

Electrochemical determination of the oxygen activity in tin melts by means of the solid electrolyte method

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The measurements of oxygen activity in the tin melt were carried out under inert (light oxidizing) as well as under reducing (N_2 with 2 vol.% H_2 and 10 vol.% H_2 , respectively) conditions. As solid electrolyte (SE) material Y_2O_3 -, CaO- and MgO-stabilized zirconia was used in the form of a long tube closed at one end. A short SE tube closed at one end within an alumina tube was applied as industrial probe. The galvanic cells worked with a Pt/air and Me/MeO reference electrode and with electrical leads of steel, tantalum as well as rhenium wires. Under inert conditions (argon with 30 vol.ppm O_2) a saturation of the tin with oxygen is always obtained and SnO_2 is formed. Under reducing conditions the saturation of the melt with oxygen does not take place and no SnO_2 is formed. An equilibrium is adjusted between oxygen in the atmosphere and solute oxygen in the melt. At extremely low oxygen contents no equilibrium will be achieved. The lower operating temperatures of the probes were between 500 and 700 °C. The data taken from the literature were confirmed by EMF measurements (solubility of oxygen in liquid tin, molar free solution enthalpy of oxygen in tin, molar free standard enthalpy of formation of SnO_2). This kind of investigations is new as to the behaviour of the tin melt under forming gas and the defined addition of elements and compounds to the tin melt (Na_2SnO_3 , Na_2O , Na, Fe_2O_3 , Fe, MgO, Mg). Under reducing conditions and the addition of sodium or magnesium to the tin melt a quick decline of the oxygen activity can be recognized at the moment of addition. The melt becomes strongly deoxidized by the addition of these metals. The subsequent processes of deoxidation, which are different from metal to metal, have still to be investigated. No change of the oxygen activity in the melt was observed by addition of iron in the ppm range to the tin melt.

For the measurements alumina and a fireclay brick were used as crucible materials. The tin surface was either in immediate contact with the gas phase or was covered with a float glass melt. The oxygen activity of the tin melt was influenced by the crucible material and the float glass melt, too.

Elektrochemische Bestimmung der Sauerstoffaktivität in Zinnschmelzen nach der Festelektrolytmethode

Die Messungen der Sauerstoffaktivität in der Zinnschmelze sind sowohl unter inerten Bedingungen (leicht oxidierend) als auch unter reduzierenden Bedingungen (N_2 mit 2 Vol.-% bzw. 10 Vol.-% H_2) ausgeführt worden. Als Festelektrolyt (FE)-Material wurde Y_2O_3 -, CaO- und MgO-stabilisiertes ZrO_2 in Form eines einseitig geschlossenen Langrohres eingesetzt. Für die Industriesonde kam ein einseitig geschlossenes kurzes FE-Röhrchen in einem Sinterkorundrohr zum Einsatz. Die galvanischen Zellen arbeiteten mit einer Pt/Luft- bzw. Me/MeO-Vergleichselektrode und mit elektrischen Ableitungen aus Stahl-, Tantal- bzw. Rheniumdraht. Unter inerten Bedingungen (Argon mit 30 Vol.ppm O_2) wird stets eine Sättigung des Zinns mit Sauerstoff und damit die gleichzeitige Bildung von SnO_2 erreicht. Unter reduzierenden Bedingungen bleibt die Sättigung des Zinns mit Sauerstoff und damit die Bildung des SnO_2 aus. Es stellt sich ein Gleichgewicht zwischen dem in der Atmosphäre befindlichen und dem in der Schmelze gelösten Sauerstoff ein. Bei extrem kleinen Sauerstoffgehalten im System kommt es zu keiner Gleichgewichtseinstellung. Die unteren Einsatztemperaturen der Sonden lagen zwischen 500 und 700 °C. Durch EMK-Messungen konnten die Erkenntnisse aus der Literatur über die Sauerstoffaktivität in der Zinnschmelze bestätigt werden (Löslichkeit von Sauerstoff in flüssigem Zinn, molare freie Lösungsenthalpie von Sauerstoff in Zinn, molare freie Standardbildungsenthalpie von SnO_2). Neu sind die Untersuchungen zum Verhalten der Zinnschmelze unter Formiergas und beim definierten Hinzufügen von Elementen und Verbindungen zur Zinnschmelze (Na_2SnO_3 , Na_2O , Na, Fe_2O_3 , Fe, MgO, Mg). Bei Zugabe von Natrium bzw. Magnesium zur Zinnschmelze unter reduzierenden Bedingungen ist ein schnelles Absinken der Sauerstoffaktivität zum Zeitpunkt der Dotierung zu verzeichnen. Durch die Zugabe dieser Metalle wird die Schmelze stark desoxidiert. Die der Desoxidation nachfolgenden Prozesse, die von Metall zu Metall unterschiedlich sind, sind noch zu klären. Durch Zugabe von Eisen im ppm-Bereich zur Zinnschmelze konnten keine Veränderungen der Sauerstoffaktivität in der Schmelze beobachtet werden.

Für die Messungen wurden als Tiegelmaterial Sinterkorund und Schamottestein eingesetzt. Die Zinnoberfläche stand entweder direkt im Kontakt mit der Gasphase oder war mit einer Floatglasschmelze abgedeckt. Auch das Tiegelmaterial und die Floatglasschmelze beeinflussen die Sauerstoffaktivität in der Zinnschmelze.

1. Introduction

Since its development in the fifties by the British company Pilkington Brothers Ltd. the float glass process has revolutionized and widely replaced the conventional manufacturing processes flat and plate glass [1]. The hitherto usual processes of flat glass manufacture were based on variants of different drawing methods, which were characterized by technical problems and qualitative difficulties till the end [2]. The novelty of the float glass technology consists of transferring the hot glass melt by charge onto the tin bath into a glass ribbon of controllable thickness and extraordinarily high homogeneity. The contact of the hot glass melt with the metal bath under reducing conditions leads to process-caused interactions, which generate different glass defects in the production process [3]. In order to obtain a deeper understanding of the occurring corrosive action a careful control of several impurities is required. In the protective atmosphere and in tin the oxygen takes a key function in the float glass process. At constant temperature the activity of oxygen is influenced by the concentration and the oxygen affinity of the impurities in tin. The resulting compounds exceed their solubility limits in tin and slag formation occurs. For the measurement of oxygen activity in tin melts the solid electrolyte method is an alternative. In contrast to the conventional chemical analysis the electrochemical determination has three great differences. Firstly, it is not applicable to the sampling, secondly, the measurement result is yielded practically without delay and, thirdly, the activity of the elements as measured quantity is obtained. Besides a continuous notification is possible over longer periods.

The present paper deals with the measurement of the oxygen activity in tin melts by the use of the solid electrolyte method. The special points of view are considered which appear with the use of tin melts in the float glass industry.

2. Fundamentals

2.1 Solid electrolyte measuring method

The ceramic materials based on ZrO_2 and ThO_2 doped with bivalent or trivalent oxides have a high oxygen ion conductivity at higher temperature. Furthermore, these materials must have good thermal and chemical stability against oxidizing and reducing agents as well as against acid and basic oxides and sufficient thermo mechanical properties. All these properties make them suitable for the construction of solid electrolyte sensors for the meas-

urement of oxygen activity in melts. The solid electrolyte is manufactured by a ceramic process and sintered at $1700^\circ C$. The ceramic sample must have a high density and must be free of pores and cracks. The chemical compound has to match the conditions in the present melt. The solid electrolyte probes use the interaction of the chemical component with the solid state for signal representation. In [4 to 6] references are collected as to solid electrolyte materials and the possibility for insertion. The probes (Heraeus Electro-Nite, Houthaler (Belgium); Ferrotron, Moers (Germany)) are available for the measurement of the oxygen in steel and copper melts and for redox control in glass melts (Kühnrich & Meixner, Frankfurt/M. (Germany)). The development of this probe is based on [7].

Hitherto the oxygen measurements were carried out with probes in gases, in copper, steel, sodium and lead melts, which were developed in our research group [8 to 10]. In copper melts the measurement of oxygen activity took place over longer periods, in steel melts for the moment with the one-way probe as well as in sodium and lead at lower temperatures. The analysis method with solid electrolytes is a special measuring technique which has to be adapted to the system. Furthermore, definite conditions have to be accomplished in respect of ionic conductivity, temperature and oxygen partial pressure that can be applied to the probe.

The electrochemical determination of oxygen supposes two oxygenous cell compartments which are separated by an oxygen ion-conducting solid electrolyte. Such a system is linked over metallic leads, so that a cell voltage (*EMF*) is measured at various oxygen partial pressures in the cell compartments. The unknown oxygen partial pressure $p_{O_2, Me}$ can be calculated by the relation according to C. Wagner at a fixed oxygen partial pressure $p_{O_2, ref}$ and known temperature.

$$EMF = \frac{RT}{4F} \int_{p_{O_2, ref}}^{p_{O_2, Me}} t_{ion} d \ln p .$$

t_{ion} is the ionic transport number which is a function of the oxygen partial pressure. The Nernst equation is obtained with $t_{ion} = 1$:

$$EMF = \frac{RT}{4F} \ln \frac{p_{O_2, Me}}{p_{O_2, ref}} .$$

The numerical value of the oxygen activity in the melt is obtained from the measured *EMF*, the free standard solution enthalpy from the oxygen in the melt, the substitution of the oxygen partial pressure $p_{O_2, Me}$ in the melt by the adequate oxygen activity and the oxygen partial pressure of the reference electrode (for instance, oxygen pressure of air or oxygen pressure of the system metal/metal oxide). The calculation of the oxygen activities from the values of the cell voltage (*EMF*) takes place on the base of the equation

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$$\lg a_{[\text{O}]} \equiv \lg e : \left(- \frac{2 \cdot EMF \cdot F + \Delta_S G_{[\text{O}]}^{\circ}}{R \cdot T} + \ln p_{\text{O}_2, \text{ref}}^{1/2} \right)$$

where:

- $a_{[\text{O}]}$ = activity of oxygen for the standard condition 1 atom% solution (Henry's law, $f_{\text{O}}^{\circ} = 1$),
 EMF = current-free measured cell voltage (EMF) of the solid electrolyte cell in V,
 F = Faraday constant ($9.648456 \cdot 10^4$ C/mol),
 R = gas constant (8.31441 J K $^{-1}$ mol $^{-1}$),
 $\Delta_S G_{[\text{O}]}^{\circ}$ = standard molar free enthalpy of solution of oxygen after the reaction $1/2 \text{O}_2$ (1 bar) \rightarrow $[\text{O}]_{\text{Sn}}$ (1 atom%) in J mol $^{-1}$,
 $p_{\text{O}_2, \text{ref}}$ = oxygen partial pressure of the reference electrode in bar,
 T = temperature in K.

It is supposed that the stabilized ZrO_2 is a pure ion conductor in the measurements of the oxygen activity in the tin melt. In doped ZrO_2 an electronic conductivity appears at extremely lower oxygen activities. It causes a partial internal short circuit of the oxygen concentration chain and the cell voltage is decreased. In solid electrolyte no noticeable electronic conduction occurred at the measured temperature about 700°C under reducing conditions. The use of the equations considering the electronic conductivity in solid electrolyte is dispensed with.

2.2 Activity

The activity of oxygen in tin defines the relationship between its thermodynamic efficiency in the state of solution and its thermodynamic efficiency in the standard state. The ratio number $a_{[\text{O}]}$ is dimensionless and refers to a basically randomly obtainable standard state. The solution of oxygen in tin is based on the Henry law. It usually extends from $0 \leq x_{[\text{O}]} \leq 0.01$, frequently also until $x_{[\text{O}]} \leq 0.1$.

$$a_{[\text{O}]}^{\text{H}} \equiv \gamma_{[\text{O}]}^{\text{H}} \cdot x_{[\text{O}]}$$

is valid.

The Henry activity coefficient $\gamma_{[\text{O}]}^{\text{H}}$ determines how far the behaviour of the real solution deviates from the ideal behaviour of the infinitely diluted solution. $x_{[\text{O}]}$ is the mole fraction of oxygen in tin.

The advantage of the standard state "infinitely diluted solution" consists in the fact that within the range of low concentrations no noticeable deviation of the real behaviour of solution from the Henry straight line occurs. Thus, the Henry activity values in this range correspond to the mole fractions of the solved component.

A special interpretation of the Henry activity represents the "activity percentage" $a_i^{\text{H},\%}$, which is very often used in practice. To obtain activity values which directly give the percentage of mole fraction x_i (in atom%) a standard state "1 atom% solution" is defined. This means that the activity of solution with a mole fraction of the component i of $x_i = 0.01 = 1$ atom% is determined to be the value 1. The relationship

$$a_i^{\text{H},\%} = \gamma_i^{\text{H},\%} \cdot x_i$$

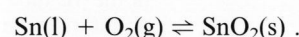
again consists of the activity percentage $a_i^{\text{H},\%}$, the percentage activity coefficient $\gamma_i^{\text{H},\%}$ and the mole fractions x_i of the dissolved component.

Generally it is assumed that the behaviour of the solution under investigation follows the Henry line by the interval from $0 \leq x_i \leq 1$ atom%. Thus, $\gamma_i^{\text{H},\%}$ reaches the value one, and the activity percentage $a_i^{\text{H},\%}$ defines the mole fraction x_i of the dissolved component in atom%. In metallurgical practice the activity of the dissolved substance is intended to be given in weight percent.

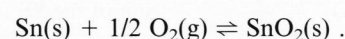
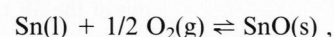
It is started from the fact that in the range of the strongly diluted solution the mole fraction x_i and the mass fraction c_i of the dissolved component are nearly proportional. Therefore, it is possible to switch from the determination of mole fraction in atom% over to the concentration definition in wt%, where simultaneously a new standard state "1 wt% solution" is defined. In this paper all the oxygen activities $a_{[\text{O}]}$ will correspond to Henry activities $a_{[\text{O}]}^{\text{H},\%}$ with reference to the standard state "1 atom% solution". Although the activity $a_{[\text{O}]}^{\text{H},\%}$ actually has the unit one, it is linked to the unit atom% due to the above mentioned relationships. The use of the exponent indices "H" and "%" is often eliminated in literature for the sake of a clearer style of writing.

2.3 Tin-oxygen

In the interpretation of the results from the experiments under oxidizing conditions, it has been generally presumed that the reaction product of the oxidation of tin consisted under the given test conditions exclusive of tin oxide SnO_2 . This assumption is based upon literature [11 and 12]. Above 400°C SnO_2 is formed via the reaction

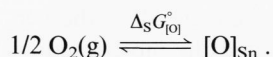


The formation of SnO_2 is also possible by the sub-reaction



In [11] it has been confirmed on the basis of calorimetric measurements that during gentle oxidation of tin melts the formation of SnO up to a temperature of 1370 K does not play any part. Below this temperature exclusive solid SnO₂ is formed.

Under reducing conditions the saturation of tin with oxygen and thus simultaneously the formation of tin dioxide does not take place. An equilibrium between the oxygen of atmosphere and that dissolved in the melt is formed according to the reaction



For the given case of equilibrium the Sievert law is valid. Oxygen activity in the melt $a_{[\text{O}]}$ and the oxygen partial pressure in the atmosphere (p_{O_2}) above the melt are directly proportional. The quotient from activity $a_{[\text{O}]}$ and the root of partial pressure p_{O_2} is dependent on temperature. Under the assumption that melt and atmosphere are thermodynamically in equilibrium, it is thus possible to calculate the oxygen activity in the melt from the oxygen partial pressure in the atmosphere above the melt. The oxygen solubility in the melt is determined by the equilibrium between solution pressure of oxygen and the formation pressures of tin oxides. This means a strong temperature dependence of oxygen solubility. At higher temperatures gaseous oxygen in pure tin melts is soluble at considerable amounts [11 to 14]. It is about 1 atom% oxygen at a temperature of 1354 K. With measurements in oxygen solutions above 1354 K it must be considered that the condition $x_i \leq 1$ atom% is no longer fulfilled.

While in the binary Sn–O solution up to saturation at good approximation an activity coefficient $f_{[\text{O}]} = 1$ (ideal behaviour) can be expected, the influence of accompanying elements (X) in the ternary system Sn–O–X on the activity of oxygen has to be considered

additionally [15 to 19]. The impurities of tin are not considered in the determination of the oxygen content of tin.

3. Preliminary measurements of oxygen in tin melts

In the literature concerned with tin melts [13, 14, 18 and 20 to 26] for the variation of the oxygen content below the saturation limit, the method of colorimetric titration under pure argon atmosphere was applied. The contributions gave some important information concerning the principal configuration of measuring probes. Basically, the used solid electrolytes were shaped like a tube closed at one end, which can also have the form similar to a crucible. The position of the two cell compartments was chosen in a way that the tin melt (cell compartment I) was placed in the tube and the reference material (cell compartment II) was situated outside the tube. Different solid electrolytes with different reference electrodes and leads were used. The essential characteristics of the oxygen probes described in these papers are given in table 1.

All the sensor types used seem to operate fairly well. Comparisons of the measured values of different sensor types, which were obtained under similar measuring conditions, were initially made only in single cases [18, 20 and 22]. From the statements of the authors it may be concluded that no essential differences between the measured results of the individual sensor types were found. In [25] pin sensors were applied for the measurement of oxygen activity in tin melts. Onto a nickel electrode the powder of the reference electrode (Ni–NiO mixture) was deposited by the flame spraying process, and the solid electrolyte material ZrO₂ (CaO) was deposited by plasma spraying. The next step consisted of

Table 1. Short description of the used probes

solid electrolyte (SE)	reference electrode	location of tin melt (cell room I)	leads in the tin melt (cell room I)	leads in the reference system (cell room II)	reference
ThO ₂ (Y ₂ O ₃)	Ni/NiO	in the SE tube	Os	Pt	[13]
ZrO ₂ (CaO)	Pt/air	in the SE tube	Ni–Cr	Pt	[14]
ZrO ₂ (Y ₂ O ₃)	Pt/O ₂ +N ₂	no information	no information	no information	[20]
ZrO ₂ (Y ₂ O ₃)	Pt/Pt+(U _{0.38} Sc _{0.62})O _α	no information	no information	no information	
ZrO ₂ (CaO)	Cu/Cu ₂ O	in the SE tube	Ni–Cr	Ni–Cr	[21]
ZrO ₂ (CaO)	Ni/NiO	no information	Pt/cermet	Pt	[22]
ThO ₂ (Y ₂ O ₃)	Ni/NiO	no information	Ni–Cr	Ni–Cr	
no information	Pt/air	no information	Pt	Pt	[23]
ZrO ₂ (CaO)	Pt/air	in the SE tube	Re	Pt	[24]
ZrO ₂ (Y ₂ O ₃)	Pt/air	in the SE tube	Ni–Cr	Pt	[18]
ZrO ₂ (CaO)	Pt/air	in the SE tube	Ni–Cr	Pt	
ZrO ₂ (CaO)	Ni/NiO	out of the SE tube	Ni	Ni	[25]
pin probe stab. ZrO ₂	Sn/SnO ₂	out of the SE tube	Re	Re	[26]

Table 2. Impurities in tin

element	content in wt.ppm	element	content in wt.ppm	element	content in wt.ppm
As	289	Ag	15	Mo	0.11
Ni	100	In	8.7	Cl	0.08
Bi	90	Co	8.1	Si	0.05
Ge	53	Tl	0.61	Al	0.03
Fe	49	Te	0.35	Zn	0.03
Sb	45	Cd	0.32	Cr	0.02
Cu	38	Au	0.29	Se	0.01
Pb	18	S	0.22	Na	<0.01

welding the electrical leads (nickel wire) onto the coated electrode. For short-time measurements these probes are applicable. The measurements of oxygen activity in tin melts are therefore subjected to errors, since a pore-free SE material can hardly be produced. Heraeus Elektrotechnik also developed a sensor which used Sn/SnO₂ as reference material and stabilized ZrO₂ as SE material [26]. Performance periods of this probe type are not known to us. The problem of a restricted corrosion resistance of the outer leads is indicated with all the probes applied.

A selection of papers presented in literature, which are concerned with the determination of oxygen activities in tin melts, is compared with our results in section 5. of this paper. By means of the developed probes it was intended to test above all, whether reliable oxygen activity measurements are possible in tin melts under reducing conditions. In the tests differently strong reducing atmospheres must have been applied. Respective data have scarcely been found in literature.

4. Experimental

4.1 Materials used

Small-piece pure tin was used as basic material. In order to determine its chemical purity material specimens were investigated by the recognized testing laboratory of NE-Metall GmbH, Freiberg (Germany), using glow discharge mass spectrometry, and the weight fractions of 74 different elements were estimated. Table 2 presents the weight fractions of all the elements which have been found in the analysis of tin as basic material by amounts above the respective detection limit. Sodium has been added to the list. If the weight fractions of accompanying impurities listed in table 2 are added, then a total content of contaminations of about 716 wt.ppm is obtained. This means that the basic material for all tests was tin at a purity degree of 99.9 wt%. In order to determine the purity degree according to DIN 1704 [27], only the elements antimony, arsenic, bismuth, copper, iron, lead, aluminium, cadmium and zinc are considered.

For oxygen measurements in tin melts differently doped ZrO₂ is used:

ZrO₂ (+ 8 mol% Y₂O₃) delivered by Zircoa, Solon, OH (USA),

ZrO₂ (+ 10.4 mol% CaO) delivered by Friatec AG, Mannheim (Germany),

ZrO₂ (+ 9 mol% MgO) delivered by Herbst GmbH, Dürrröhrsdorf (Germany).

The material was delivered as tubes which are closed at one end. On the basis of the given SE materials a suitable engineering solution for an industrial-scale probe was developed.

A 430 mm long sintered corundum tube with an external diameter of 15.4 mm and an internal diameter of 10.3 mm was chosen as mechanically resistant base of the industrial-scale probe. The sensor ceramic was cemented to the lower end of the corundum tube according to a procedure taken from literature [28]. As reference system air was used. The internal contacting was performed conventionally with platinum paste. The inner lead equipped with a ball-like platinum top was put onto the contact layer. The outer lead consists of similar material as the inner one. In this way thermoelectric voltage could be eliminated. As lead materials steel, tantalum and rhenium wires were used.

4.2. Sensor design

Concerning the use in tin baths, where the sensors could be applied during float glass production, a mechanically resistant oxygen sensor on the basis of the oxygen ion-conducting solid electrolyte ZrO₂ (MgO) with air electrodes was constructed, built and applied at different temperatures for the determination of oxygen activities in the tin melt (figure 1).

Besides the industrial-scale probes the laboratory-scale probes made from ZrO₂ (Y₂O₃) and ZrO₂ (CaO), respectively with longer SE tubes were used (figure 2). The former were also equipped with an air electrode, the

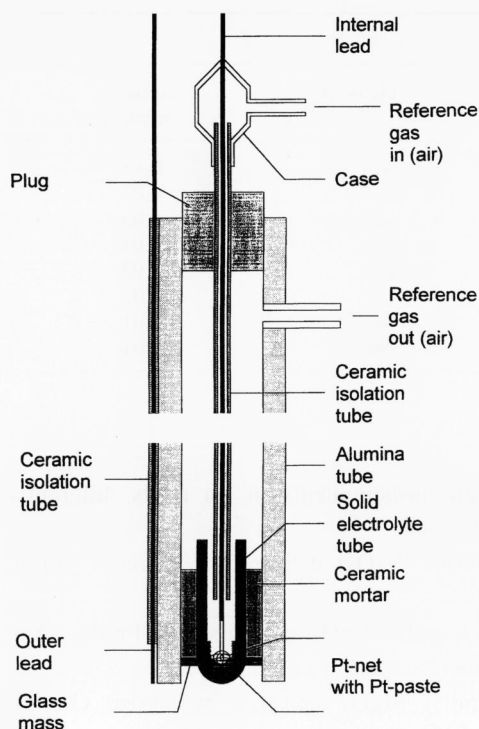


Figure 1. Design of the industrial-scale probe for measurement of the oxygen activity in tin melts.

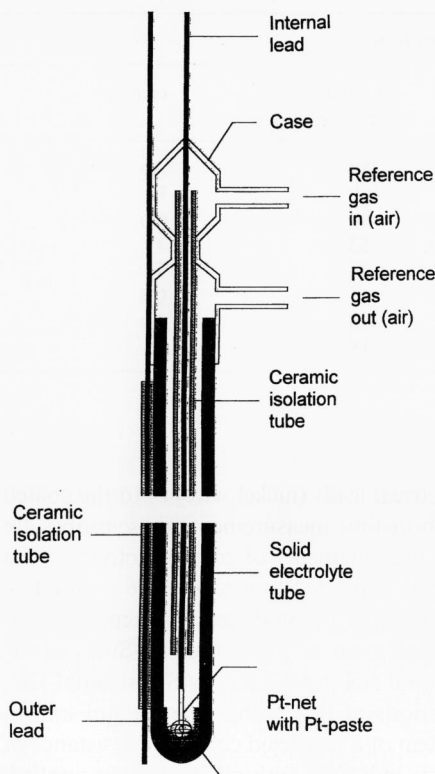


Figure 2. Laboratory probe with a long solid electrolyte tube and air as reference electrode.

latter optionally with air or Cu/Cu₂O. With all the probe types oxygen activity measurements were carried out in tin melts.

4.3 Experimental set-up

The different sensor types were applied for the measurements of oxygen activity both under inert (slightly oxidizing) and under reducing conditions in the experimental set-up schematically described in figure 3. The oxygen content of the supplied gas was steadily controlled by a device on SE base, type Ursalyt G (Junkalor, Dessau (Germany)).

The galvanic cell was adjusted to measuring temperature by an electric furnace via Eurotherm controller (Eurotherm Regler GmbH, Limburg a. d. Lahn (Germany)). The measurements were possible up to a temperature of 950 °C. The *EMF* value of the cell was determined by a high-ohmic digital voltmeter.

4.4 Doping

The measurements of oxygen content in tin melts were extended to investigations under forming gas and on the behaviour of tin melt at defined addition of elements and compounds (Na₂SnO₃, Na₂O, sodium, Fe₂O₃, iron,

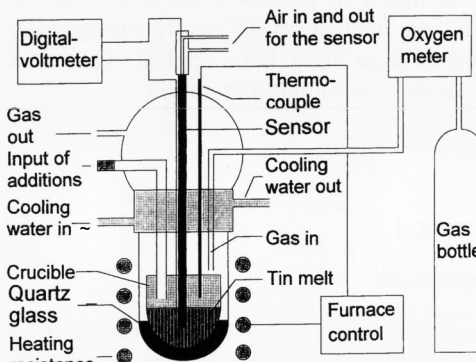


Figure 3. Set-up for the measurement of the oxygen activity in tin melts.

MgO, magnesium). These experiments should contribute to a deeper understanding of the corrosion processes under large-scale conditions as well as lead to findings concerning the interactions of these elements with the glass and the tin melt.

The experimental apparatus was equipped with a tubular opening for material addition. This was accomplished by small tin capsules containing the dopant material.

Table 3. Data for the relation $EMF = D \cdot T + L$ and the limiting temperatures for various sensor types

sensor type	D in 10^{-4} V/K	L in V	correlation coefficient	T_{limit} in K
ZrO ₂ (Y ₂ O ₃) with air electrode	-5.4800	1.4659	0.9997	773
ZrO ₂ (CaO) with air electrode	-5.1806	1.4434	0.9994	743
ZrO ₂ (CaO) with Cu/Cu ₂ O electrode	-1.0152	0.5587	0.9934	923
ZrO ₂ (MgO) with air electrode (industrial sensor)	-5.1998	1.4423	0.9996	973

Note: D = slope of the straight line in the EMF/T diagram; L = ordinate section of the straight line in the EMF/T diagram.

4.5 Sampling and analysis

For the withdrawal of tin samples from the experimental set-up a special dipper was developed. Quartz glass tubes of about 450 mm in length, 5 mm internal diameter and 1 mm wall thickness were molten together at one end. About 20 mm above the tube ground an intake hole was cut out. Into the prepared tubes closed at one end tight quartz glass tubes were pushed until reaching a mark shortly before the intake hole. In this way samples could be taken from the tin. The oxygen content in tin was determined according to the hot extraction process with the device ON-mat 8000 by Ströhlein Instruments, Kaarst (Germany). To determine sodium in tin, an analysis method had to be elaborated. For the proper determination of sodium the ICP-OES method (Inductively Coupled Plasma-Optical Emission Spectroscopy) was applied. The iron content in tin could also be determined by this method.

5. Results and discussion

5.1 Inert conditions (slightly oxidizing)

The total evaluation of results is based on the simplifying assumption that the basic material tin had a purity of 100%. The influence of the impurities found during tin analysis was neglected. In the interpretation of the results obtained from the experiments under oxidizing conditions, it was basically presumed that the reaction product in tin oxidation consisted exclusively of tin dioxide SnO₂ under the given test conditions. This assumption is based on [11]. On the basis of calorimetric investigations it was established that during gentle oxidation of tin melts the formation of tin monoxide (SnO) up to a temperature of 1370 K does not matter. Below this temperature exclusively solid SnO₂ is formed.

For the differently designed sensors table 3 summarizes the results of the temperature dependence of EMF with oxygen-saturated tin melts. According to theory the EMF of the oxygen concentration chain is directly proportional to the molar free reaction enthalpy ΔG_R of cell reaction. Since ΔG_R is directly proportional to temperature, it follows that plotting of EMF versus temperature

Table 4. Data of $\Delta_B H_{\text{SnO}_2}^\circ$ and $\Delta_B S_{\text{SnO}_2}^\circ$ from the literature

temperature range in K	$\Delta_B H_{\text{SnO}_2}^\circ$ in $\text{J} \cdot \text{mol}^{-1}$	$\Delta_B S_{\text{SnO}_2}^\circ$ in $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	reference
773 to 983	-586 910	-215.7	[13]
673 to 1167	-571 400	-203.0	[20]
773 to 1380	-578 600	-208.5	[29]
773 to 1173	-575 090	-207.0	[21]
990 to 1371	-575 450	-207.5	[22]

must result in straight lines. T_{limit} is the lowest temperature at which the sensor still gives reliable values. The limit temperature is dependent on SE material and on the reference electrode. The course of the EMF below the limit temperature is analogous for every probe, such that the evaluation of the measurements is of no use within this range.

A good accordance between the experimental results and the data taken from literature could be reached concerning the dependence of molar free standard enthalpy of formation $\Delta_B G_{\text{SnO}_2}^\circ$ on temperature. $\Delta_B G_{\text{SnO}_2}^\circ$ (in $\text{J} \cdot \text{mol}^{-1}$) follows the relationship:

$$\Delta_B G_{\text{SnO}_2}^\circ = \Delta_B H_{\text{SnO}_2}^\circ - \Delta_B S_{\text{SnO}_2}^\circ \cdot T$$

where $\Delta_B H_{\text{SnO}_2}^\circ$ is the molar standard enthalpy and $\Delta_B S_{\text{SnO}_2}^\circ$ is the molar standard entropy of reaction $\text{Sn(l)} + \text{O}_2(\text{g}) \rightarrow \text{SnO}_2(\text{s})$ (table 4). The values $\Delta_B H_{\text{SnO}_2}^\circ$ and $\Delta_B S_{\text{SnO}_2}^\circ$ calculated from the values measured by the four sensor types (table 3) lie quite closely by around the mean value, at a standard deviation $\sigma_{n=1} = 0.93\%$ for $\Delta_B H_{\text{SnO}_2}^\circ$ and $\sigma_{n=1} = 3.17\%$ for $\Delta_B S_{\text{SnO}_2}^\circ$. Substituting the results the complete equation is:

$$\Delta_B G_{\text{SnO}_2}^\circ = 558\,306 (\pm 5176) + 189.6 (\pm 6.0) \cdot T$$

This, strictly speaking, is only valid within the temperature range from 973 to 1148 K. Due to the small deviations between the individual equations it is assumed that the equation derived from the mean values is still valid in the extended range of temperature from 743 to 1191 K.

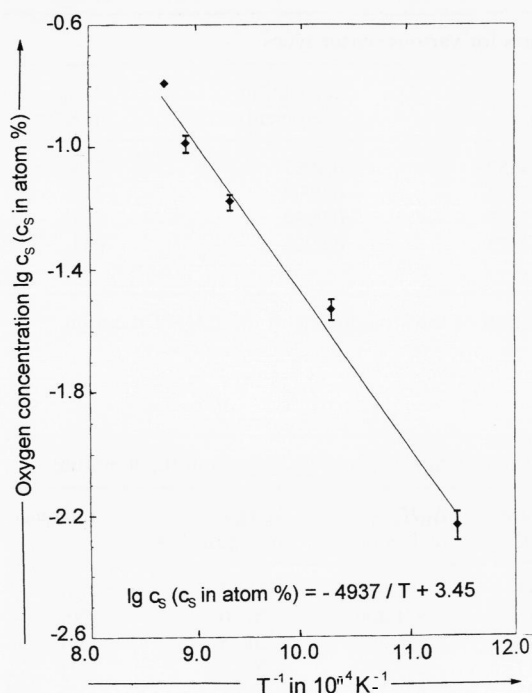


Figure 4. Saturation concentration of oxygen in liquid tin as a function of temperature.

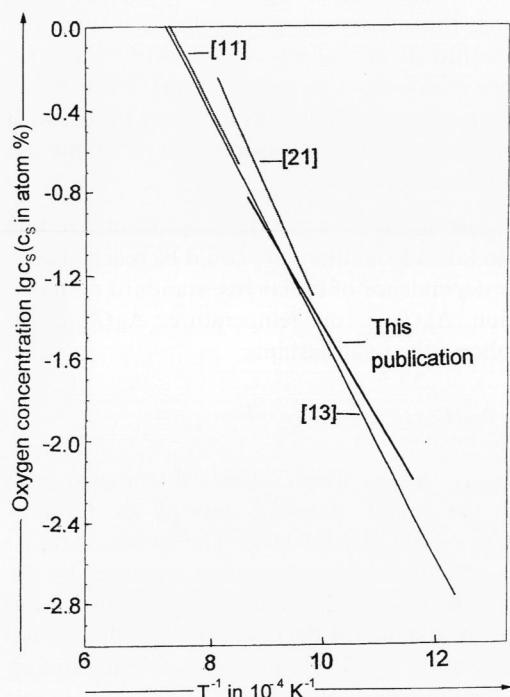


Figure 5. Saturation concentration of oxygen in liquid tin as a function of temperature in comparison with data from literature.

Furthermore, the solubility of oxygen in liquid tin was determined. The oxygen contents of the oxygen-saturated tin samples taken at various temperatures are

Table 5. Data of $\Delta_S H_{[O]}^\circ$ and $\Delta_S S_{[O]}^\circ$ from the literature

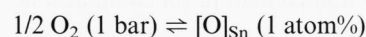
temperature range in K	$\Delta_S H_{[O]}^\circ$ in $J \cdot mol^{-1}$	$\Delta_S S_{[O]}^\circ$ in $J \cdot mol^{-1} \cdot K^{-1}$	reference
809 to 1024	-183 675	-65.90	[13]
1023 to 1223	-167 470	-6.87	[14]
1073 to 1223	-183 000	-24.89	[18]
1053 to 1453	-192 844	-50.16	[23]
973 to 1173	-176 300	-20.52	[24]

presented in figure 4. Appropriately, the saturation concentration c_s (in atom%) is presented logarithmically versus reciprocal temperature $1/T$. The equation of regression lines is

$$\lg c_s = -4937/T + 3.45$$

at a correlation coefficient of $r = 0.9948$. The range of validity reaches from 873 to 1153 K. For the purpose of comparison the experimentally determined solubility data of oxygen in liquid tin are presented with the values taken from literature in figure 5 [11, 13 and 21]. The accordance with the data from literature can be considered to be quite good.

Knowing the functions $\Delta_B G_{SnO_2}^\circ(T)$ and $\lg c_s(T)$ the dependence of molar free standard enthalpy of solution $\Delta_S G_{[O]}^\circ$ of the reaction



on temperature can be derived. The equation presents the course of solution of gaseous oxygen in liquid tin. The additions (1 bar) and (1 atom%), respectively, give the standard state of gaseous oxygen and oxygen solution, respectively. $\Delta_S G_{[O]}^\circ$ (in $J \text{ mol}^{-1}$) can be presented as

$$\Delta_S G_{[O]}^\circ = \Delta_S H_{[O]}^\circ - \Delta_S S_{[O]}^\circ \cdot T$$

as a function of temperature, where $\Delta_S H_{[O]}^\circ$ is the molar standard enthalpy, and $\Delta_S S_{[O]}^\circ$ is the molar standard entropy of solution according to the above mentioned equation. The values of $\Delta_S H_{[O]}^\circ$ and $\Delta_S S_{[O]}^\circ$ taken from literature are presented in table 5. The relationship for the molar free standard solution enthalpy $\Delta_S G_{[O]}^\circ$ (in $J \text{ mol}^{-1}$), which we determined, is

$$\Delta_S G_{[O]}^\circ = 184 635 (\pm 2588) + 28.7 (\pm 3) \cdot T.$$

It is valid for the temperature range 873 to 1153 K. The error information is obtained from the range of uncertainty of the value equation for $\Delta_B G_{SnO_2}^\circ$. The absolute term is $\pm 1.4\%$, and the slope is $\pm 10.5\%$. The range of scattering of the presented values is very large. Only three of the pairs of values ($\Delta_S H_{[O]}^\circ$, $\Delta_S S_{[O]}^\circ$) taken from literature lie completely or partially within the range of error of our value equation.

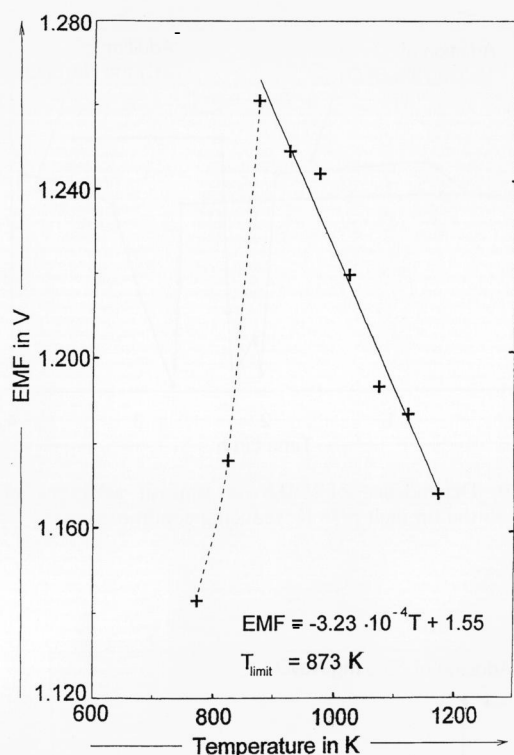


Figure 6. Dependence of EMF on temperature for the tin melt under reducing conditions ($p_{O_2} = 4.6 \cdot 10^{-26}$ bar).

This fact supports the assumption that our equation resembles the real relation relatively strongly. Additionally, the value equations given outside of the error limits are of earlier origin [13 and 23]. In all the subsequent calculations for the determination of oxygen activities in unsaturated tin melts, in which the function $\Delta_S G_{[O]}^{\circ}(T)$ is important, the above mentioned equation is used without restrictions.

5.2 Under reducing conditions

Under reducing conditions the saturation of tin with oxygen does not take place and, simultaneously, neither does the formation of tin dioxide. An equilibrium is formed between the oxygen present in the atmosphere and that solved in the melt. During EMF measurements under reducing conditions only CaO-stabilized ZrO_2 and air as reference electrode were used. Figure 6 presents the temperature dependence of EMF under strongly reducing conditions ($p_{O_2}(T = 973 \text{ K}) = 4.6 \cdot 10^{-26}$ bar in the rinsing gas).

The limiting temperature for the application of the sensor under reducing conditions is at $T = 873 \text{ K}$. Under inert conditions (slightly oxidizing), $T = 743 \text{ K}$. From the EMF values the oxygen activities could be calculated. It is obvious that the measured oxygen activities

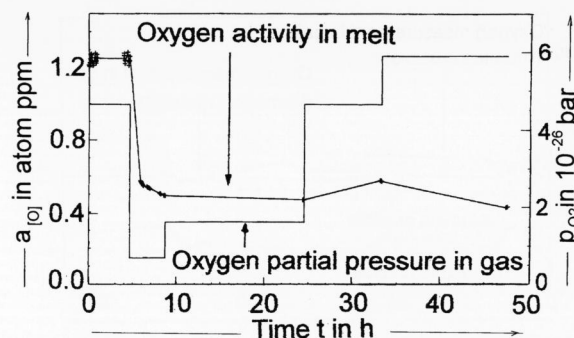


Figure 7. Oxygen activity $a_{[O]}$ of the tin melt and oxygen partial pressure above the melt as a function of time.

at low temperatures take very low values. While the oxygen activity e.g. at $T = 1173 \text{ K}$ still has the value 2.2 atom ppm, it is at $T = 873 \text{ K}$ only about 0.04 atom ppm. Figuratively speaking, at $a_{[O]} = 0.04$ atom ppm no more than four oxygen atoms are applicable to 10^8 tin atoms. The efficiency of the solid electrolyte method is considerable concerning the determination of lowest oxygen activities.

If there are other oxygen partial pressures in the reducing gas, then also the oxygen activities of the melt are changed under these conditions.

5.2.1 Inert gas atmosphere and tin melt

At constant temperature of 1073 K the tin melt was subjected to a reducing atmosphere, the oxygen partial pressure of which was varied. The oxygen partial pressure in the gas atmosphere was measured by an SE device (Ursalyt). In figure 7 the oxygen activities in the tin melt and the oxygen partial pressure in the gas as a function of time are presented. At the beginning of the test an oxygen partial pressure was adjusted in the gas ($p_{O_2} = 4.6 \cdot 10^{-26}$ bar). This resulted in an oxygen activity of $a_{[O]} = 1.24$ atom ppm in the melt. In the subsequent reduction of the oxygen partial pressure to $0.7 \cdot 10^{-26}$ bar the oxygen activity of the tin melt was also decreased (0.49 atom ppm). A repeated increase of oxygen partial pressure above the melt did not result in an essential increase of oxygen activity in the melt. These adjusted values proved to hold a high constancy of time. The described behaviour of the oxygen activity in the melt upon changes of oxygen partial pressure in the inert gas atmosphere leads to the conclusion that the kinetics of absorption of gaseous oxygen from the atmosphere is severely hindered by the tin melt at low oxygen partial pressures. The release of dissolved oxygen to the atmosphere, however, seems to occur quite quickly under the precondition of a corresponding oxygen potential gradient.

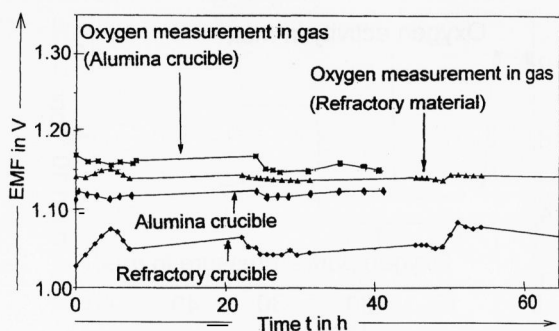


Figure 8. Time dependence of *EMF* on tin melt in refractory and in alumina crucible.

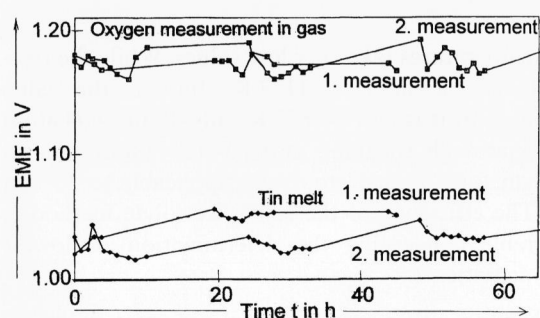


Figure 9. Time dependence of *EMF* on tin melt in the presence of float glass in alumina crucible.

5.2.2 Under industrial-scale conditions

In these investigations the tin melt (about 140 g) was in a crucible made from a material which is similar to that of the lining of the ground basin of the float glass plant (Verral 40 FT, composition in wt%: 55 SiO₂, 40 Al₂O₃, 1.2 Fe₂O₃). For comparison purposes measurements were also performed in the sintered corundum crucible under forming gas (98 vol.% N₂, 2 vol.% H₂). The time dependence of *EMF* on the tin melt is presented in figure 8. The *EMF* values of the measurements on tin situated in the tin bath stone crucible are lower than those of the tin in the Al₂O₃ crucible. That means that the oxygen content in the tin melt is adjusted by the crucible material. If the melt is covered by float glass, then the glass melt also participates in the adjustment of the oxygen content in the tin melt (figure 9). The measurement of oxygen content in tin in the tin bath stone (Ursalyt) in the presence of glass still needs to be investigated.

5.2.3 Addition of compounds and elements

The investigations concerned the following additions:

a) Sodium compounds and sodium

In further tests it was to be shown that the addition of sodium compounds and sodium at a temperature of

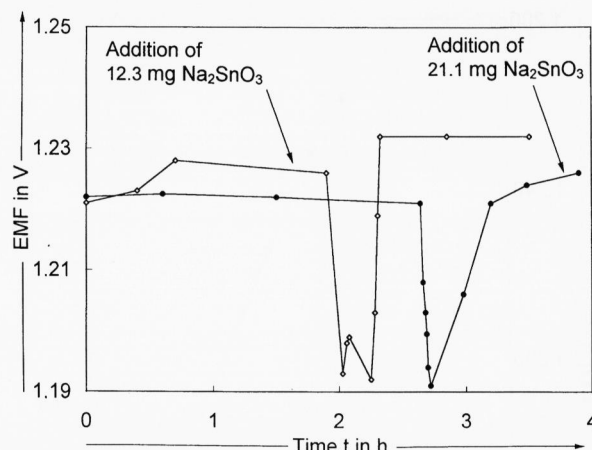


Figure 10. Dependence of *EMF* on time at additions of Na₂SnO₃ to the tin melt (973 K, reducing conditions).

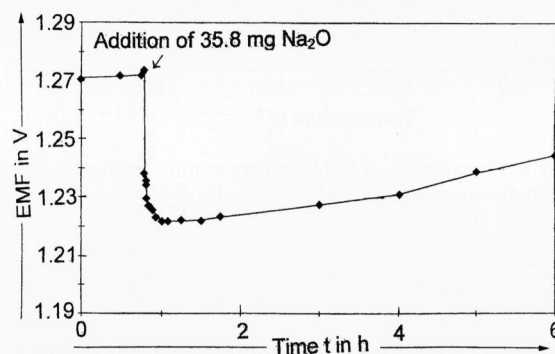


Figure 11. Dependence of *EMF* on time under addition of Na₂O to the tin melt (973 K, reducing conditions).

973 K influences the oxygen activity in the tin melt ($p_{O_2} = 4.6 \cdot 10^{-26}$ bar in the rinsing gas, various doping contents). The pure melt was heated to working temperature and under testing atmosphere the adjustment of a constant *EMF* at the sensor was expected. Then Na₂SnO₃, Na₂O and sodium were added.

Under the addition of Na₂SnO₃ a rapid increase of oxygen activity in the tin melt is recorded. After a short time the earlier *EMF* value adjusts again (figure 10). By the addition of Na₂O the *EMF* decreases, but again increases very slowly with time (figure 11). If sodium is added to the tin melt, the *EMF* increases again (figure 12).

Finally it can be stated that by the addition of sodium to the tin melt the oxygen in the melt will be combined to sodium, while on adding the other two compounds oxygen is released. In the case of stannate it is assumed that it is adsorbed oxygen. The final state is reached very fast. Stannate seems to be very stable under these experimental conditions. During retesting of the tin melt Na₂SnO₃ was proved (X-ray investigation).

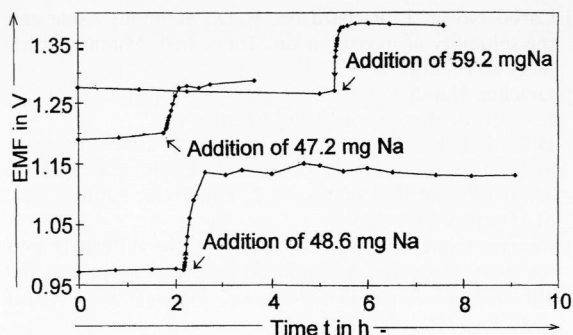


Figure 12. Dependence of EMF on time under addition of sodium to the tin melt (973 K, reducing conditions).

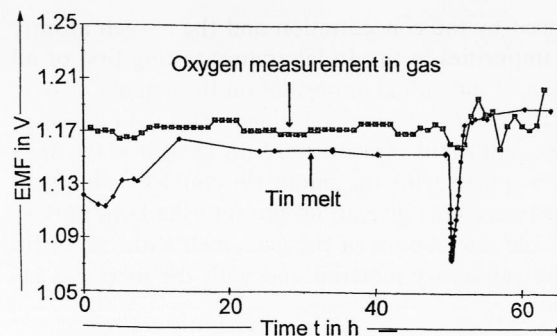


Figure 14. Dependence of EMF on time under addition of Fe_2O_3 (32.5 mg) to the tin melt (1073 K, reducing conditions).

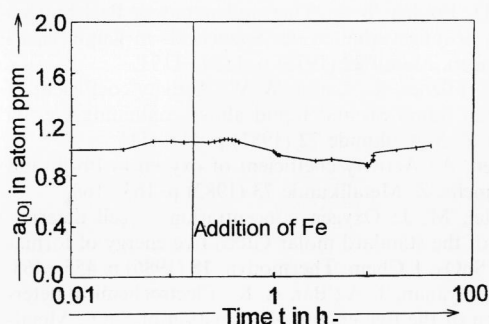


Figure 13. Dependence of oxygen activity in the tin melt on time under addition of iron (45 mg) to the tin melt (1073 K, reducing conditions).

b) Magnesium oxide and magnesium

Measurements on doping of the tin melt by MgO and magnesium, respectively, were carried out. The evaluation of the series was as follows: a strong gettering of oxygen in tin occurs by magnesium. The old EMF value is reached again after about 15 h. Under the addition of MgO the oxygen contents become higher (lower EMF values) in tin. It seems, MgO is stable in the tin melt.

c) Iron oxide (Fe_2O_3) and iron

Furthermore, it had to be explained how the addition of pure iron and Fe_2O_3 at a temperature of 1073 K influences the oxygen activity in the tin melt ($p_{O_2} = 4.6 \cdot 10^{-26}$ bar in the rinsing gas, doping content: 94 wt.ppm, lead: tantalum).

The pure melt was heated up to working temperature, and under test atmosphere the adjustment of a constant EMF was been expected at the sensor. The dopant iron was added to the melt. This moment of iron addition is shown in figure 13 by a vertical line intersecting the time axis. After doping of the melt the behaviour of EMF was observed over a longer period. This is also shown in figure 13. At the time of doping and afterwards changes of oxygen activity in the tin melt could not be observed. It can be concluded that under the selected

test conditions (temperature, atmosphere, doping degree) there are no interactions between the iron solved in the melt and oxygen.

Figure 14 shows the time behaviour of EMF of the cell under addition of Fe_2O_3 . The EMF decreases shortly after doping to lower EMF values, i.e. the iron oxide passes its oxygen over to the tin melt. Then EMF increases again, and the values of the melt correspond to those of the gas phase.

The above-described dopings indicate how the oxygen content of the tin melt is influenced. Those elements and compounds, respectively, were selected as additions which are important for the float glass process. The present investigations are far from being completed. Further elements and compounds as well as their concentration and temperature dependence on the adjusted oxygen content in the tin melt must be tested. Also the basic oxygen content of the tin melt is important for the subsequent reactions. Within the scope of the project it has to be shown that by the use of the oxygen sensors built a much deeper insight into the interactions glass melt–tin melt–atmosphere and refractory material can be obtained.

6. Concluding remarks

As a result of these investigations it can be summarized that a dependable determination of oxygen activities in tin melts with the applied systems, described in this paper, on the outer leads, solid electrolyte and on the reference electrode is possible. Also in tin melts under reducing atmosphere the applied sensor types were proved to perform well.

In the process of float glass production the oxygen partial pressure belongs to the most important variables of influence. Due to the exact mode of operation of the SE sensors it is possible to investigate the variable oxygen in the float glass process in greater detail. The activity of the dissolved oxygen at constant temperature is

influenced by the concentration and the oxygen affinity of the impurities in tin. In laboratory testing first of all the effect of individual impurities on the activity of oxygen in the tin melt were determined. Also data concerning the equilibrium adjustment of the oxygen of the inert gas atmosphere with the liquid tin could be obtained. The measurements give an insight into the large variety of possible interactions of the glass melt with tin, of tin with the refractory material and with the inert gas atmosphere.

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