

THE EFFECT OF ELECTRIC FIELD ON THE CORROSION OF SnO_2 BY FUSED BORAX

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Relation between the free convective corrosion of SnO_2 specimens in borax melt at 1100 °C and the density of DC applied between SnO_2 and the melt was studied experimentally. The corrosion losses at and below the surface level of the melt increased linearly with time. In the case of cathodic connection of SnO_2 the corrosion rate increase linearly as the current density increased. In the case of anodic connection of SnO_2 the surface level corrosion rate decreased as the current density increased, while the rate of the sub-surface corrosion showed a rising trend as a result of turbulence caused by development of bubbles.

INTRODUCTION

The effect of electric field on the rate of dissolution (corrosion) of electrically conductive refractories in glass melts was studied experimentally from the point of view of possible protectoin of refractory furnace linings [1] as well as in connection with the use of these materials as electrodes for electric melting of glass [2]—[5]. The problem was dealt with theoretically by Hrma [6]—[9] who showed that when no additional side effects of the electric field take part in the process (penetration of mobile ions into the refractory, developments of gas bubbles, etc.) then, under the conditions of steady free convection in the melt, the following relation holds between the rate of dissolution u and the current density i :

$$u = u_0 + \alpha i, \quad (1)$$

where u_0 is the rate of dissolution in a current-free state, α is a coefficient defined as follows:

$$\alpha = \frac{1}{5} (4 + \rho_{1\infty}/\rho_{10}) (\rho_{20}/\rho_S) (\nu_1 e/kT) (D/\sigma), \quad (2)$$

where ρ_{10} and $\rho_{1\infty}$ is the density*) of the mobile (e.g. alkaline) component of the melt at the boundary and far from it respectively, ρ_{20} is the density of the material being dissolved in the melt at the boundary, ρ_S is the density of the body being dissolved, ν_1 is the number of elementary charges of the mobile cation, e is the electron charge, k is the Boltzmann constant, T the temperature, D the diffusion coefficient and σ the electric conductivity of the melt. The Nernst—Einstein relationship does not hold between D and σ , because D is related to particle mobility of the dissolved substance, while σ depends on the mobility of the mobile ions (e.g., the alkaline ones). Relationship (1) holds under the assumption that

$$(u/u_0 - 1)(\rho_{1\infty}/\rho_{10} - 1) \ll 1, \quad (3)$$

*) The density of a mixture component is defined as the mass of that component contained in a volume unit of space. Its physical dimension is ML^{-3} . It should be distinguished from the density in the pure state.

i.e., that either a) the relative increase in the dissolution rate as compared to that in current-free state is low, or b) the relative concentration jump at the boundary is small.

If the material being dissolved is a cathode, $i > 0$ and $u > u_0$, if it is an anode, $i < 0$ and $u < u_0$.) According to (1) at positive polarity of the refractory it should be possible to slow down or even eliminate its dissolution. Such a phenomenon was actually observed by Darcy [10] in a ZrO_2 -based material. On the other hand, Pavlovskij et al. [4], when using a positive polarity of SnO_2 , determined a still faster dissolution than at the same value of cathodic polarization. Matěj et al. [5] report a similar effect, although less remarkable and limited to low current densities only. They explained it by the development of gas bubbles arising as a product of the electrode reaction. The bubbles agitate the boundary layer not only by their own movement but also by the much more intensive surface convection.

The aim of the present study is to measure the dependence between the rate of the surface level and sub-surface corrosion of SnO_2 in molten borax and the density of dc at both polarities under the conditions of free convection. That particular experimental system was chosen because it is simple (it comprises only three oxidic components) the ratio between the melt and the refractory conductivity is extraordinarily favourable and the system is experimentally convenient (low melting temperature, easy removal of residual melt of specimens). The evaluation of the corrosion rate from the experimental data (which exhibited a relatively large dispersion) was carried out as described in the last section, where the results are discussed and compared with the relations (1) and (2).

EXPERIMENTAL

A platinum crucible conductively connected to the DC source was placed in the heating furnace on a supporting column (of Akor steel). An adapted camera tripod was employed for introducing the experimental specimen into the melt in the crucible. The vertical stand traverse was fitted as a holder carrying a corundum container in which the specimen was fixed by a corundum pin and provided with platinum current supply leads.

The direct current was supplied from a stabilized DC source Mesit YE-2T allowing stepped adjustment by 0.1 V. A milliamperemeter was fitted in the circuit.

The temperature was measured and controlled by Ni/Ni, Cr thermocouples. The measuring sensor was connected to a pyrometric millivoltmeter, the control sensor to a chopper bar controller. The system was calibrated by means of a standard Pt/Pt, Rh thermocouple.

All the experiments were carried out at 1100 ± 15 °C.

The test specimens $7 \times 7 \times 70$ mm in size contained at least 98.5% tin dioxide; the rest consisted of doping copper and antimony oxide additions.

Sodium tetraborate dehydrate A.R. was dehydrated by fusion in a platinum dish. Amounts of 30 g were used in each individual experiment.

The corrosion experiments were carried out at an immersion depth of 20 mm, while the submerged specimen end was at a distance of 5 mm from the crucible

*) Conventionally, cathodic current density is considered as being negative. However, when defining vector current density as a flow of electrons, then the scalar cathodic current density has a positive sign. As in most of the present experiments the specimen was a cathode, the later possibility was chosen. The sign in equation (1) should therefore be understood in this sense.

bottom. The corrosion proceeded in current-free state, as well as under constant current which was adjusted manually. When neglecting the change the surface area of specimens due to corrosion the current density in the anodic connection was 39 mA/cm² and that in the cathodic connection was 18 and 19 mA/cm². The experiments took from 0.5 to 10 hours.

After the experiment the residual melt was removed from the specimen by 1-hour etching in a mixture of concentrated HCl — 30% H₂O₂ — H₂O (1 : 1 : 2). The loss of material at various immersion depths was then measured (at measuring intervals of 3 mm ± 0.02 mm) with an accuracy of ± 0.01 mm.

EXPERIMENTAL RESULTS

The corrosion at the surface level and that below it formed two separate regions divided by a discernible edge. The corrosion profiles at the surface level showed the typical neck shape. The sub-surface corrosion profiles after eight-hour exposure are shown in Fig. 1. At the cathodic connection and in the current-free experiment the profiles were virtually linear, and thus did not correspond to the theoretical relationship

$$y = y_0(x + x_0)^{-1/4}, \quad (4)$$

where y is the corrosion loss, x is the depth below level, y_0 is a coefficient depending on the physical properties of the system, and x_0 is a correction for the effect of the surface level corrosion. The profiles in Fig. 1 indicate that the bottom part of the

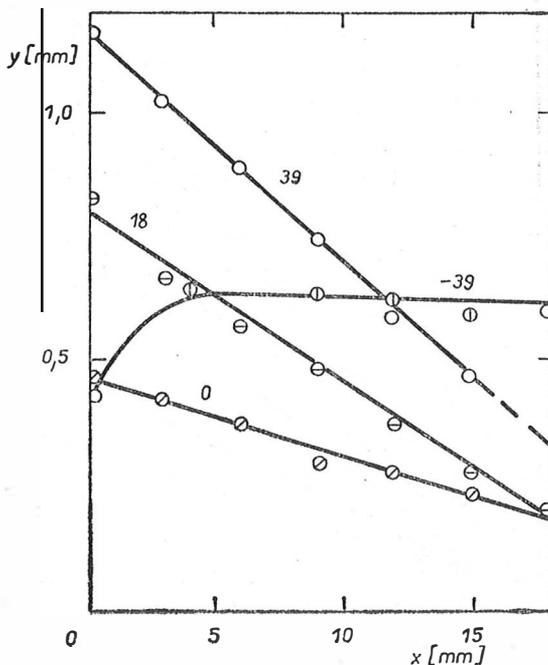


Fig. 1. Corrosion profiles after 8 hours. The numbers at the curves specify the current density in mA/cm².

specimen was relatively protected. This may be due to temperature and current density non-uniformities along the specimen. In the case of the anodically connected specimen the corrosion was virtually uniform, independent of the depth of immersion, with the exception of the part closely at the surface level exhibiting somewhat slower dissolution. That uniformity of dissolution implies that the process was not controlled by free convection. As the development of gas bubbles was observed in the neighbourhood of the specimens, the turbulent flow was probably brought about by the growth and movement of bubbles as well as by the surface tension gradient rising on their surfaces due to non-uniform concentration field.

The time dependence of corrosion loss was approximated for both types of corrosion by a straight line corresponding to the equation

$$y = u(t + t_0) \tag{5}$$

where t_0 is the correction for the transient period during which the steady state was established. In the case of sub-surface corrosion the losses were taken in a depth of $x = 9$ mm below the level of melt, e.i., approximately at the middle of the immersed part of the specimen. The parameters in equation (5) were determined under the assumption that t_0 did not depend on current density, so that the approximating straight lines pass through one point at coordinate t , the position of which depends

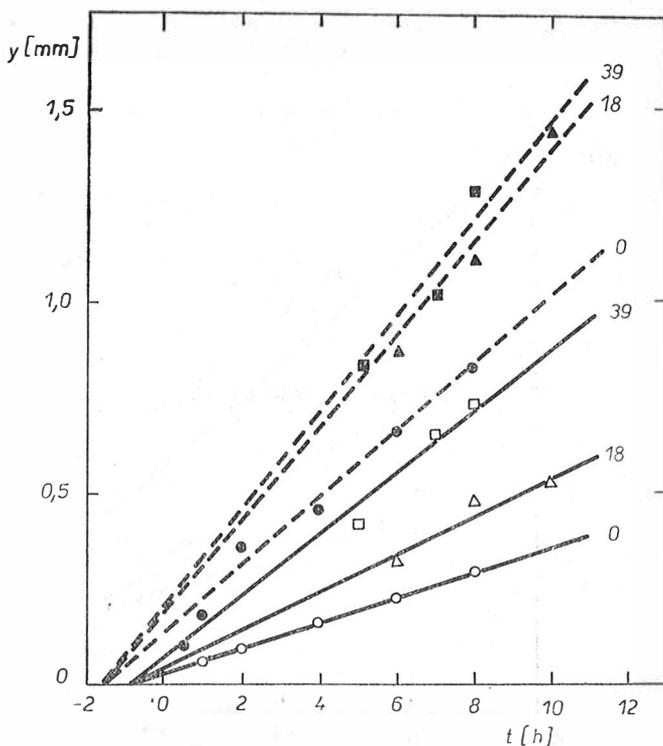


Fig. 2. The time dependence of corrosion. The full and dashed lines approximate the experimental data for the corrosion at and below the surface level, respectively. The numbers at curves specify the current density in mA/cm².

on the respective type of corrosion. For $i > 0$ these straight lines together with the experimental points are plotted in Fig. 2 and the corrosion rates for all the experimental values i are summarized in Table I.

Table I
The corrosion rates in 9 mm depth and at the surface level in terms of current density

i [mA/cm ²]	$10^8 u_0$ [m/s]	
	9 mm below the surface level	At the surface level
0	0.889	2.44
18	1.380	2.44
39	2.240	3.51
-39	2.200	1.98

When joining (1) and (5) one obtains

$$y = (u_0 + \alpha i)(t + t_0). \tag{6}$$

Fig. 3, where the difference $u - u_0$ is plotted in terms of i , indicates that equation (6) holds only for cathodic connection of the specimen, i. e., for dissolution controlled by free convection. The coefficients u_0 , α , and t_0 for the both types of corrosion are listed in Table II. The coefficient α is vitrually independent of the type of corrosion.

In order to compare quantitatively the experiments with theory, let us suggest an order estimate of α according to relationship (2). When taking $\frac{1}{5} (4 + \rho_{1\alpha}/\rho_{10}) \approx \approx 1$, $\rho_{20}/\rho_S \approx 0.2$, $v_1 e/kT \approx 8S/A$, $D \approx 10^{-11} \text{m}^2/\text{s}$ and $\sigma \approx 1S/\text{m}$, hence $\alpha \approx \approx 2 \times 10^{-11} \text{m}^3/\text{As}$. This result is in a very satisfactory agreement with the experimental value $\alpha = 3 \times 10^{-11} \text{m}^3/\text{As}$.

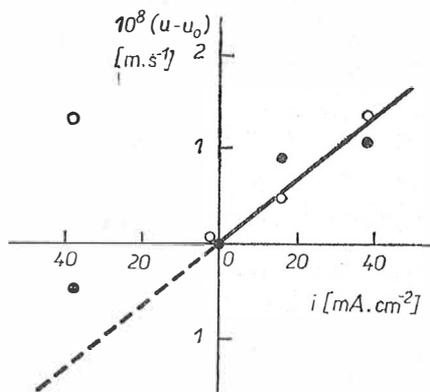


Fig. 3. Increment of corrosion rate vs. current density for the corrosion below the surface level (rings) and at the surface level (full dots). The straight line approximates this dependence at $i \geq 0$.

Table II

The parameters of the approximation function (6)

Type of corrosion	$10^8 t_0$ [m/s]	$10^{11} \alpha$ [m ³ /As]	$10^{-3} t_0$ [s]
Below the surface level	0.889	3.240	3.350
At the surface level	2.440		5.620

Fig. 3 and Table I show that in anodic connection of the specimen the rate of dissolution below the surface level exceeds considerably that corresponding to relationship (1) using the constant α from Table II. This is probably due to the turbulent flow induced by the developments of gas bubbles mentioned above. The rate of level corrosion is reduced as compared to the current-free state and is only slightly higher than would correspond to equation (1).

The different control mechanisms involved with cathodic and anodic connection are also indicated to by the temperature dependence of corrosion rate as measured by Pavlovskij et al. [4]. Whereas with anodic connection the activation energy was close to that of current-free dissolution and correspondent to a diffusion-hydrodynamic mechanism, the rate of SnO₂ dissolution with cathodic connection was virtually independent of temperature. Taking $u \gg u_0$ in equation (1) (which holds likewise for forced convection [6] dealt with by Pavlovskij et al.) then, if the condition (3) is satisfied, the dependence of u on temperature is given by the temperature dependence of α . This, however, is negligible according to (2), because the growth of D with temperature is compensated for by the increase in electric conductivity σ .

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VLIV ELEKTRICKÉHO POLE NA KOROZI SnO₂ ROZTAVENÝM BORAXEM

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Byla experimentálně sledována podhlinová a hladinová koroze SnO₂ v boraxu při 1100 °C za podmínek volné konvekce v závislosti na hustotě stejnosměrného proudu protékajícího mezi SnO₂ a taveninou. Velikost koroze y v závislosti na čase t a proudové hustotě i při katodickém zapojení SnO₂ lze aproximovat funkcí (6), kde $u_0 = \partial y / \partial t|_{t=0}$ je rychlost koroze při $i = 0$, t_0 je koeficient vyjadřující korekci na počáteční neustálené období a α je koeficient, jehož hodnota je rovna $3,2 \cdot 10^{-11} \text{ m}^3 \text{ A}^{-1} \text{ s}^{-1}$ a není závislá na druhu koroze. Teoretický vztah mezi α a vlastnostmi

систému byl odvozen v práci [8] a je vyjádřen rovnicí (2), kde ρ_{10} a $\rho_{1\infty}$ značí hustotu pohyblivé (např. alkalické) složky v tavenině na rozhraní a daleko od něj, ρ_{20} je hustota rozpouštěného materiálu v tavenině na rozhraní, ρ_s je hustota rozpouštěného žárovzdorného materiálu, ν_1 je počet elementárních nábojů pohyblivého kationtu, e náboj elektronu, k Boltzmannova konstanta, T teplota, D difúzní koeficient a σ měrná elektrická vodivost taveniny. Ačkoli přesné hodnoty některých z těchto veličin nejsou známy, hodnota odhadnutá podle (2) se shoduje s experimentálním výsledkem. Je-li SnO_2 anodou, platí sice vztah (5), kde $u = \partial y / \partial t$ je rychlost koroze, avšak podhladinová koroze je mnohem větší než odpovídá vztahu (6) s $\alpha = 3,2 \cdot 10^{-11} \text{ m}^3 \text{ A}^{-1} \text{ s}^{-1}$. Příčinou je vývin bublin vznikajících následkem elektrodové reakce. Bubliny působí silnou turbulenci, a to 1. vyrovnáváním povrchového napětí v neuniformním koncentračním poli, 2. svým růstem, 3. vztakovým pohybem. V hladinovém menisku je při anodickém zapojení SnO_2 rychlost koroze menší než při bezproudovém stavu, ale větší, než by odpovídalo extrapolaci z oblasti $i > 0$ podle vztahu (6).

- Obr. 1. Korozní profily po 8 hodinách koroze. Čísla u křivek udávají proudovou hustotu v mA/cm^2 .
 Obr. 2. Závislost koroze na čase. Plná čára aproximuje experimentální data pro podhladinovou a čárkovaná pro hladinovou korozi. Čísla u křivek udávají proudovou hustotu v mA/cm^2 .
 Obr. 3. Závislost přírůstku korozní rychlosti na proudové hustotě pro podhladinovou (prázdná kolečka) a hladinovou (plná kolečka) korozi. Příímka aproximuje tuto závislost při $i \geq 0$.

ВЛИЯНИЕ ЭЛЕКТРИЧЕСКОГО ПОЛЯ НА КОРРОЗИЮ SnO_2 ПЛАВЛЕННОЙ БУРОЙ

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Исследовали экспериментальным путем коррозию под уровнем и на нем SnO_2 в буре при 1100°C в условиях свободной конвекции в зависимости от плотности тока одного направления, протекающего между SnO_2 и расплавом. Величину коррозии y в зависимости от времени t и плотности тока i при катодном включении SnO_2 можно аппроксимировать функцией (6), где $u_0 = \partial y / \partial t |_{i=0}$ — скорость коррозии при $i = 0$, t_0 — коэффициент, выражающий коррекцию на исходный неустойчивый период и α — коэффициент, величина которого равна $3,2 \cdot 10^{-11} \text{ м}^3 \cdot \text{А}^{-1} \cdot \text{с}^{-1}$ и не зависит от вида коррозии. Теоретическое отношение между α и свойствами системы выведено в работе [8] и выражено уравнением (2), где ρ_{10} и $\rho_{1\infty}$ обозначает плотность подвижного (напр. щелочного) компонента в расплаве на пределе и далеко от него, ρ_{20} — плотность растворяемого материала в расплаве на пределе, ρ_s — плотность растворяемого огнеупорного материала ν_1 — число элементарных зарядов подвижного катиона, e — заряд электрона, k — константа Больцмана, T — температура, D — коэффициент диффузии и σ — удельная электропроводность расплава. Хотя некоторые величины точно неизвестны, величина, предполагаемая согласно (2) совпадает с экспериментальным результатом. Если SnO_2 служит анодом, то справедливо отношение (5), где $u = \partial y / \partial t$ — скорость коррозии, однако коррозия под уровнем гораздо больше, чем этому соответствует отношение (6) с $\alpha = 3,2 \cdot 10^{-11} \text{ м}^3 \cdot \text{А}^{-1} \cdot \text{с}^{-1}$. Причиной является развитие пузырьков, образующихся в результате последующей электродной реакции. Пузырьки вызывают сильную турбулентцию 1. выравниванием поверхностного напряжения в неuniformном концентрационном поле, 2. своим ростом, 3. поддерживающей силой. В мениске уровня при анодном включении SnO_2 скорость коррозии меньше, чем при состоянии без тока, но больше, чем это соответствовало бы экстраполяции из области $i > 0$ согласно отношению (6).

- Рис. 1. Коррозионные профили после 8 часов коррозии. Числа у кривых приводят плотность тока в mA/cm^2 .
 Рис. 2. Зависимость коррозии от времени. Сплошная линия аппроксимирует экспериментальные данные для коррозии под уровнем и штриховая линия для коррозии на уровне. Числа у кривых обозначают плотность тока в mA/cm^2 .
 Рис. 3. Зависимость прироста скорости коррозии от плотности потока для коррозии под уровнем (кружочки) и коррозии на уровне (полные кружочки). Прямая аппроксимирует эту зависимость при $i \geq 0$.