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MEASUREMENT OF THE OXYGEN POTENTIAL OF NON-FERROUS SLAGS WITH AN EX-SITU ELECTROCHEMICAL DEVICE

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Abstract

A method using an ex-situ electrochemical measurement device was developed to determine the oxygen potential of non-ferrous metallurgical slags. The electrochemical cell consists of the molten slag sample, an inert Ir electrode, a stabilized ZrO_2 solid electrolyte and a Ni/NiO reference electrode. Different slags from non-ferrous pyrometallurgical processes were analysed at 1100 and 1200 °C and pO_2 values between 10^{-3} and 10^{-12} bar were obtained. The measurements were evaluated with thermodynamic calculations and using processing considerations. It was found that the reproducibility and stability of the measurement was significantly improved by shielding the molten slag from the atmosphere by a thin layer of carbon, especially for slags with a low oxygen potential.

Introduction

The oxygen potential of a slag affects its reactivity with the metal, the matte and the lining of the reactor. Therefore, an accurate measurement of the oxygen potential is important to the product quality as well as the process efficiency.

The measurement of the oxygen activity of metals using an in-situ electrochemical method has been well established during the last century, e.g. (1). Also the in-situ electrochemical determination of the oxygen potential of the slag or equivalently its activity of FeO has been investigated, e.g. (2). Recently it has been found that an in-situ electrochemical measurement of the oxygen potential of the slag by submersion of a slag sample in the liquid metal may result in a systematic deviation (3), and for some processes an in-situ measurement is not practical.

In this article an ex-situ electrochemical technique is described that allows to measure the oxygen potential of typical non-ferrous slags. We will demonstrate that the technique may be used for slags exhibiting a wide range of oxygen partial pressures, if measurement conditions are properly adopted.

Experimental procedure, materials and calculations

Description of the Measurement Technique

The measurement equipment was originally developed by Heraeus Electro-Nite for the measurement of the redox potential of glass (4). It consists of an electrochemical cell using a Ni/NiO reference electrode, a MgO-stabilized ZrO_2 solid electrolyte and an Ir conductor which is partially covered by silica.

$$\text{Ni (a=1)/NiO (a=1)//ZrO}_2\text{ (MgO)//slag/Ir} \qquad (1)$$

The oxygen activity of the slag can be calculated at a fixed temperature T (K) by

$$E_{cell} = 10^3 \cdot \frac{RT}{4F} \ln \frac{pO_2(slag)}{pO_2(ref)} \tag{2}$$

where E_{cell} is expressed in mV and $pO_2(ref)$ represents the oxygen partial pressure at the Ni/NiO reference electrode. With the standard Gibbs free energy of NiO the following expression for $pO_2(slag)$, expressed in bar, may be obtained

$$\log(pO_2(slag)) = \frac{20.171 \cdot E_{cell} - 24{,}420}{T} + 8.88 \tag{3}$$

From equation (2) it follows that slags with an oxygen potential lower than that of the reference exhibit a negative voltage. As the difference between the oxygen potential of the slag and that of the reference increases, the current also increases and measurement errors occur due to polarisation and to contact as well as electrolyte resistance. It is therefore ideal to have a close match between the oxygen potentials of the reference and the slag. To minimize the mass transport overpotential in the slag the crucible is rotated. A typical error on E_{cell} is 2 to 5 mV.

The apparatus consists of a resistance heated furnace, a crucible which is loaded in the furnace through the bottom and a sensor assembly (Figure 1), which is lowered into the crucible through an opening in the top which is closed off by a hatch during the melting stage. The crucible is rotated at a speed of 4 rpm and the sensor is eccentrically positioned. This limits the polarisation and improves the homogenisation of the melt. The temperature of the furnace is monitored with a thermocouple Ni/NiCr which is located inside the furnace next to the crucible. There is a gas inlet to regulate the furnace atmosphere. The appropriate heating cycle may be programmed. During the course of a measurement the temperature, the cell potential and the corresponding oxygen partial pressure (equation 3) are logged.

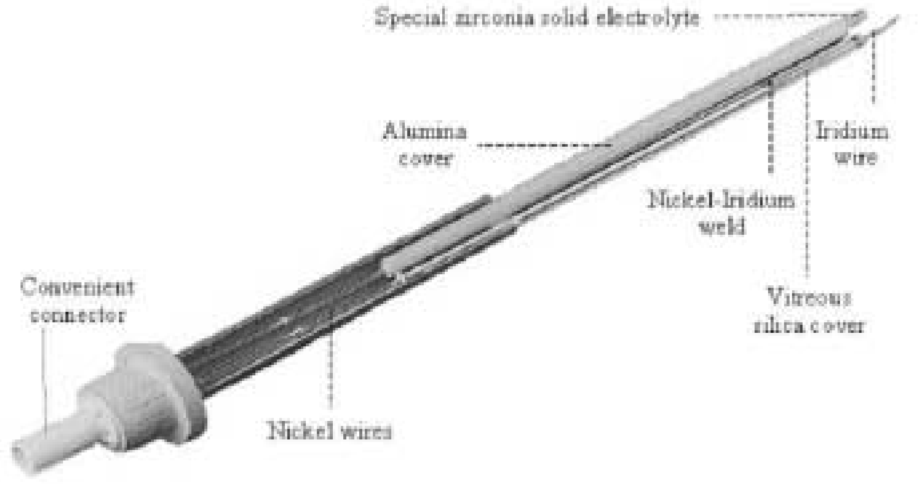


Figure 1 The sensor of the Rapidox system (from (4))

A typical example of a temperature-time curve is shown in Figure 2. At the beginning of the experiment the gas flow (60 l/h) is started and the furnace is heated at a rate of about 7 °C/min until a temperature 50 °C above the measurement temperature is reached. This temperature is maintained for 15 minutes. Thereafter it is lowered to the measurement temperature. After a holding time of 15 to 20 minutes the measurement can be started. The hatch is opened and the sensor is inserted in the liquid melt. After about 5 minutes a constant potential is reached. The duration of the measurement is limited by the degradation of the sensor. After the measurement the gas flow is closed off and the furnace is allowed to cool down.

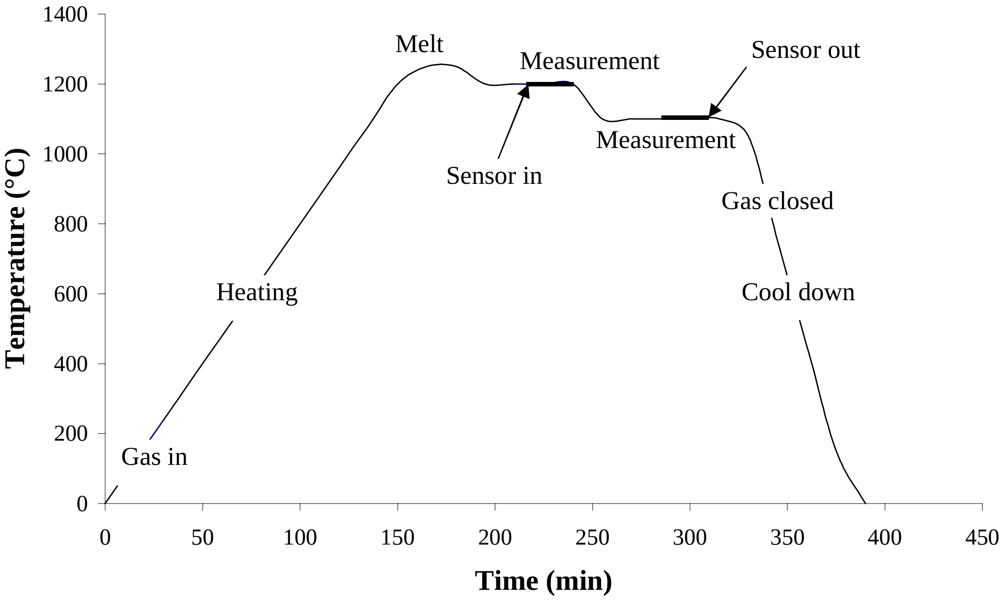


Figure 2 Temperature-time curve for a typical measurement at two different temperatures.

The crucible material is either alumina or silica. The alumina crucibles are in general more resistant to slag corrosion, but are more prone to thermal shock.

A correct control of the atmosphere is crucial otherwise oxygen may dissolve in the slag and change its potential. Different methods were evaluated: (1) nitrogen (99.8 %); (2) nitrogen + 5% hydrogen; (3) nitrogen and a thin layer of carbon black fine cokes (30 to 40 g), which will be indicated by N_2, N_2 + 5% H_2 and N_2 + C, respectively.

Description of the Slag Samples

Different slag samples were obtained from non-ferrous smelting operations. Their compositions are for the oxygen potential determining constituents are listed in Table 1. Slag 1 was obtained from a lead blast furnace operation. Slag 2 is a cleaned lead blast furnace slag. Slag 3 is a reduced lead blast furnace slag. Slag 4 was taken from a lead-copper smelter. Slag 5 is a copper convertor slag.

Table I Composition of the evaluated slags in mass%

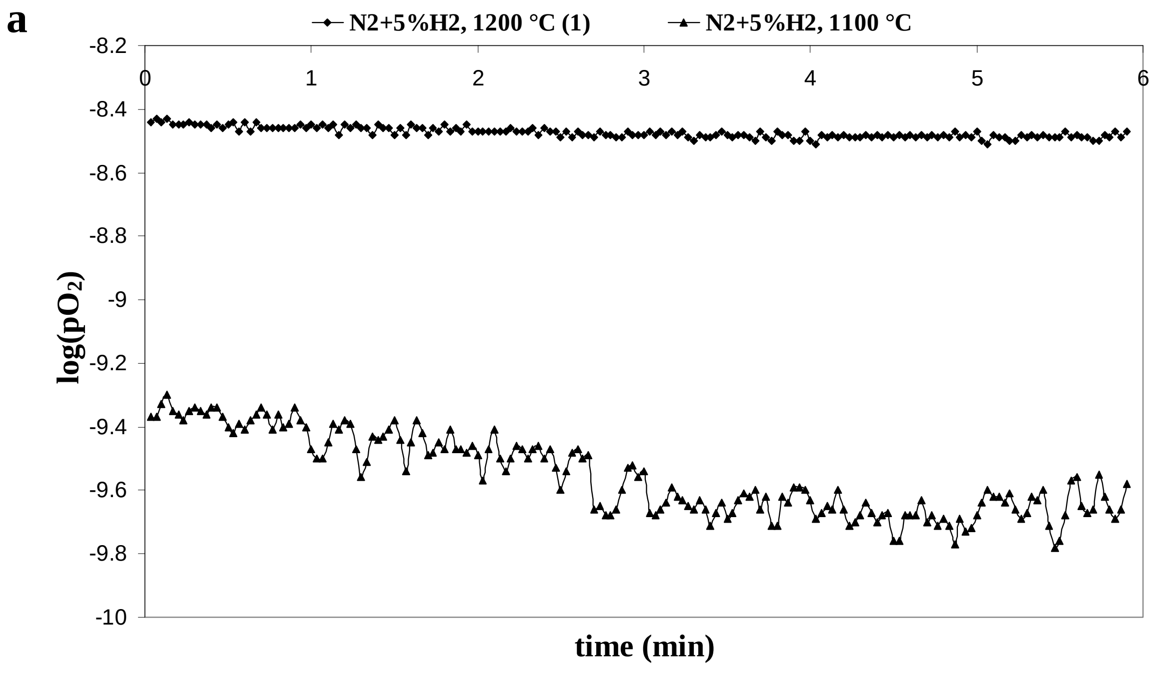
	Pb	Cu	Ni	Zn	Fe
Slag 1	2.5	0.2	<0.1	5.9	25.0
Slag 2	0,74	0.30	<0.02	5.1	21.5
Slag 3	<0.1	0.10	<0.1	0.7	0.3
Slag 4	29.9	2.7	1.7	3.6	10.1
Slag 5	36.0	24.0	5.6	1.3	3.0

Description of the Calculations

The oxygen activity of the slags was calculated using the thermodynamic software FactSage (5). The slags are equilibrated with another phase to ensure the meaningfulness of the calculated values (3). The second phase was chosen to be the metal in equilibrium with the slags. Therefore, slags 1, 2 and 3 were equilibrated with a lead rich metallic phase and slags 4 and 5 with a Cu rich metallic phase. 100 grams of slag is equilibrated with 1 gram of metal in the calculation. The slag components are supposed to be oxides during the experiments. The small metal addition does not change the slag composition much. This procedure ascertains that a reliable oxygen potential of the oxide-metal system is calculated.

Results and Discussion

Slag 1 was tested under N_2 + 5% H_2 and N_2 + C atmosphere. The measurement of the log(pO_2) in a N_2 + 5 % H_2 atmosphere at 1200 °C gave a value of –8.4 with a very stable signal (Fig. 3a). After one hour the sensor showed signs of strong corrosion in comparison with similar measurements in glass melts. At 1100 °C a value of –9.5 was found, although the signal was much less stable and the slag was already too viscous for proper evaluation (Fig. 3a). In the N_2 + C atmosphere, at 1200 °C the log(pO_2) was equal to –9.0, at 1100 °C to –10.8. Table II gives an overview of the measured and calculated oxygen potentials. There is a fairly good agreement between the measured and calculated oxygen potential of Slag 1. The use of carbon improves the correspondence between the values. The unstable signal at 1100 °C is probably due to the large solid fraction of the slag at that temperature. Calculations show that only 14 wt% of the system is liquid at 1100 °C.



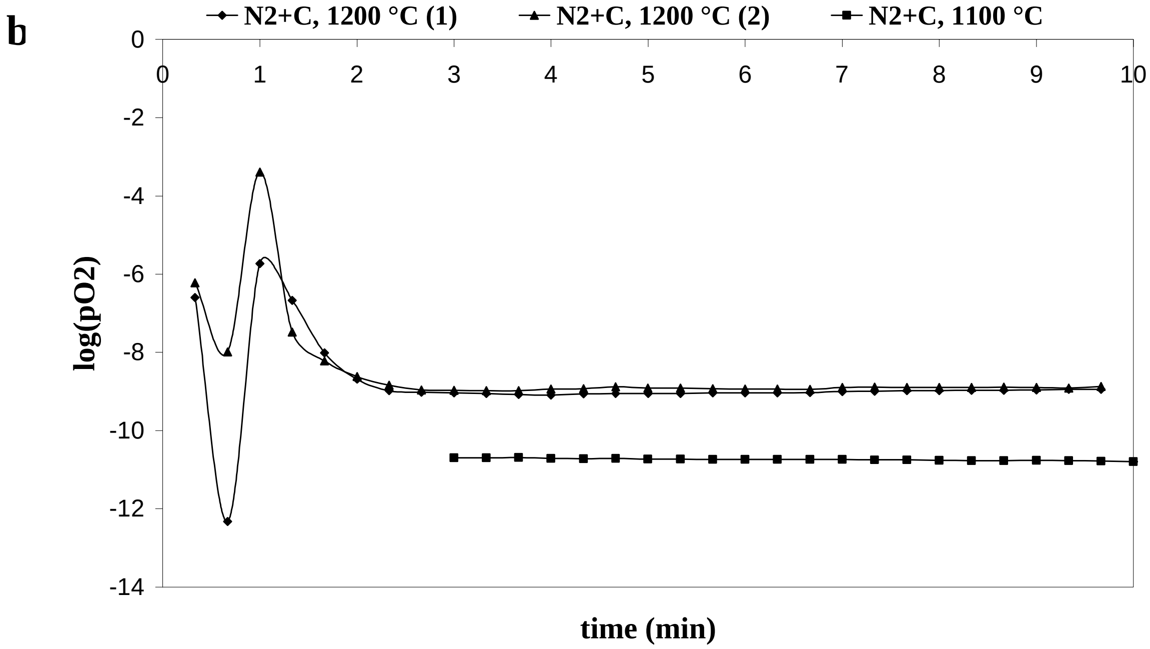


Figure 3 Measurement of Slag 1 (a) at 1100 and 1200 °C in a N_2 + 5% H_2 atmosphere; (b) at 1100 and 1200 °C in a N_2 + C atmosphere

Table II Overview of the measured and calculated oxygen potentials

Slag	Measured log(pO_2)					Calculated log(pO_2)	
	N_2 (+ 5% H_2)			N_2 + C			
	1100 °C	1200 °C	1300 °C	1100 °C	1200 °C	1100 °C	1200 °C
1	-9.5	-8.4		-10.8	-9.0	-10.5	-9.6
2		-7.7	-6.6			-10.7	-10.3
3					-10.6	-11.3	-10.4
4		-6.5			-6.4	-8.1	-7.1
5		-3.7					-6.8

The melting point of Slag 2 is higher than that of Slag 1 and therefore measurement temperatures of 1200 °C and 1300 °C were chosen. Measurements were made only in N_2 + H_2. At 1200 °C a very stable signal was obtained which corresponds to a log(pO_2) of –7.7. At 1300 °C the value equals –6.6. After some 10 minutes however the signal became unstable, probably due to corrosion of the silica protection tube around the Ir conductor, which caused the measured potential to go up. It was attempted to measure at 1100 °C but the slag was too viscous. The thermodynamic calculations predict only 1.3 wt% liquid fraction of the oxides at 1100 °C. It is generally accepted that the oxygen potential of a slag is determined by its least stable components. As Slag 2 has less iron oxide in the slag, it would be expected that Slag 2 has a lower oxygen potential than Slag 1. Therefore it is remarkable that the measured oxygen potential of Slag 2 is higher than that of Slag 1. This is probably caused by atmospheric oxygen that reoxidises the slag or that makes contact with the Ir conductor. Covering the slag with a carbon layer can prevent both phenomena.

Slag 3 was obtained after reduction of blast furnace slag with CO gas at 1300 °C. It was measured at 1200 °C in a N_2 + C atmosphere and the log(pO_2) was found to equal –10.6. The measurement of Slag 3 corresponds well with the calculated log(pO_2) at 1200 °C. The signal was very stable for a long time and the corrosion of the sensor was minimal. At 1150 °C the slag was too viscous to be measured.

Slag 4 was measured in N_2 and N_2 + C atmosphere at 1200 °C. A value of –6.5 was found in N_2 and –6.4 in N_2 + C (Fig. 4). Slag 4 was also measured at 1250 °C. No stable value could then be determined. The measurements at 1200 °C showed that the results are reproducible. The difference between the measurements with and without a carbon layer is small. At these relatively high oxygen potential the small amount of oxygen in the N_2 gas seems not to disturb the measurement. The measured value is somewhat higher than the calculated values.

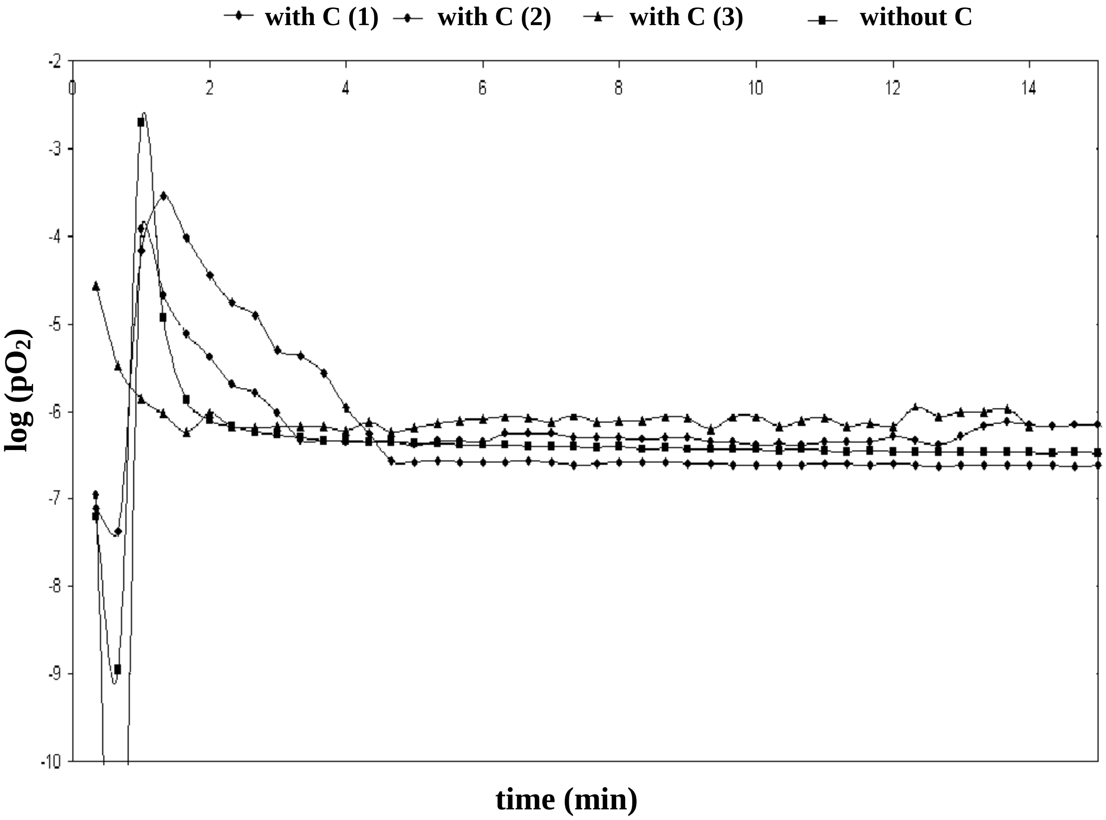


Figure 4 Measurements of Slag 4 at 1200 °C

Slag 5 was only measured under N_2 atmosphere at 1200 °C. A value of log(pO_2) equal to –3.7 was found. The measurement was performed twice. In the first experiment the measurement was done at 1100 °C and subsequently the temperature was increased to 1200 °C. The measured values were unstable but on average they corresponded with the second test. In the second experiment the temperature was increased at once to 1200 °C. The measured values were rather stable in this case. Probably the measurement at 1100 °C caused that much damage to the sensor that the values at 1200 °C were variable during the first test. The difference between the measured and calculated value is quite large. In this case, the assumption for the calculation (equilibrium with Cu metal) may be less accurate to describe the state of the slag.

Conclusions

The experiments described in this paper confirm that the Rapidox technique may be used to measure the oxygen potential of non-ferrous slags in a range of 10^{-3} to 10^{-12} bar accurately if the necessary precautions are taken. A protective carbon layer on the slag surface seems to be of use when measuring oxygen partial pressures below 10^{-6} bar in addition to a flow of nitrogen. The temperature at which the measurement is best taken depends on the slag system. At too high a temperature the slag becomes too aggressive and starts to corrode the sensor, at too low a temperature the slag becomes too viscous. The ideal measurement temperature seems to correspond to the tapping temperature.

The slag measurements appear to be less accurate than the glass measurements as reported in (4). This may be caused by a dissolution of the silica protection layer on the Ir electrode. A more resistant coating could avoid this problem. Possibly also a faster rotation speed is helpful. To extend the measurement range other crucible materials and eference electrodes different from Ni/NiO may need to be used.

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