

Influence of alternating current frequency on the corrosion behaviour of molybdenum electrodes in glass melts

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Literature data that show the complicated course of the frequency dependence of the corrosion rate with a maximum and a minimum were confirmed for several glass types. The results obtained for lead glasses demonstrate that in the region of corrosion retardation the depolarization and the corrosion rates are a function of the ratio of current density to the square root of frequency. At the frequency of minimum corrosion rate, local maxima of mean electrode potential and of voltage are found, which are related to the course of the potential in the anodic half-period. The proposed explanation of this behaviour is based on the effect of protective layers that would be destructed by oxygen evolution at lower frequencies.

Einfluß der Wechselstromfrequenz auf das Korrosionsverhalten von Molybdänelektroden in Glasschmelzen

Die vorliegende Arbeit bestätigt für verschiedene Gläser Literaturdaten über den komplexen Verlauf der Frequenzabhängigkeit der Korrosionsgeschwindigkeit mit einem Maximum und einem Minimum. Die an Bleigläsern erhaltenen Ergebnisse zeigen, daß im Bereich der Verzögerung der Korrosion die Depolarisation und die Korrosionsgeschwindigkeit vom Verhältnis der Stromdichte zur Quadratwurzel der Frequenz abhängig sind. Bei der Frequenz, bei der die geringste Korrosionsgeschwindigkeit auftritt, wurden lokale Maxima des mittleren Elektrodenpotentials und der Spannung gefunden, die mit dem Potentialverlauf während der anodischen Halbperiode im Zusammenhang stehen. Eine mögliche Erklärung für dieses Verhalten wird darin gesehen, daß Schutzschichten durch Sauerstoffentwicklung bei niedrigen Frequenzen zerstört werden.

1. Introduction

In electric glass melting, electrode corrosion may be a limiting factor. The corrosion of molybdenum electrodes is due to molybdenum oxidation by some glass melt components, particularly by the oxides of lead, arsenic, antimony and by sulphate anions. It proceeds as metal corrosion in the electrolyte in which the mentioned substances act as corrosion depolarizers. The alternating current (a. c.) as such would speed up corrosion considerably. This effect is explained by Dévay's theory [1] according to which the alternating current may increase the mean value of the anodic current which is a measure of corrosion. According to this theory, the corrosion rate rises with current density and drops with its frequency.

The results of a previous paper [2] demonstrate that the frequency dependence of the corrosion rate within the range of tens to hundreds Hertz is more complicated, having a maximum and a minimum mostly at frequencies lower than 50 Hz. This was confirmed for several glass types containing various depolarizers: four lead glasses, a barium crystal glass, two TV glasses, a soda-lime-silica glass and a Pyrex-type glass refined by NaCl [2 and 3]. In all lead glasses studied the courses of frequency dependence of the corrosion rate and those of lead precipitation

rate were quite similar. The maximum and minimum frequencies increase with increasing current density.

These findings have been used in Czechoslovakia for several years to reduce the corrosion of molybdenum electrodes in electric melting of lead glasses by the application of a current of lowered frequency. This is why it is of great importance to explain the complicated shapes of current frequency-corrosion curves. This paper presents a survey of the main findings obtained so far.

2. Corrosion rate as a function of current density to frequency ratio

The dependence of the corrosion loss and of the amount of precipitated lead on the frequency and density of the alternating current passing through the electrodes at the glass melting temperature was measured.

2.1. Experimental procedure

The used glass contained more than 10 wt% PbO and was refined by arsenic trioxide. The electrodes consisted of molybdenum wire with up to 30 ppm carbon.

A ceramic crucible with glass cullet was put into a vertical resistance-heated tube furnace. After the

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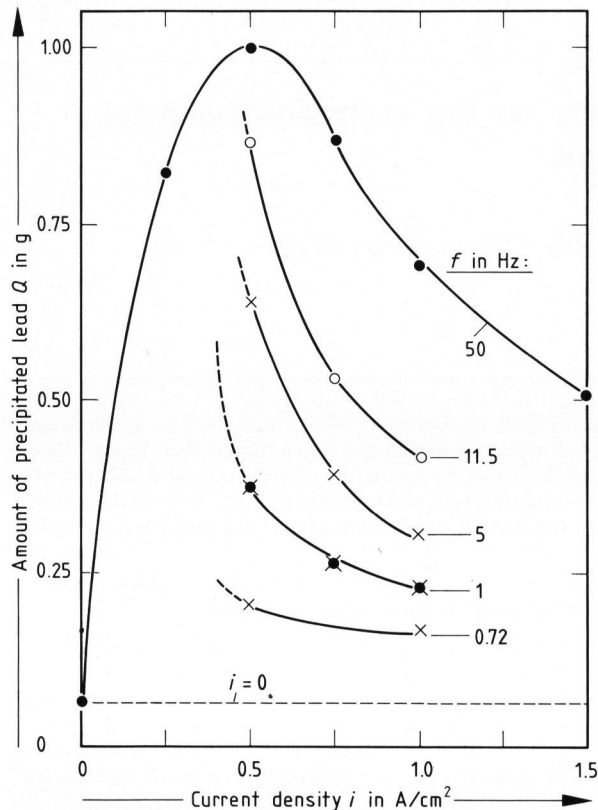
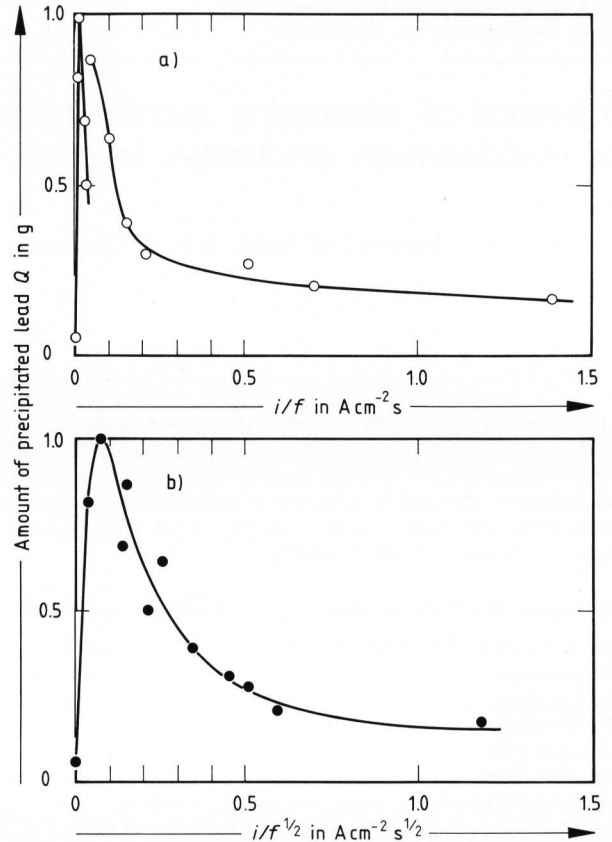


Figure 1. Amount of precipitated lead Q from the glass melt as a function of current density i with the frequency f as parameter.



Figures 2a and b. Amount of precipitated lead Q for various frequencies (see figure 1) as a function of the ratios i/f (figure a) and $i/f^{1/2}$ (figure b).

Table 1. Current density and frequency values at maximum corrosion rates in lead glass melts [2]

| | f in s^{-1} | i in $A\ cm^{-2}$ | i/f in $A\ cm^{-2}\ s$ | $i/f^{1/2}$ in $A\ cm^{-2}\ s^{1/2}$ |
|------------------------------|-----------------|---------------------|--------------------------|--------------------------------------|
| see [2, figure 2] | 30 | 0.50 | 0.017 | 0.091 |
| | 150 | 1.00 | 0.0067 | 0.082 |
| | 300 | 2.00 | 0.0067 | 0.115 |
| see [2, figure 7] | 10 | 0.25 | 0.025 | 0.079 |
| | 50 | 0.50 | 0.010 | 0.071 |
| | 200 | 1.50 | 0.0075 | 0.106 |
| mean value: | | | 0.01215 | 0.0906 |
| relative variation range: | | | 151 % | 49 % |
| relative standard deviation: | | | 61 % | 19 % |

glass was melted, two vertical parallel electrodes were introduced. Their upper parts were protected against corrosion by silica glass capillaries extending into the glass melt. The working area of each electrode was $0.75\ cm^2$ and the amount of molten glass in the crucible was 75 g.

In most cases the electrodes were fed by a frequency converter operating as a cycloconverter. The results for 50 Hz given in figures 1, 2a and b and table 1 were obtained for the main current feeding via a regulating and separation transformer, while the other data in table 1 resulted from the feeding by an amplifier controlled by a generator.

After 7 h the experiment was finished by quick temperature lowering, followed by self-cooling in the furnace. The crucible with the electrodes and the glass was cut into plates perpendicular to the axis with the aid of a diamond saw. Then the loss of electrode diameters was measured by means of a microscope. The precipitated lead was separated mechanically from the bottom section, the glass residues were etched away by hydrofluoric acid and the total lead amount was weighed.

2.2. Results

Figure 1 shows the amount of precipitated lead on the molybdenum electrode in a lead glass melt at frequencies between 0.72 and 50 Hz and for current densities from 0.25 to $1.5\ A/cm^2$. In figures 2a and b these values are plotted as a function of the current density to frequency ratio (figure a) and as a function of the current density to the square root of frequency ratio (figure b). This range comprises the maximum corrosion rate as well as considerable corrosion suppression, without attainment of the corrosion minimum. It is obvious that the function of $i/f^{1/2}$ describes the whole range better. The dependence shows a fast rise from zero values to a sharp maximum and a decline towards higher values of the $i/f^{1/2}$

ratio. Table 1 contains the current density and frequency values from [2] at which the lead precipitation attains its maximum. This comparison shows also a considerably smaller variation of the $i/f^{1/2}$ values than of the i/f ones. This points to a significant role of diffusion in the kinetics of the corrosion processes in the frequency range of their retardation. On the other hand, the frequencies of minimum corrosion rate yield, according to the additional results, a constant i/f ratio rather than an $i/f^{1/2}$ one.

3. Products of molybdenum oxidation

Figure 3 describes the frequency dependence of the ratio α of the amount of precipitated lead to the equivalent electrode loss, assuming the oxidation of molybdenum to Mo^{6+} . The measurement of the necessary values was done in the way described in section 2.1., the current source being a cycloconverter and the 50 Hz mains only. With the exception of the range below the minimum frequency, the value of α is lower than 1, which corresponds probably to a lower mean oxidation stage and is in qualitative agreement with the results given by Rudolph et al. [4]. At the frequency of maximum suppression of the corrosion, the lead precipitation is reduced even more, and increases again below this frequency.

The study of the interface between the electrode and the lead glass melt showed that there are in general at least four phases in contact with glass: a layer of oxidation products, the thickness of which is of the order of 10 to $10^2 \mu\text{m}$, precipitated lead, uncovered molybdenum and a gaseous phase. The layer of oxidation products (which can consist of more phases) contains (in wt%) on the average 66 Mo, 12 Pb and 3 K, the rest being oxygen. This is not true for the initial atypical period lasting 2 to 3 h when intermediate products containing molybdenum, potassium and oxygen, are formed. The proportion of described interface types is not regular, but it may be found that both the proportion and thickness of the layer of oxidation products increase within the corrosion suppression range. This layer is much less compact under the minimum frequency and its composition approaches the composition in the initial period (figures 4a and b).

4. Electrode potential and voltage

The course and mean value of the potential of the pair of electrodes fed with rectangular alternating current were measured and at the same time the interelectrode voltage was followed (figure 5).

At frequencies near to the corrosion minimum both the mean electrode potential and the electrode voltage exhibit typical courses as presented in figure 6. The minimum corrosion rate frequency corresponds to the local maximum of positive potential and

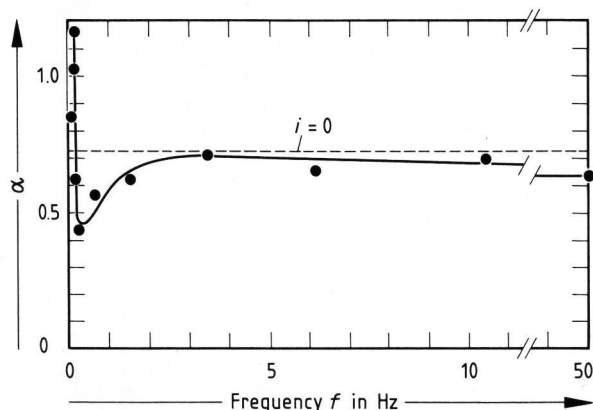
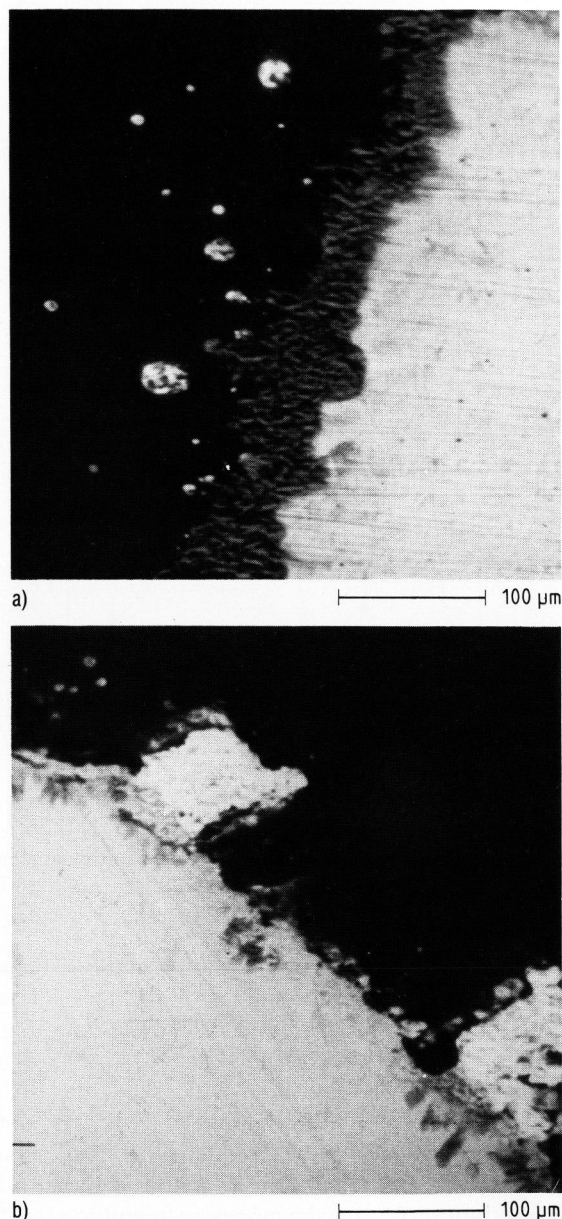


Figure 3. Frequency dependence of the ratio α of the amount of precipitated lead to the equivalent molybdenum loss.



Figures 4a and b. Electron microprobe images of the electrode with a 30% lead glass melt interface at the frequency a) above the corrosion rate minimum, b) below the corrosion rate minimum.

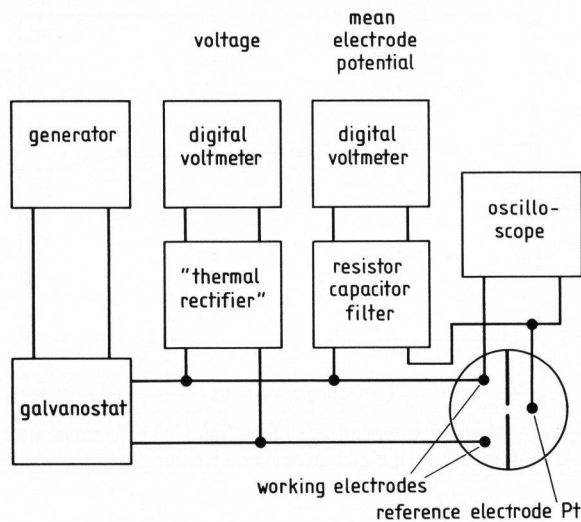


Figure 5. Measurement of electrode potential and voltage.

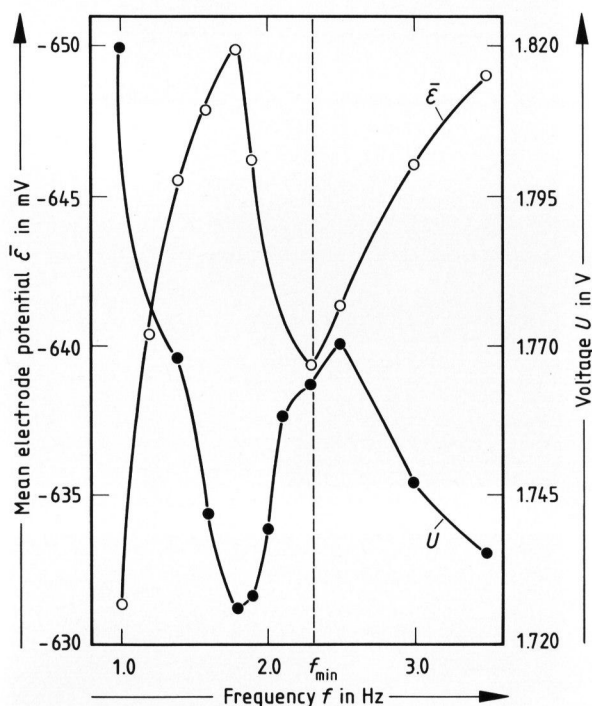
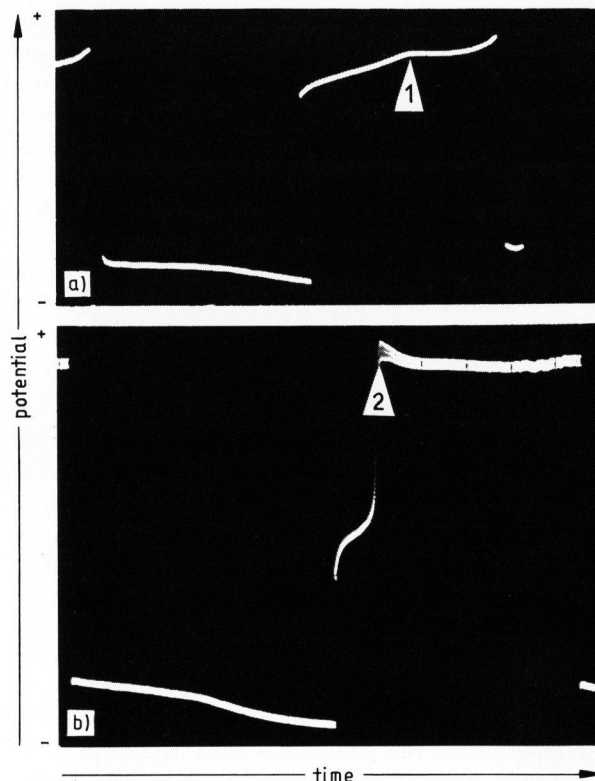


Figure 6. Typical frequency dependence of the mean electrode potential $\bar{\epsilon}$ and the voltage U . f_{min} = minimum corrosion frequency.

to the local maximum of alternating voltage. Figures 7a and b show typical courses of the molybdenum electrode potential at frequencies lower than that of minimum corrosion. In the potential course of the anodic half-period two breaks are seen, the first of which (figure 7a) is followed by a potential rise of the order of 10^3 mV if the frequency is low enough (figure 7b). The second break followed by an oscillation typical for gas development manifests itself at the lowest frequencies (figure 7b).

It was found that the onset of the first break corresponds to the minimum corrosion frequency. It



Figures 7a and b. Shape of the electrode potential course in lead glass melts, loaded by rectangular current of frequencies lower than the minimum corrosion frequency f_{min} , a) $f < f_{min}$, b) $f \ll f_{min}$.

may be shown and it was confirmed experimentally, too, that the frequency associated with the onset of the first break corresponds also to the frequency of the local mean electrode potential maximum and voltage maximum: The mean electrode potential $\bar{\epsilon}$ is given by

$$\bar{\epsilon} = \frac{2}{T} \left[\int_0^{T/2} \Delta\epsilon_a dt - \int_0^{T/2} \Delta\epsilon_k dt \right]$$

where $\Delta\epsilon_a$ and $\Delta\epsilon_k$ are the potential lifts in the anodic and cathodic half-period, T is the duration of the period and t the time. A similar equation applies also for mean voltage.

5. Discussion

The results given in section 4. show that the new process, which is followed by an increasing corrosion rate at lowest frequencies, and probably the retardation process, too, have their origin in the anodic half-period. The suppression of the corrosion may be caused either by the formation of a layer of oxidation products persisting also in the cathodic half-period, or by the formation of a layer deficient in alkali ions as carriers of conductivity. Increased occurrence of the layer of oxidation products was found in the corrosion suppression range. In any case, this suppression

involves a slow diffusion process, which is in agreement with the significance of the $i/f^{1/2}$ ratio shown in section 2.2. Diffusion overvoltage under a. c. conditions is proportional to the $i/f^{1/2}$ ratio [5]. This ratio and the $it^{1/2}$ product, respectively, are also involved in other equations describing the kinetics of non-stationary diffusion-controlled processes. From the viewpoint of Dévay's theory, slow diffusion as the rate-determining step does not agree with his assumptions and is responsible for the change of the polarization curves. The alternating current can then even lower the mean value of the anodic and cathodic currents [5].

An additional information can be provided by comparison of the corrosion behaviour of molybdenum and tin oxide electrodes. Figure 8 shows the courses of the mean potential and voltage for tin oxide electrodes. These courses are similar to those for the molybdenum electrodes. The reason for the break in the potential course in the anodic half-period should be then the same for both materials. In addition, there are also frequencies which are associated with reduced corrosion of the tin oxide electrodes [6]. Since it is hardly possible to assume passivation in the tin oxide electrodes, this decrease of corrosion must be caused by another process, which is probably the formation of a layer deficient in alkali ions. It is possible that this phenomenon takes also part – in addition to passivation – in the molybdenum electrode corrosion reduction before the first break in the potential course is attained. As for the new process which sets on at the minimum corrosion rate frequency and which is responsible for the destruction of the protective layers it is most probably the oxygen development by oxygen anion oxidation. The oxygen development may occur both on the molybdenum and tin oxide electrodes.

Direct observation of molybdenum electrodes in a special silica glass crucible by a slow-speed movie camera showed, however, that it is the second break which is associated with visible gas development from the electrodes. The onset of this break was followed at the same time by a sharp voltage drop and a potential lift drop. This may be explained by the fact that an extensive convection induced by the development of bubbles will damage the glass melt layer deficient in alkali ions near the electrodes, the formation of which is associated with the potential increase following the first break. The first break accompanied by the drop of the positive potential and increased corrosion is likely to be associated with the development of small oxygen bubbles that erode the layer of oxidation products. At the end of the anodic half-period these bubbles are not big enough to be released from the electrode and thus will be resorbed

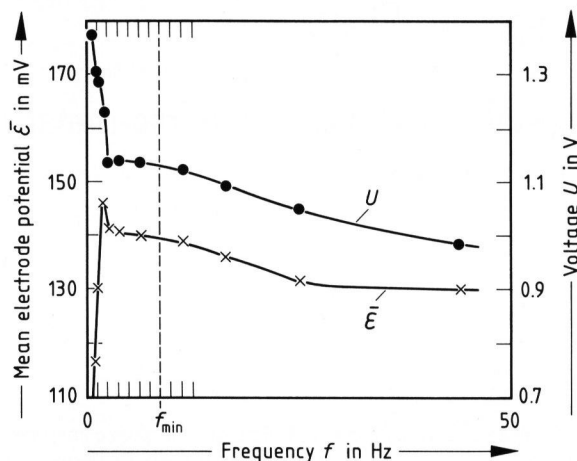


Figure 8. Frequency dependence of the mean electrode potential \bar{E} and the voltage U for tin oxide electrodes in a bottle glass.

again in the cathodic half-period. At frequencies below the corrosion minimum a pulsating electrode image was observed [7]. The rhythm of this pulsation was identical with the alternating current frequency. The development of oxygen as a competition process to molybdenum dissolution explains also the high values of α in the lowest frequency range.

The verification and perfectioning of this preliminary interpretation will require a number of additional experimental data.

6. References

- [1] Dévay, J.; Mészáros, L.: Mathematische Untersuchungen über die Wirkung des Wechselstromes auf die Korrosion. T. 1. Über die Möglichkeit der Beschreibung der auf einer homogenen Metalloberfläche stattfindenden anodischen und kathodischen Vorgänge durch Tafelsche Gleichungen des gleichen Typs. *Acta Chim. Acad. Sci. Hung.* **43** (1965) p. 25–31.
- [2] Matěj, J.; Staněk, J.: Electric glass melting with low-frequency current. *Glastech. Ber.* **61** (1988) no. 1, p. 1–4.
- [3] Hromádka, L.: Corrosion of electrodes for electrical melting of glass. (Orig. Czech.) Institute of Chemical Technology, Prague, thesis 1989.
- [4] Rudolph, T.; Bryan Balazs, G.; Rüssel, C. et al.: Electrochemical study on the corrosion of molybdenum electrodes in lead glass melts. *Glastech. Ber.* **61** (1988) no. 7, p. 177–183.
- [5] Erdey-Grúz, T.: Kinetics of electrode processes. Budapest: Akadémiai Kiadó 1972. p. 128–131, 314–319.
- [6] Matěj, J.; Bernard, V.: The effect of alternating current on the corrosion of tin oxide electrodes in lead crystal glass. (Orig. Czech.) In: Proc. 8th Conference on Electric Glass Melting, Prague 1989. Ústí n. Labem: Dům techniky ČSVTS 1989. p. 22–28.
- [7] Matěj, J.; Němec, L.; Freivolt, Š.: Behaviour of molybdenum electrodes in molten glass under the influence of very low frequency current. (Orig. Czech.) In: Proc. 7th Conference on Electric Glass Melting, Ústí n. Labem 1986. Ústí n. Labem: Dům techniky ČSVTS 1986. p. 52–60. 90R0827