The influence of polyvalent metal cations on the corrosion rate of molybdenum in molten glass

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Abstract

The corrosion behavior of molybdenum in a silicate melt has been studied using electrochemical techniques. The aim was to examine whether or not polyvalent metal ions such as iron (Fe^{3+}), nickel (Ni^{2+}) and cobalt (Co^{2+}) are able to influence the corrosion behavior of molybdenum and, if so, to which extent. In addition the impact of the temperature of the melt on the corrosion rate has been addressed.
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1. Introduction

The electric melting of glass has become a method with increasing importance in the glass and enamel production industry as a result of various technical and ecological advantages [1–4]. The procedure involves bringing heat into the glass melt by means of the Joule effect using an ac current through electrodes.

Today, molybdenum is commonly used as electrode material for glass melting. It has a high melting point, a high thermal and electrical conductivity and it is mechanical stable up to temperatures of 1600 °C. However, the most important problem associated with the electrical glass melting and the use of molybdenum electrodes is the significant corrosion of the electrode material [5–7]. This corrosion process causes the molybdenum electrodes to be damaged.

One of the more important factors which influences the corrosion of molybdenum electrodes is the chemical composition of the melt. Since molybdenum is one of the less noble metals, it will be oxidized in the presence of nearly all other polyvalent ions in the melts. The temperature and viscosity of the melt and the density and frequency of the heating current are other factors that may well influence the corrosion.

Several studies on the corrosion behavior of molybdenum electrodes in glass melts have been published [2–17]. Two categories can be distinguished here: studies which investigate the corrosion reaction and the influence of different parameters on it [2–9] and studies concerning the corrosion protection [9–17]. The study of the corrosion reaction has already been approached through a great number of methods, including electrochemical techniques [2–5,9,10,16]. These electrochemical methods are quite suitable for this purpose because of the electrochemical nature of the corrosion process and the good conductivity of molten glass.

In this study the influence of iron, nickel and cobalt on the corrosion of molybdenum in a molten enamel is investigated using electrochemical techniques. The aim is to examine whether or not these polyvalent metal ions are able to influence the corrosion behavior of molybdenum

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and, if so, to which extent. In addition, the influence of the temperature of the melt on the corrosion rate is addressed.

2. Experimental procedures

In order to select a relatively simple and representative primary glass, a large number of compositions were compared. A composition, containing no electroactive species, but with a satisfactory electrical conductivity was selected. The chemical composition of this basic melt is given in Table 1. All reagents used to prepare the melts were of analytical grade.

A preliminary study existed in determining the standard reduction potentials of the redox couples, Fe^{3+}/Fe^{2+}, Ni^{2+}/Ni, Co^{2+}/Co^+, $Mo^{(x+n)}/Mo^{x+}/Mo$, using square wave voltammetry. For each redox couple 1 wt% of the oxide of the metal under investigation (i.e. Fe_2O_3, Ni_2O_3, Co_3O_4 or MoO_3) was added to the basic glass melt and the current–potential curves were acquired at a platinum electrode with a frequency between 200 and 10 Hz. The choice of using these oxides as sources for the various redox couples is based on previous research results [18–20]. All reagents used were of analytical grade.

The extent of the impact of their presence was performed by adding different concentrations of the various oxides to the basic melt. For each melt composition three types of electrochemical experiments were carried out. First the corrosion potential (E_{corr}) was measured as a function of time. Even though this parameter will not give direct information with regard to the corrosion rate or mechanism, it provides useful information with regard to the surface reactivity. Once a stable potential was reached electrochemical impedance measurements were performed to obtain information on the electrolyte resistance. Finally, linear potential sweep voltammograms were recorded in a small potential region around E_{corr} to obtain the polarization resistance, which is directly related to the corrosion rate. In addition mass loss experiments were performed, providing additional information about the corrosion behavior.

The influence of the temperature on the corrosion rate was determined by measuring the polarization resistance in a temperature range of 1473–1173 K using one melt of each metal.

Table 1
Chemical composition of the melt (= basic glass melt)

Oxide	Content in wt%
SiO_2	62.8 ± 0.3
Na_2O	18.2 ± 0.2
CaO	7.8 ± 0.1
B_2O_3	4.9 ± 0.1
MgO	3.5 ± 0.1
Al_2O_3	1.8 ± 0.1
K_2O	0.8 ± 0.1

2.1. Electrochemical experiments

A vertical tube furnace was modified to be powered with dc current in order to avoid the effect of an ac current on the electrochemical experiments, as previously described by Rüssel et al. [21,22]. A water cooled flange of stainless steel was placed on top of the furnace. In this flange the reference and counter electrode are attached.

The reference electrode is a rod of yttria stabilized zirconia, the upper part of which is cemented into an alumina tube with a ceramic mortar. Inside this tube a pressure contact with the zirconia is made with the aid of a platinum wire and as reference gas air is blown through the tube [23]. All potentials mentioned in this paper refer to this reference. The counter electrode is a platinum plate with a surface area of approximately 3 cm^2.

The working electrode is an inlaid disc electrode. For the preliminary study a platinum electrode is used, whereas for the corrosion study it is a molybdenum electrode. These inlaid disc electrodes are constructed according to a paper by De Strycker et al. [24]: a platinum rod (3 mm diameter; 99.95% pure) respectively a molybdenum rod (5 mm diameter; 99.98% pure) is fixed in an alumina tube (8 mm inner diameter; 99.7% pure) with a ceramic binder in such a way that only the cross section of the rod is used as electrode surface. A fresh surface of the working electrode is obtained by polishing with SiC-emery paper, type 1200 grit for 30 s. To smoothen this relatively rough surface it was further polished on a polishing cloth with alumina powder of successively 1.0 and 0.05 μm particle size for respectively, 5 and 10 min. The polishing sequence was carried out on a disk polishing machine. To remove any adsorbed alumina particles an ultrasonic cleaning step was introduced. Contact is made with a platinum wire on top. The alumina tube was purged with pure nitrogen to avoid contact between the molybdenum and the air.

The electrochemical cell, which is an alumina oxide crucible, filled with the melt was lifted in the furnace with the aid of an alumina tube placed on two lab jacks. This system allows one to control the position in the furnace very precisely. Checking of the contact between electrodes and the melt was carried out through electrical conductivity measurements. After dipping in the reference and counter electrode the furnace was flushed with pure nitrogen and the working electrode was immersed and attached in the water cooled flange. Subsequently the atmosphere is changed by blowing air in the furnace. The operating temperature for all tests (except for the temperature dependence tests) was 1473 K.

For all electrochemical experiments a PC controlled potentiostat and software package type GPES 4.5 (Autolab PGSTAT20 from ECO Chemie) was used. The potentiostat was extended with a frequency response analyzer module to perform EIS (FRA 4.5). Impedance measurements were performed between 100 and 100 mHz. The resistance ranged between 10 and 1 kHz, depending on the measurement performed.

2.2. Mass loss experiments

In these experiments rods (30 mm length, 5 mm diameter) of molybdenum were positioned in an alumina crucible. The crucible was filled with the basic melt and placed in a chamber furnace at 1473 K for 10 days. After 10 days the entire content of the crucible was poured in water at room temperature. Due to the fast cooling and the difference in shrinkage coefficient between the glass and molybdenum, the glass in general does not adhere to the metal surface. To remove small, adhering pieces of glass, the rods were cleaned with hydrofluoric acid (Vel 48–51%). Hence an accurate determination of the mass loss is possible.

3. Results

3.1. Preliminary study

The spontaneity of a redox reaction in a particular solvent, be it in an aqueous solution or in a glass-forming melt, can be predicted by determining the reduction potentials of the redox couples. In this study the reduction potentials of Fe^{3+}/Fe^{2+}, Ni^{2+}/Ni, Co^{2+}/Co^+, $Mo^{(x+n)}/Mo^{x+}/Mo$ were determined using square-wave voltammetry. The latter technique was used as it has previously shown to obtain a high sensitivity under the conditions measured [18]. Fig. 1 shows the square wave voltammetric curves. The peak potentials in this plot are equal to the reduction potential of the attributed redox pair. It is generally accepted that the potential of the reference electrode used in this study would be zero if the reference gas was pure O_2. In other words the $ZrO_2/Pt/air$ electrode fulfils the same function as the Normal Hydrogen Electrode in aqueous solutions [25,26]. The latter implies the standard potentials of the redox pairs can be obtained by correcting the peak potentials for the use of air instead of pure O_2. Fig. 2 gives the order of the redox couples in the investigated glass at 1473 K arranged by their standard reduction potential.
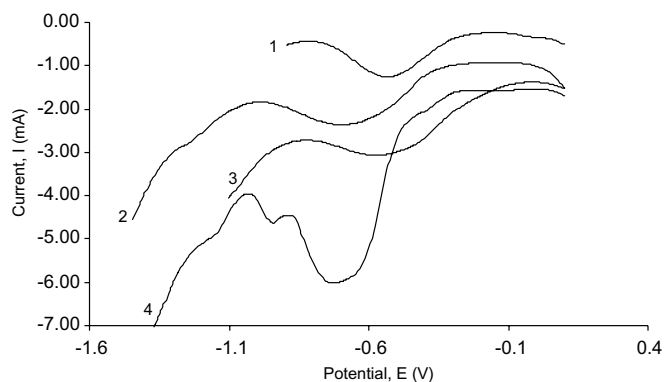

Fig. 1. Square wave voltammetric curves recorded at a platinum electrode in the basic glass melt modified with different oxides. (1) 1 wt% Ni_2O_3, $f = 10$ Hz, (2) 1 wt% Co_3O_4, $f = 50$ Hz, (3) 1 wt% Fe_2O_3, $f = 50$ Hz, (4) 1 wt% MoO_3, $f = 50$ Hz. Square wave amplitude = 50 mV; temperature = 1473 K. The reference electrode is a rod of yttria stabilized zirconia.
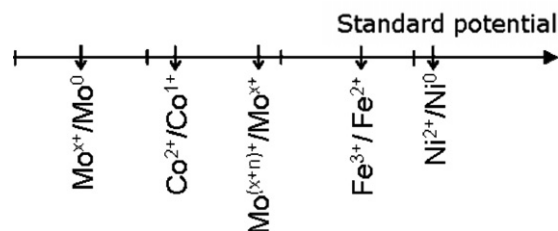

Fig. 2. Redox reactions arranged by their standard potential at 1473 K in the basic glass melt. Absolute values are not given as they depend on the composition of the melt they have been measured in.

3.2. Corrosion study

The surface reactivity of molybdenum was studied by determining the corrosion potential of the metal when immersed in the glass melt containing one of the oxides and this under various concentrations. The time required to reach a non-fluctuating value depends on the composition of the melt and takes between 2 and 16 h. The stable E_{corr} values for the various melt compositions are given in Table 2. Although the corrosion potentials are all situated within a range of 150 mV, in each series of measurements a clear tendency can be observed. With the exception of 2.5 wt% Co_3O_4, the corrosion potential increases (becomes less negative) with increasing cation concentration.

Linear potential sweep voltammetry was used to determine the polarization resistance. The latter is commonly used for corrosion rate monitoring and is defined by the slope of the (linear) potential sweep voltammogram at E_{corr}.

$$R_p = \left(\frac{\Delta E}{\Delta I} \right)_{E_{corr}} \tag{1}$$

However, by using linear potential sweep voltammetry, the data may suffer from the contribution of capacitive currents and Ohmic drop effects. The capacitive currents are proportional to the potential sweep rate. The latter implies that if the slope of the curves is not affected by the scan

Table 2
Average stable E_{corr} values

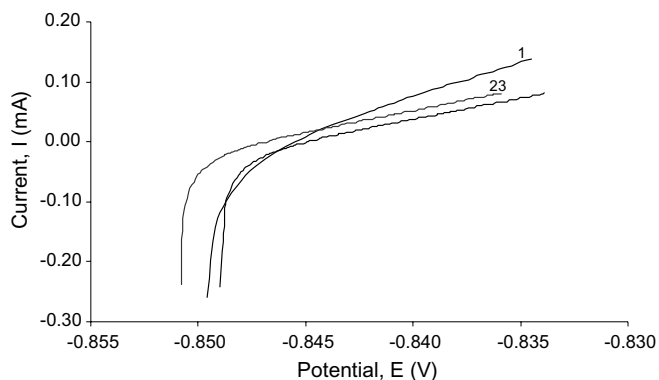| Compound	Quantity (wt%)	E_{corr} (mV)
Fe_2O_3	2.5	-808 ± 21
	5.0	-790 ± 6
	7.5	-733 ± 4
	10.0	-703 ± 2
Ni_2O_3	0.5	-825 ± 17
	1.0	-818 ± 10
	1.5	-809 ± 5
	2.5	-763 ± 6
Co_3O_4	0.5	-826 ± 23
	1.0	-821 ± 17
	1.5	-810 ± 14
	2.5	-819 ± 4

Fig. 3. Linear sweep voltammetric curves recorded with different potential sweep rates at a molybdenum electrode in the basic glass melt at 1473 K. Sweep rates are (1) 0.2, (2) 0.05, (3) 0.01 mV s^{-1}. The reference electrode is a rod of yttria stabilized zirconia.

Table 3
Mass loss data of molybdenum in various glass melts

Compound	Quantity (wt%)	Δm (mg cm^{-2})
Fe_2O_3	2.5	15.0
	5.0	59.5
	7.5	237.1
	10.0	330.9
Ni_2O_3	0.5	9.5
	1.0	29.8
	1.5	91.3
	2.5	196.1
Co_3O_4	0.5	3.5
	1.0	10.0
	1.5	18.8
	2.5	39.1

rate, there is no significant contribution from capacitive currents. Fig. 3 shows three current–potential curves obtained by linear sweep voltammetry in the basic glass melt. The curves were recorded at three different potential sweep rates (0.2 mV s^{-1}, 0.05 mV s^{-1}, 0.01 mV s^{-1}). The highest scan rate gives rise to a steeper slope, the other curves are parallel, indicating there is not any significant influence of capacitive currents. In order to comply with this and at the same time keep the duration of the measurements to a minimum, data were acquired with a scan rate of 0.05 mV s^{-1}. The Ohmic resistance on the other hand, was determined using electrochemical impedance measurements and is of the same order as R_p (i.e. ca 2 Ω cm^2). The latter implies the need for taking the Ohmic resistance into account when determining the polarization resistance.

The inverse R_p values of molybdenum as a function of the various oxide concentrations are presented in Fig. 4. The values are averaged over at least 5 measurements performed between 24 and 28 h after immersion of the elec-
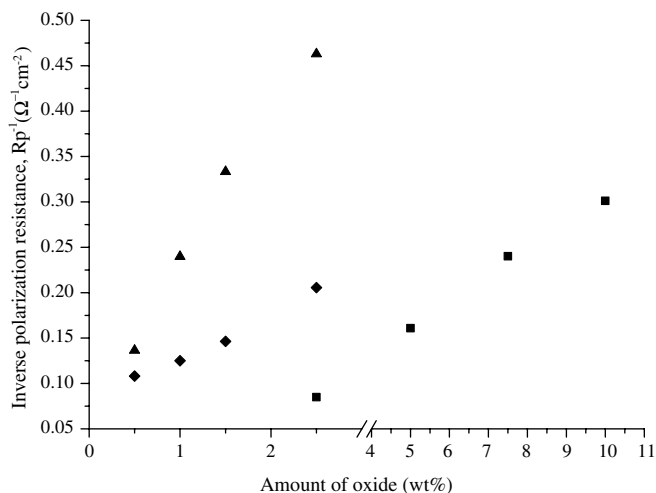
trode into the glass melt. In accordance with the practical experience, the inverted polarization resistance increases with increasing oxide concentrations or in other words the corrosion rate is augmented at a higher Fe_2O_3, Ni_2O_3 or Co_3O_4 concentration. The results of mass loss experiments performed in glass melts with the same composition are given in Table 3. They show a clear increase in mass loss of the molybdenum rod with higher concentrations of the metal cations.

3.3. Influence of temperature

In order to obtain information about the influence of the temperature on the corrosion rate, the polarization resistance was determined for a temperature range from 1173 K to 1473 K in the basic melt and three melts were modified with the lowest Fe_2O_3, Ni_2O_3 and Co_3O_4 concentration. The results are shown in Fig. 5 in the form of Arrhenius plots.

4. Discussion

The ranking of the standard reduction potentials for the various metal ions, presented in Fig. 2, confirms that molybdenum has the most negative standard potential. The latter indicates that iron, nickel and cobalt can act as an oxidizing agent (electron acceptor) with respect to molybdenum.

Their actual involvement is demonstrated by the shift of the E_{corr} data to less negative values as a function of the oxide concentration (Table 2). This trend can be explained by a theoretical current–potential curve of a corrosion system (Fig. 6). In case iron, nickel and cobalt act as oxidizing agent (or electron acceptor) in the corrosion reaction of molybdenum, an increasing concentration of these metal ions results in a raised cathodic current, depicted as the dashed curve in Fig. 6. The latter implies that the E_{corr} value ($i_M = -i_{EA}$) shifts to a more positive value (or to the right on the figure).

The polarization resistance values (Fig. 4) as well as the results of mass loss experiments given, in Table 3, show

Fig. 4. Inverse of the polarization resistance of molybdenum at 1473 K plotted versus (▲) Fe_2O_3, (♦) Ni_2O_3 and (■) Co_3O_4 concentration in the glass melt.
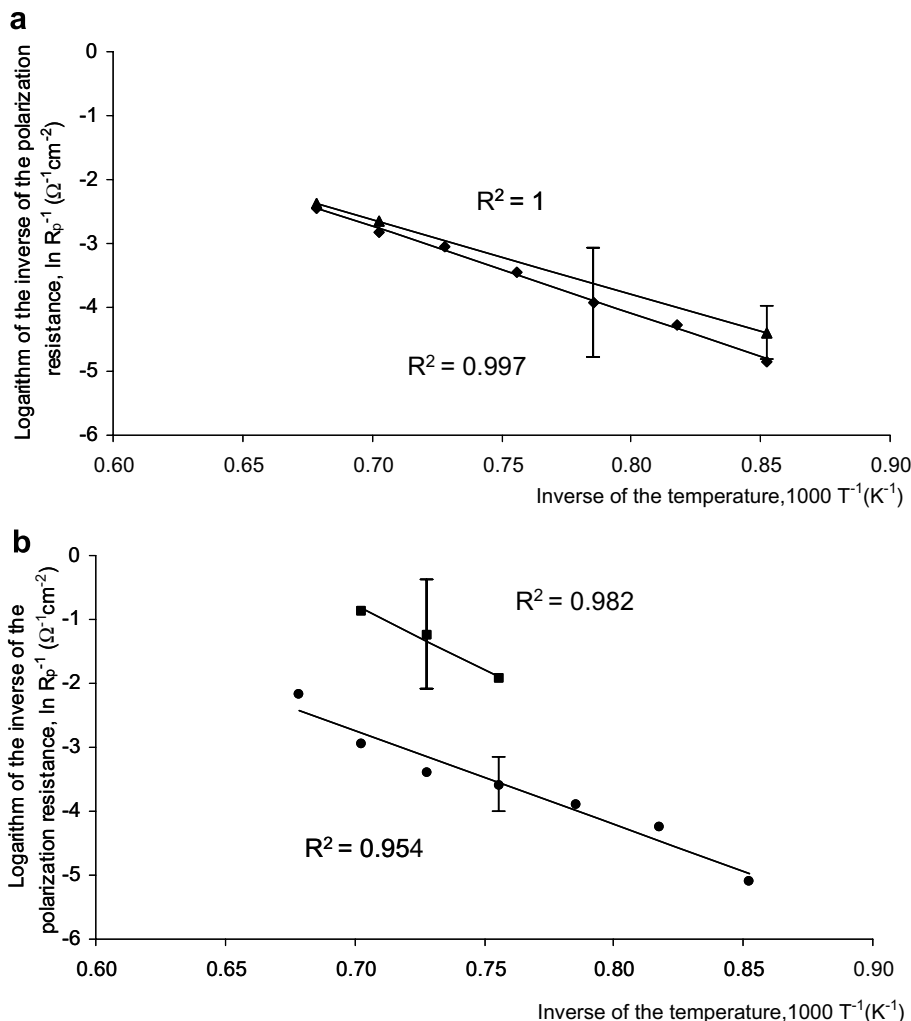
Fig. 5. Arrhenius plot of the inverse of the polarization resistance of molybdenum at 1473 K. (a) (♦) in the basic glass melt, (▲) in the basic glass melt modified with 2.5 wt% Fe_2O_3. (b) (■) in the basic glass melt modified with 1.0 wt% Ni_2O_3, (●) in basic glass melt modified with 1.0 wt% Co_3O_4. Each set of data has been fitted by the method of least squares.
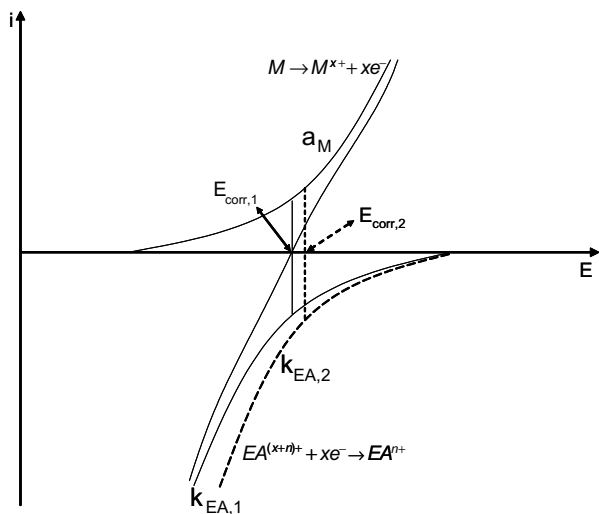

Fig. 6. Schematic of a current–potential curve of a corroding system. a_M: anodic curve of the metal (M), $k_{EA,1}$ and $k_{EA,2}$: cathodic curves for different the electron acceptor (EA) concentrations. $k_{EA,1}$ lowest concentration, $k_{EA,2}$ highest concentration.

that the corrosion rate of molybdenum increases with higher Fe_2O_3, Ni_2O_3 or Co_3O_4 concentrations. The mass loss results, moreover, show nickel to be the most aggressive metal ion and iron the least aggressive metal ion.

In spite of the fact that the polarization resistance is already a relative measure for the corrosion rate and t, the real reaction rate (I_{corr}) requires the knowledge of the Stern–Geary constant. This relationship is known as the Stern–Geary equation:

$$I_{corr} = \frac{B}{R_p} \qquad \text{with} \qquad B = \frac{\beta_a \cdot \beta_c}{2.303(\beta_a + \beta_c)}, \qquad (2)$$

where R_p is the polarization resistance, B the Stern–Geary constant β_a and β_c the anodic and cathodic Tafel slopes. In Tafel plots the current is plotted in a logarithmic way versus the potential.

Fig. 7 shows a current–potential curve obtained at a molybdenum electrode in the basic glass melt. This Tafel representation, however, does not show a decade of linearity necessary to determine the Tafel slopes. The latter can
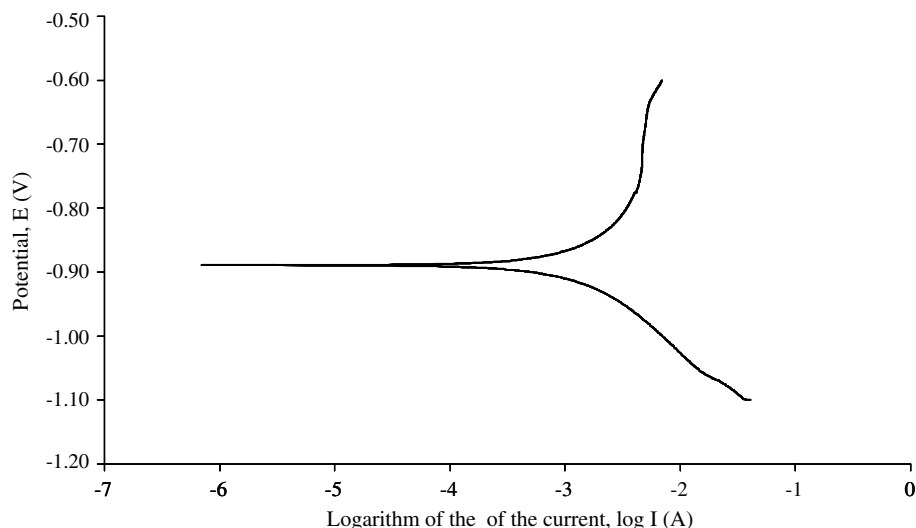
Fig. 7. Tafel representation of a current–potential curve recorded at a molybdenum electrode in the basic glass melt at 1473 K. The reference electrode is a rod of yttria stabilized zirconia.

be explained by the high temperature of the melt. Tafel slopes are defined according to the following equation:

$$\beta_a = \frac{2.3RT}{F\alpha_a} \qquad \beta_c = \frac{2.3RT}{F\alpha_c}, \tag{3}$$

where β_a and β_c are the anodic and respectively cathodic Tafel slopes, R the gas constant (8.314 J mol^{-1} K^{-1}), T the temperature in K (1473 K), α_a and α_c the anodic and respectively cathodic transfer coefficient and F the Faraday constant (96485 C mol^{-1}). With the exception of the transfer coefficients α_a and α_c all factors are known. For a one electron-step the transfer coefficients vary between 0 and 1. Assuming these values equal to 0.5 leads to $\beta = 583$ mV/decade. The latter implies that the linearity of at least one decade can occur when no other reaction takes place in that interval. This condition is rarely fulfilled in glass melts.

ASTM procedures to determine the corrosion rate describe several possibilities to obtain the Stern–Geary constant in a non-electrochemical way by for example coupling of mass loss and polarization resistance measurements [27]. A combination of Faraday's law (4) and Eq. (2) predicts a linear relationship between the mass loss per time unit and the inverted polarization resistance (5).

$$i_{corr}t = nF\frac{\Delta m}{M_R} \tag{4}$$

$$\Delta m_{time} = \frac{M_R B}{nF} \cdot R_P^{-1} = constant \cdot R_P^{-1}, \tag{5}$$

where Δm and Δm_{time} are the mass loss in g cm^{-2} and respectively mass loss per time unit in g s^{-1} cm^{-2}, M_R the molecular weight in g mol^{-1}, t the time in s, n the number of transferred electrons, F the Faraday constant (96485 C mol^{-1}), R_p the polarization resistance in Ω cm^2 and i_{corr} the corrosion current in A cm^{-2}. The mass loss per time (Δm in mg s^{-1} cm^{-2}) unit as a function of the inverted polarization resistance (R_p^{-1} in Ω^{-1} cm^{-2}) when Fe_2O_3 is present in the melt is plotted in Fig. 8. This curve
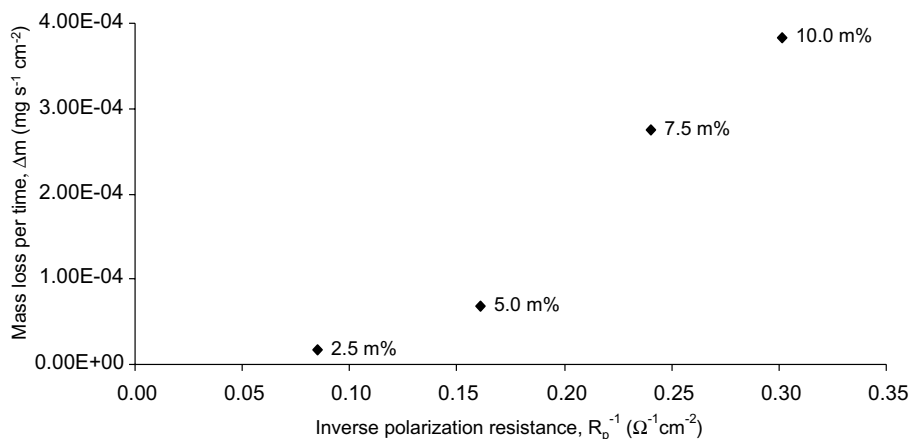

Fig. 8. The mass loss per time (Δm in mg s^{-1} cm^{-2}) unit as a function of the inverse of the polarization resistance (R_p^{-1} in Ω^{-1} cm^{-2}) of a molybdenum electrode in glass melts with varying Fe_2O_3 concentrations.

does not show the expected linear relationship. Similar results were obtained for Ni_2O_3 en Co_3O_4. An explanation for this discrepancy could be found in the different duration of the experiments. On the one hand, the mass losses are time averaged results of the corrosion reaction that took place during ten days. On the other hand, the inverted polarization resistance is a measure for the corrosion rate at a given moment. Considering the fact that the rate of corrosion processes does not proceed linearly as a function of time these results could be different.

The above-mentioned results have shown that it is not possible to obtain the Stern–Geary constant in the glass melt environment. For this reason, the inverted polarization resistance is further used to investigate the influence of the temperature on the corrosion rate of molybdenum in the basic melt and three melts modified with the lowest Fe_2O_3, Ni_2O_3 and Co_3O_4 concentration. The Arrhenius plots of the inverted polarization resistances shown in Fig. 5 reveal a good linear fit for each melt composition. The straight line indicates that the same corrosion mechanism is valid over a wide temperature range. Moreover the Arrhenius-type diagrams reveal an activation energy of 113, 97, 166 and 121 kJ mol^{-1} for the corrosion reaction of molybdenum respectively in the basic melt and melts modified with Fe_2O_3, Ni_2O_3, and Co_3O_4.

5. Conclusions

This study focused on the influence of polyvalent metal ions of iron, nickel and cobalt on the corrosion behavior of molybdenum rods in glass melts. Using corrosion potential measurements, it was possible to identify iron, nickel and cobalt as reduction partners in the corrosion of molybdenum. In addition, nickel could be classified as the most aggressive ion, and iron the least aggressive ion.

The polarization resistance method was used to investigate the corrosion rate and the effect of the temperature on it. The results showed an increased corrosion rate with higher concentration of iron, nickel and cobalt ions. The temperature dependence study showed a constant corrosion mechanism across the temperature range of 1173–1473 K and allowed us to determine the activation energies of the corrosion processes.

In spite of the fact that the polarization resistance is already a relative measure for the corrosion rate, the real reaction rate requires the knowledge of the Stern–Geary constant or Tafel slopes. Different methods to obtain the Stern–Geary constant were evaluated but none of them were satisfactory to retrieve the value of the constant for molybdenum in molten glass. For this reason, the inverted polarization resistance remains to be used as a measure for the corrosion rate despite its limitations.

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