   c) τ + 5 min

Figure 15. Potential courses in borosilicate glass melt in the non-stability region (1225°C, 180 mA·cm⁻², 47.5 Hz, 2.0 V/d).

cathodic half-period decreases up to a load of 120 mA·cm⁻² to almost −0.7 V. Beginning with 180 mA·cm⁻², the cathodic potential attains two very different levels (cf. Figures 15, 16a). The potential stays on the moderately positive level of about 0.1 V during most of the half-period. The potential at the end of half-period decreases gradually up to 0.7 V and its fluctuation occurs between 120 and 180 mA·cm⁻². At a temperature of 1100°C (Figure 6), the limit at about 80 mA·cm⁻² where the anodic potential attains about 0.65 V manifests itself as well. Above this current density, very extensive fluctuations of the ultimate anodic potential between a lower and a higher value appear, where both the values rise with increasing current density. The ultimate cathodic potential also shows very extensive fluctuations between 100 and 180 mA·cm⁻² that attain two levels to settle at 250 mA·cm⁻² at a similar value as is seen in Figure 5, i.e. −0.6 V. No substantial change in the course of the dependence was found if a molybdenum reference electrode was used instead of a platinum one.

In the model soda-lime-silica glass melt (Figure 7), a hint of a delay on the increase of anodic potential at about 0.3 V manifests itself between 30 and 80 mA·cm⁻² and the anodic potential then increases again up to about 0.6 to 0.7 V at a current density of 350 mA·cm⁻². The potential in the cathodic half-period decreases up to about 150 mA·cm⁻² where it attains values of −0.6 to −0.7 V that do not further change appreciably.

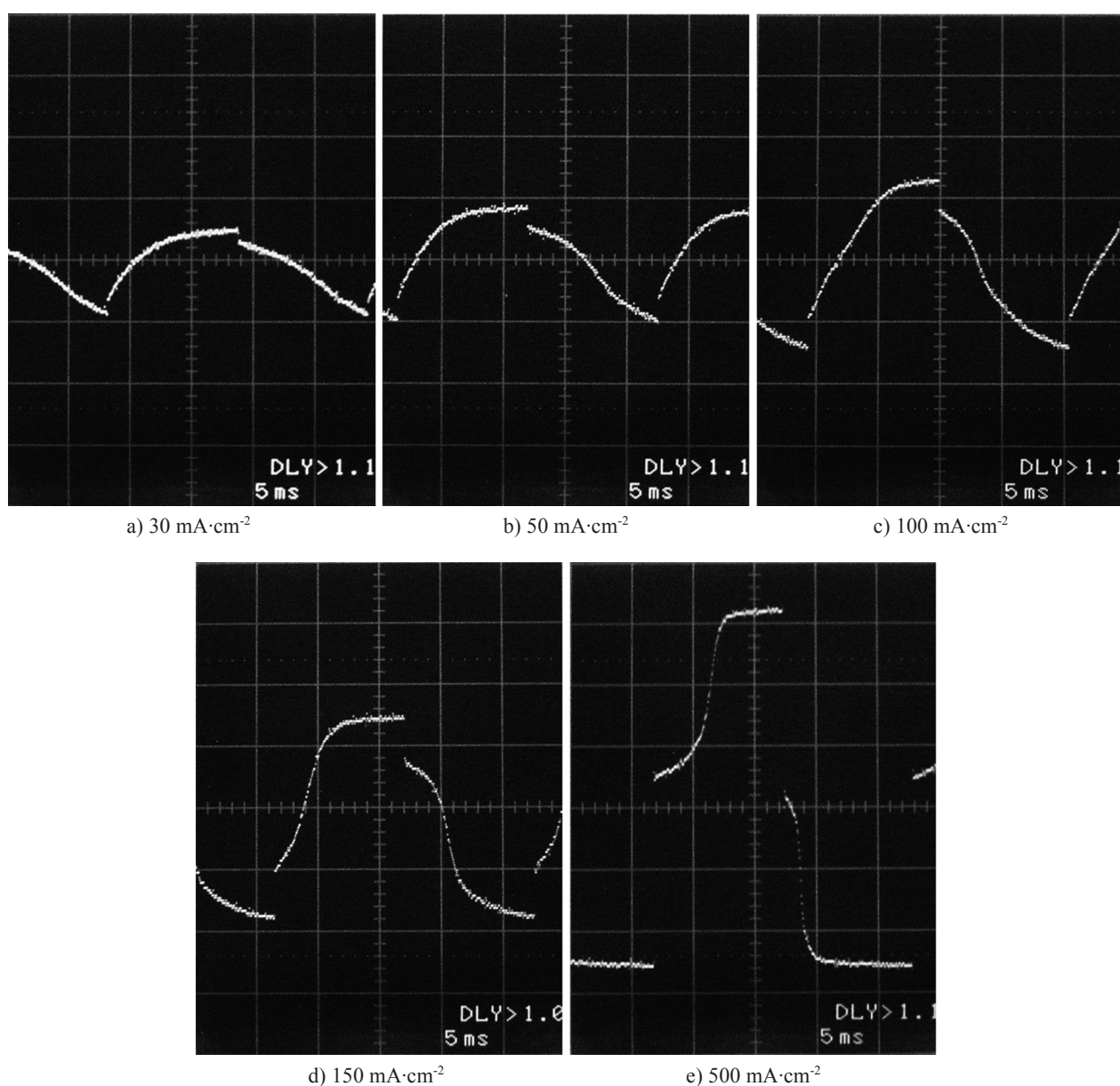a) 30 mA·cm⁻²   b) 50 mA·cm⁻²   c) 100 mA·cm⁻²

d) 150 mA·cm⁻²   e) 500 mA·cm⁻²

Figure 17. Potential courses in soda-lime-silica glass melt. 1225°C, 47.5 Hz, 0.5 V/d. a – 30 mA·cm⁻², b – 50 mA·cm⁻², c – 100 mA·cm⁻², d – 150 mA·cm⁻², e – 500 mA·cm⁻².

A possible explanation of the limits in
bubble development and a possible
association between bubble development
and the increased corrosion of
platinum by alternating current

Direct observation of bubble development has shown that there are three more or less distinct limiting current densities in that development. It has also been shown that the changes found in the course of the electrode potential correspond principally to those limits.

The limits of rapid bubble development at 220 or 250 mA·cm^{-2}, respectively, found in borosilicate glass melt represent about half of the limits for oxygen bubble development found by Higgins [1]. On the contrary, the corresponding ratios of current density to frequency of 4.4×10^{-3} and 5.0×10^{-3} A·sec·cm^{-2}, respectively, are about two-times higher than the average value of 2.4×10^{-3} A·sec·cm^{-2} given by Higgins [1]. Hence, taking into account the different experimental conditions, there is no principal contradiction.

According to the results of a number of papers involving different electrolytes summarized by Erdey-Grúz [12], oxygen development on a platinum anode cannot occur until an oxidic layer is formed, which needs a charge of 2×10^{-3} C·cm^{-2}. This value corresponds to a current density of 200 mA·cm^{-2} at 50 Hz, i.e. at the duration of a half-period of 10^{-2} sec. This current density is in principal agreement with the values given in the paragraph above. As the development of minute bubbles was safely found at as low a current density as about 30 mA·cm^{-2} in the presented work, it is necessary to presume that an oxidic layer persists on the electrode under the described experimental conditions. The comparatively long period of setting the constant electrode potential before the measurement enables the formation of that layer. At the lowest current densities, both anodic and cathodic current is probably transferred presumably by an alternating increase and reduction of the oxidic layer beside a small share of capacity current. The approximately linear potential courses under the effect of the rectangular current found in this area correspond to this assumption. At a current density of about 30 mA·cm^{-2}, the development of minute bubbles associated with a delay on the anodic course starts at a potential of 0.5 V at 1225°C and one at 0.65 V at 1100°C, respectively. These potentials are not much higher than the value of 0.4 V given by Maric et al. [7] as the limit for the first step in oxygen development described in the introduction. Those potentials are also in principal agreement with the potentials at the end of the first wave found for the nearest current densities and temperatures by Higgins [4]: 0.52 V at 83 mA·cm^{-2} and 1200°C and 0.58 V at 25 mA·cm^{-2} and 1100°C, respectively. In the soda-lime-silica glass melt, bubble development starts at a lower voltage of 0.30 V. As a probable consequence of oxygen development, two delays appear in the cathodic course: at the beginning and at the end. The first one that occurs at already moderately positive potentials is probably associated with a reduction of the dissolved oxygen. The comparatively short duration of that delay that represents only about 1/3 to 1/2 of the duration of the anodic period is in agreement with this interpretation. The second delay that occurs at substantially more negative potentials is probably associated with a reduction of the bubbles on the electrode. The course of the cathodic polarization curve in Figure 1 where the reduction of developed bubbles finishes at as negative a potential as −0.65 V and also the reduction of the anodic products between -0.4 and −0.9 V found by Maric et al.[7] is in agreement with this explanation.

Between 80 and 150 mA·cm^{-2}, changes in the course of the anodic potential occur in all the cases involved in Figures 5-7. After $0.6 - 0.7$ V is reached, a greater or lesser potential decrease or at least a break in potential course occurs, which is followed by fluctuation of the anodic and cathodic potentials in the borosilicate glass melt. According to Maric et al. [7], the oxidation of platinum to PtO$_2$ that does not necessarily have to be followed by oxygen development can occur at these potentials. The transition to another anodic reaction may be associated with changes in the amount of bubbles developed and in the properties of the oxidic layer on the electrode. Moreover, the release of bubbles also starts at about 100 mA·cm^{-2}. The released bubbles are not available for a backward reduction and, in addition to that, the bubble release is associated with strong convection in the vicinity of the electrode. These effects may cause a backward decrease of the anodic potential and non-stability of electrode behaviour may thus result. As the cathodic half-period follows the anodic one, the non-stability can manifest itself in both half-periods. The periodic reduction of the oxidic layer necessary for oxygen development and its reforming in the anodic half-period also cannot be excluded even if this cannot be confirmed on the basis of the cathodic courses found. The total reduction of this layer does not have to occur on the entire electrode surface.

A further increase of the current density results in a rise of the potential elevation and/or in the increasing release of bubbles. This can lead to the anodic potential maintaining a high value during most of the half-period (as is probably the case in the soda-lime-silica glass melt) or, on the contrary, the greater release of bubbles associated with increased convection can cause a greater supply of O^{2-} ions to the electrode and thus set the anodic potential at a low value. Moreover, as has already been shown, the charge transferred at current densities above 200 mA·cm^{-2} is sufficient for the reformation of the oxidic layer on the electrode. This may also contribute to the more stable electrode behaviour above 200 mA·cm^{-2}. Except for the range of the highest current densities in the borosilicate glass melt at 1100°C, the high positive values of anodic potential exceeding 1 V given by Higgins [4] for oxygen development were not found.

The differences observed in the behaviour of the platinum electrodes in the three investigated instances, i.e. at both temperatures in the borosilicate glass melt

and in the soda-lime-silica glass melt are apparently associated with differences in the parameters affecting electrode behaviour, especially the rate of oxygen diffusion from the electrode, the oxygen solubility in the glass melt and the concentration of oxygen ions in the glass melt.

There is another possible consequence of the release of oxygen bubbles out of the reach of their backward reduction above about 100 mA·cm⁻². In an arrangement with a pair of identical electrodes where the rectifying effect is excluded, the resulting deficit of anodic products can be compensated only by another cathodic reaction. The reduction of Fe(III) to Fe(II), reduction of Fe(II) to Fe(0) and reduction of Si(IV) to Si(0) can be taken in consideration. The total amount of iron of only 0.03 wt. % as Fe_2O_3 was found by the RFA method in both of the investigated glasses. The course of the cathodic polarization curve found for the original surface with no conclusive effect between −0.4 and −0.6 V in Figures 1 and 2 is in accordance with the low iron content. On the other hand, the continuous and progressive increase of the cathodic current starting at about −0.8 V indicating the starting reduction of Si(IV) as a major glass component can be seen especially in Figure 2. The cathodic potential attained in both glass melts under the effect of alternating current is not far from that value. As silicon attacks platinum, which has also been demonstrated by Higgins [1], the platinum corrosion observed along with high oxygen bubble development may be associated with the oxygen development via the resulting reduction of silicon even if the oxidation of platinum by oxygen cannot be excluded. The suggested mechanism of secondary platinum corrosion could explain particularly the release of the comparatively large platinum particles observed in the quoted paper. A distinctive blackening of the glass adjacent to electrodes in soda-lime-silica glass melt could be observed also in the presented work after direct observation of bubble development even if the delay at alternating current densities above 200 mA·cm⁻² did not exceed 1 hour.

The described results show that the behaviour of a platinum electrode in a glass melt under the effect of alternating current is rather a complicated phenomenon depending on the current density, glass composition and temperature. A more accurate explanation of the described behaviour would need another detailed investigation beyond the scope of the presented work.

CONCLUSIONS

1. The development of minute oxygen bubbles on a platinum electrode in borosilicate glass melt by the effect of alternating current at a frequency of 50 Hz starts at as low a current density as roughly 30 mA·cm⁻². Above approximately 100 mA·cm⁻², the bubbles alternatively appear and disappear. Bubble release from the electrode starts at approximately the same current density. The steady development of large bubbles begins between 220 and 250 mA·cm⁻².

2. Bubble development in borosilicate glass melt at a temperature of 1100°C is higher than that at 1250°C. The limits in bubble development at about 100 and especially at 220 and 250 mA·cm⁻² are also more distinct at a temperature of 1100°C.

3. The described limits in bubble development correspond to changes in the course of the electrode potential and in its mean value. An explanation of the non-stability in bubble development between 100 and 220 or 250 mA·cm⁻² based on the alternating transition between two mechanisms of oxidation of O^{2-} ions described in the literature and/or on the alternating reduction of the layer of oxidic products necessary for oxygen development has been suggested. The limit of the steady development of large bubbles is in accordance with the limiting value for oxygen development of about 200 mA·cm⁻² given in the literature.

4. Bubble development in soda-lime-silica glass melt also starts at a low current density of 40 mA·cm⁻². Less distinct fluctuations in bubble development occur above approximately 80 mA·cm⁻². No other limit in bubble development has been found up to 500 mA·cm⁻².

5. A possible association between the release of oxygen bubbles and the corrosion of the platinum material by silicon as a consequence of the deficit of anodic products able to be reduced in the cathodic half-period has been suggested.

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