

Sensor for oxygen activity measurements in glass melts

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Dedicated to Dipl.-Phys. Erich Schuster on the occasion of his 60th birthday

Traditional oxygen activity measurement in glass melts is based on Y_2O_3 -stabilized ZrO_2 which, in continuous use in the glassworks, is subjected to considerable wear. The present paper describes an oxygen sensor that is not equipped with wear parts. The new sensor is far less sensitive to temperature gradients in the surrounding area than ZrO_2 sensors; the oxygen measurement, however, is greatly disturbed at direct flame irradiation.

Sensor für die Messung der Sauerstoffaktivität von Glasschmelzen

Die herkömmliche Sauerstoffaktivitätsmessung in Glasschmelzen basiert auf Y_2O_3 -stabilisiertem ZrO_2 , das im kontinuierlichen Einsatz im Glashüttenbetrieb einem starken Verschleiß unterworfen ist. Die vorliegende Arbeit beschreibt einen Sauerstoff-Sensor, bei dessen Aufbau auf Verschleißteile verzichtet wurde. Der neue Sensor ist sehr viel unempfindlicher gegenüber Temperaturgradienten in der Umgebung als ZrO_2 -Sensoren; die Sauerstoffmessung wird jedoch bei direkter Flammeneinstrahlung stark gestört.

1. Introduction

Glass properties like colour, viscosity, visco-elastic behaviour and surface tension, but also the refining behaviour of a glass melt are influenced by the oxygen activity of the glass melt. This affects the strength and the workability of the glass as well. Therefore, there is a strong interest to better characterize the oxidation state of the glass melt at the time of processing. The oxygen activity measurement in the melt offers a possibility here by means of yttrium-stabilized zirconia. This kind of measurement has been employed for some years in laboratory melts [1 and 2] and meanwhile successfully developed for regular use under industrial conditions [3 and 4].

The zirconia, however, is subjected to a continuous corrosive attack by the glass melt, i.e. the solid electrolyte is a wear part that has to be substituted regularly. In this paper, an oxygen sensor operating without a solid electrolyte will be introduced.

$$a_{O_2}(T_0) = \exp \left[\frac{T_R}{T_G} \ln p_R + \frac{E - k_S (T_G - T_R) - k_T (T_G - T_0)}{c T_G} \right], \quad (1)$$

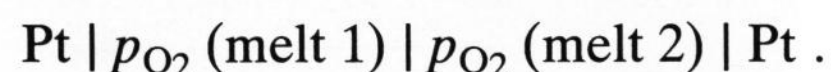
with $c = R/4F = 2.15 \cdot 10^{-5}$ V/K where R is the gas constant, F the Faraday constant, E the measured electromotive force (emf), T_R the temperature at the

2. Measurement procedure

The oxygen activity measurement of a glass melt is carried out by means of an electrochemical measuring cell. At present, only cells on the basis of solid electrolytes are used, e.g. zirconia



In principle, also a glass melt with a defined oxygen activity can be employed as reference:



The oxygen activity measurements by Csaki and Dietzel [5] were based on such an arrangement. Also Lenhardt and Schaeffer [2] describe such a cell arrangement.

For both measuring cells the oxygen activity a_{O_2} can be calculated from the reference oxygen pressure with the following equation:

reference electrode, T_G the temperature of the glass melt, p_R the oxygen partial pressure at the reference electrode, a_{O_2} the oxygen activity of the glass melt, k_S the standard Seebeck coefficient [6], k_T a temperature coefficient [3] and T_0 the temperature to which the value of the oxygen activity refers.

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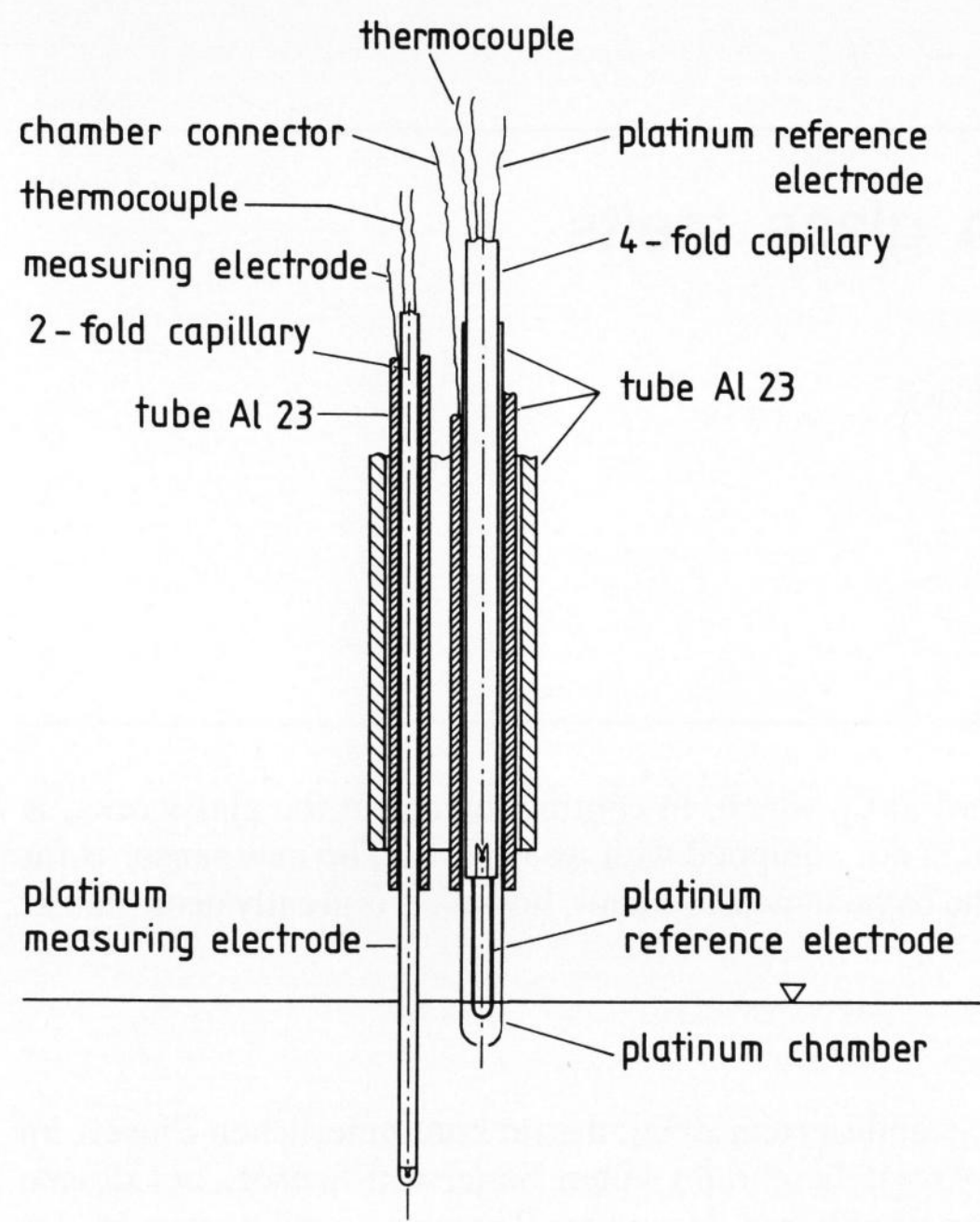


Figure 1. Schematic of the platinum sensor for the oxygen activity measurement.

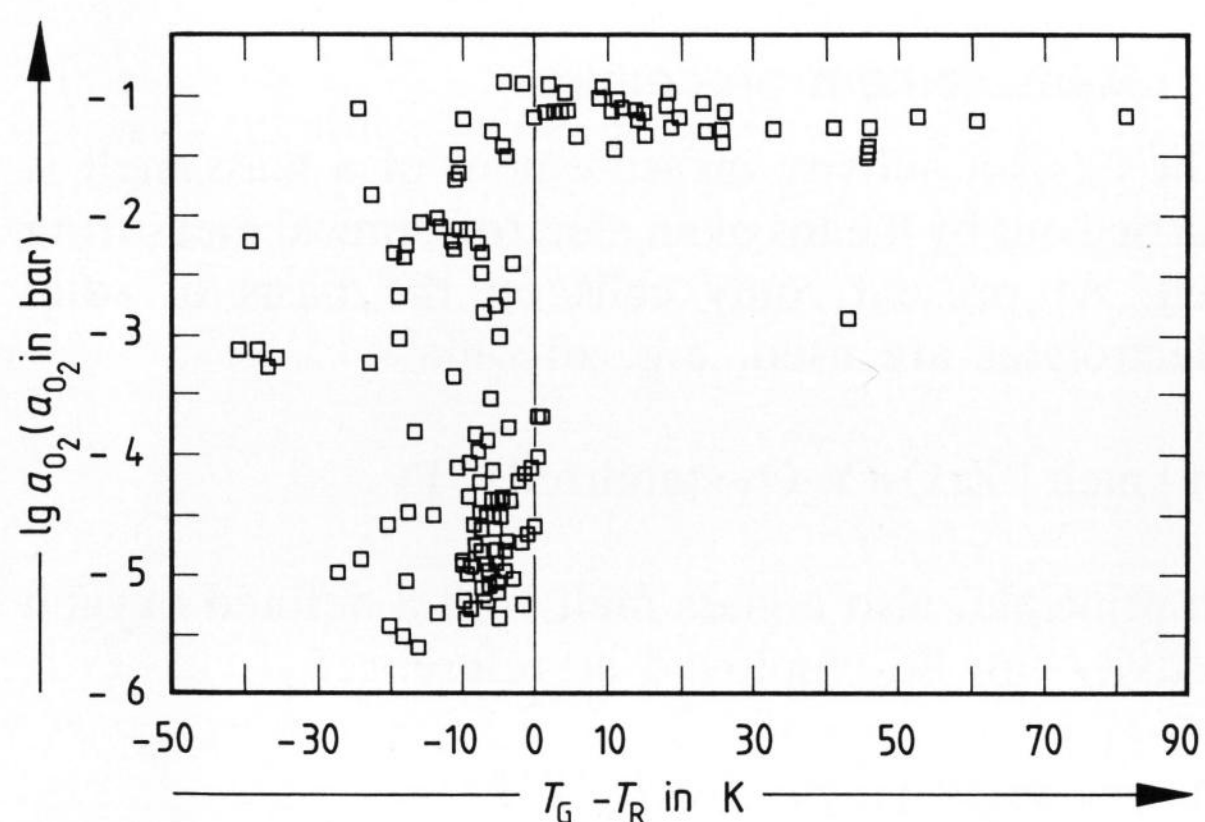


Figure 2. Dependence of the measured oxygen activity, a_{O_2} , on the temperature difference, $T_G - T_R$, between the measuring- and the reference electrodes.

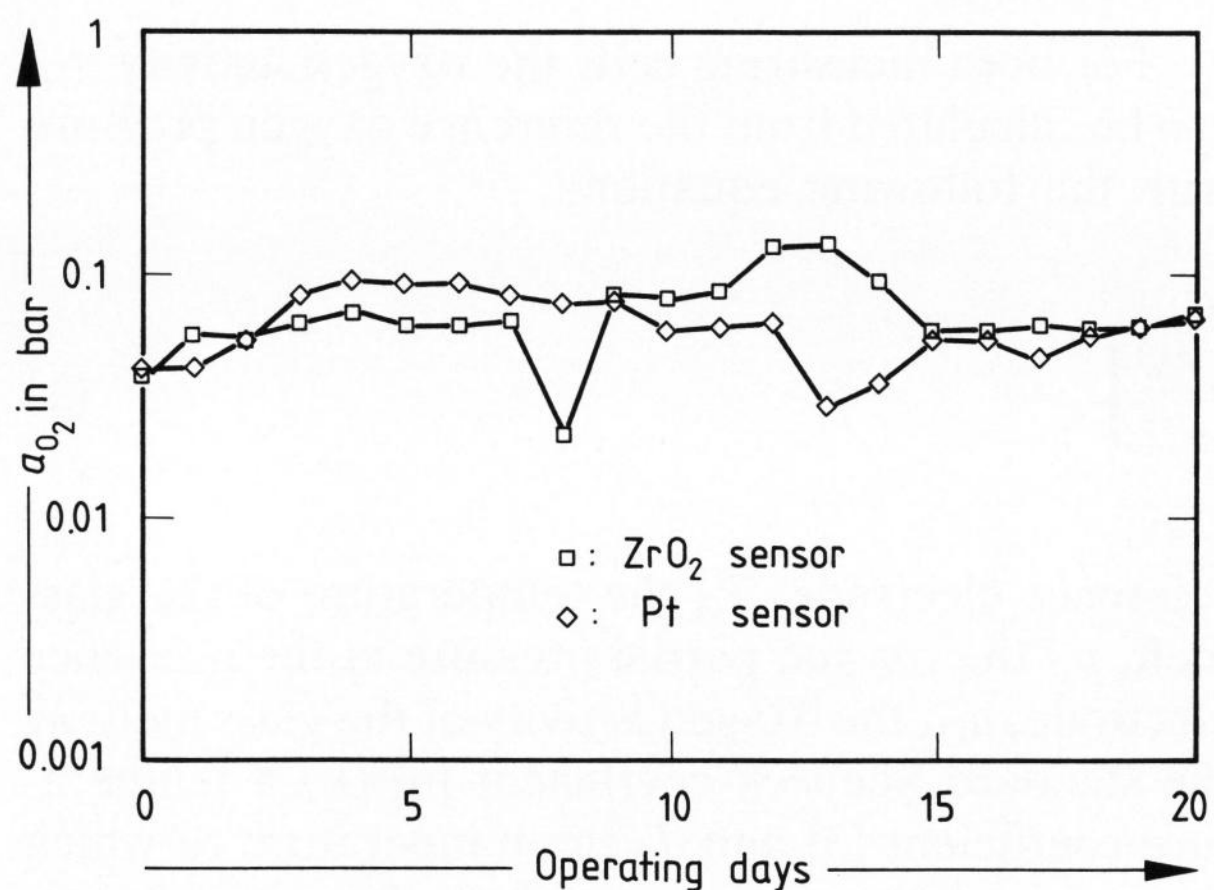


Figure 3. Comparison of the measured oxygen activity, a_{O_2} , with two different sensors at 1200 °C.

3. Sensor construction

This procedure for the oxygen activity measurement can be realized in industry with the sensor illustrated in figure 1. The platinum measuring electrode is constructed in the same way as that at the zirconia sensors presently used in industry [4]. The reference electrode consists of a loop-shaped platinum wire that is surrounded by a platinum chamber. This chamber has an opening on the bottom to establish contact to the melt. According to [2] the oxygen diffuses into the glass mostly at the two-phase boundary Pt | melt. Therefore, if one employs the sensor from figure 1 in a feeder channel the measuring electrode is still washed by the melt. The reference electrode touching the melt only at the surface is screened from the flowing melt by the platinum chamber. Thus equilibration results between the melt surrounding the reference electrode and the atmosphere in the chamber. As soon as this chamber is exposed to a gas of known composition – e.g. air – the arrangement can be used for the oxygen activity measurement of the melt.

In order to be able to take into consideration temperature dependencies known from the measuring with the zirconia sensor both of the electrodes are equipped with a PtRh-Pt thermocouple type S.

4. Results

The described sensor was employed, on a trial basis, for 4 months in the feeder channel of a flint glass furnace. At the zirconia sensor a thermally induced voltage is superimposed on the emf of the electrochemical reaction of the cell [6]. Therefore, in figure 2 the oxygen activity, calculated by equation (1) assuming k_S and k_T to be zero, has been plotted against the temperature difference between measuring- and reference electrode. The figure shows two ranges of much different behaviour. For negative $T_G - T_R$ the values of the oxygen activity scatter extremely. In this case the temperature above the glass is higher than in the glass, i.e. the respective feeder range is heated. Most probably, the sensor is interacting with the reaction products of the combustion reaction. The range in figure 2 where T_G is larger than T_R shows a constant oxygen activity to a large extent even though $T_G - T_R$ amounts to up to 90 K. This behaviour is clearly different from that of the zirconium dioxide sensor. For the new sensor the standard Seebeck coefficient is close to zero, i.e. there is no thermally induced voltage worth mentioning. The reason for this is, on the one hand, that the platinum sensor in contrast to the zirconium dioxide sensor has two equal phase boundaries Pt | melt. Moreover, because of the arrangement of the thermocouples the temperature at the phase boundary Pt | melt in the reference electrode can be assumed to lie close to the glass temperature.

In another segment of the same feeder channel a zirconia sensor was installed at the same time. Figure 3 shows the development of the day mean values of the oxygen activity at the two sensors over a period of three weeks. During the chosen period $T_G - T_R$ was always positive at the platinum sensor. The oxygen activity was calculated by means of equation (1). k_S was set zero for the platinum sensor; for the zirconia sensor $k_S = -0.45$ mV/K [3]. The dependence of the melt on the temperature T_G – and thus also the temperature coefficient k_T – must be the same at both sensors. k_T was set 0.1 mV/K. This value was found on average in flint container glass at various measurements of the authors.

Both sensors show almost the same oxygen activity. Part of the deviation can be explained by the fact that the sensors were installed several meters apart from one another in different feeder zones. Moreover, the glass flow between the two sensors was deviated by 90°. There was an overall good agreement between the signals. From this can be concluded that the melt at the reference electrode of the new sensor normally is in equilibrium with the oxygen partial pressure of the air.

5. Summary

A new sensor for oxygen activity measurements in glass melts has been developed. The sensor has the following properties:

- a) The sensor has no wear parts.
- b) The Seebeck coefficient of the measuring arrangement is extremely small, i.e. there are no signal

changes worth mentioning by thermally induced voltages.

c) The measurement is very sensitive to disturbances by the feeder heating and glass depth fluctuations.

d) The measuring results are in agreement with those of the zirconia sensor.

Further investigations are to show in which cases the new sensor is a practicable alternative to the zirconia sensor.

6. References

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