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Electrochemical behavior of glass melts: application to corrosion processes

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Abstract

Molten silicate glasses are complex media in which ionic species can be easily dissolved. That typically concerns the metallic cations or oxoanions. The as-described liquids have therefore the properties of electroactive solutions in which the ions displacements allow the electrical conduction. As a consequence, the use of electrochemical techniques adapted from those classically used in aqueous media allows the characterization of specific physico-chemical properties of the system (*i.e.* the molten silicate matrix containing the dissolved ionic species). In particular, thermodynamic characteristics, like the redox and the basicity of the molten glass, can be measured as well as kinetic properties, like the intrinsic ion mobility or the metallic alloys corrosion rates. Some of these results, from specific studies performed by IJL-UMR 7198, are summarized here. For example, an electrochemical concentration cell has been developed to determine the activity of the strong base Na₂O in silicate melts at high temperature, and the results were compared to theoretical models of basicity. A scale of formal potentials characterizing the redox couples in corrosion process was determined, allowing the prediction of the chemical reactivity with regard to thermodynamic criteria. Kinetic data evidenced the conditions leading to the passivation of the surface of alloys: it was deduced that the most efficient protection was provided by chromia. Lastly, the conditions of thermodynamic stability of Cr₂O₃ have been studied by considering the influence of temperature, basicity, and oxygen partial pressure in the melts.

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Keywords: corrosion; electrochemical methods; molten glass; basicity; redox; solubility; chromia

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1. Introduction

In glass industry, superalloys are widely used when the ductility of platinum or the fragility of ceramic is not suitable. However, these materials should have the ability to withstand such a harsh environment and thus to resist against high temperature corrosion by molten glass. Due to their structure and composition, glass media exhibit acido-basic properties as they allow the exchange of oxide ions O^{2-} . The acido-basic properties have already been described by Abdelouhab *et al.* (2008). Furthermore, the presence of dissolved oxygen O_2 in the medium, depending on the conditions of preparation of the glass, provides oxydo-reducing properties described by Claes *et al.* (1992) and Tilquin *et al.* (1997). So glass is a corrosive medium, and as it is an electrolyte, a specific apparatus devoted to electrochemical characterization has been adapted from aqueous corrosion studies to the case of the high temperature. As a consequence, experiments performed thanks to this specific device gave access to a better knowledge of the mechanisms involved in the corrosion of alloys by molten glass.

This paper presents some of the main results obtained in the lab through years of study of the corrosion of alloys by molten glass. The main properties of the glass media are summarized. First, the determination of the electroactivity domains of the glass is important to know the limit potentials where the solvent is oxidized or reduced. Then, a summary of the formal potentials of many metallic elements couples often met in glass industry is given, and can be used to explain many corrosion mechanisms and reactions. Lastly, basicity has been thoroughly studied. Experimental data have been collected giving access to the sodium oxide Na_2O activity in the melts. As Na_2O is the main strong base in many melts, these data are compared to a basicity model (optical basicity) commonly described for molten glasses by Duffy *et al.* (1976).

From this, several examples of corrosion are detailed. In a first time, the behavior of pure metallic elements commonly used in the metallic parts of industrial devices (*i.e.* Ni, Cr, Fe, Co) is presented. In a second time, the electrochemical characterization of the corrosion of a simplified chromia forming alloy is thoroughly detailed. The ability of this kind of alloy to develop a protective oxide scale is thus emphasized. During immersion, the chromium oxide scale might be dissolved in the molten glass, thus limiting the durability of the protection against corrosion. As a consequence, some general points dealing with the physico-chemistry of chromium in molten silicates are finally shown. A correlation has been directly made with the corrosion study results, highlighting the stability domains of the different oxidation states of chromium.

2. Materials and Methods

2.1. Characterization of the corrosion by electrochemical methods

The experimental apparatus used for the electrochemical characterization of corrosion by molten glass at high temperature has already been described by Di Martino *et al.* (2004). From 1 to 1.5 kg of glass contained in a Pt or in a fused-cast Al_2O_3 - ZrO_2 - SiO_2 crucible is placed in a high temperature furnace. The three electrodes are immersed in the molten glass through the top of the furnace and linked to an acquisition system. The electrodes are home made by using specific materials as mullite tubes, platinum wires, refractory cements. The working electrode consists in a platinum wire (diameter = 1 mm) for the characterization of a glass, or in a metal rod (diameter = 5.5 mm, polished to 1200 grid SiC paper) for the corrosion studies. The counter electrode is a platinum plate (surface $\sim 1\text{ cm}^2$) for the current collection. The reference electrode consists in yttria stabilized zirconia (YSZ) stick (diameter = 5 mm), as this material is good conductor of oxide ions O^{2-} . The electrode is flushed with air through a syringe needle. So the reference used for the electrochemical potentials is the O_2/O^{2-} couple.

2.2. Measurement of sodium oxide activity in molten glass

The determination of Na_2O activities in silicate melts by EMF measurement has been optimized by Abdelouhab *et al.* (2008). The principle is based on a concentration cell, with two cells containing the reference and the working melt respectively, and separated by a Na - β "-alumina electrolyte. Platinum electrodes are immersed in both half-cells.

The anodic reaction of this cell is:



And the cathodic reaction is:



The overall reaction can be written as:



where $Na_2O_{(R)}$ is the sodium oxide in the reference melt and $Na_2O_{(W)}$ is the sodium oxide in the working melt. As the oxygen partial pressure is assumed to be the same in both cells, the activity of sodium oxide in the working melt, $a(Na_2O_{(W)})$, can be calculated from the Nernst equation as follows:

$$\log a(Na_2O_{(W)}) = \log a(Na_2O_{(R)}) - (nF\Delta E)/(2.3RT) \quad (4)$$

where ΔE is the EMF (V) of the cell, R is the universal gas constant, F is the Faraday constant and n the number of electrons exchanged during the reaction.

2.3. Determination of chromium oxide solubility in molten glass

The specific reactor allowing the determination of solubility as a function of glass composition, oxygen fugacity and temperature has been described by Mathieu *et al.* (2008). The sample consists in glass ball (diameter = 2 mm) added with an excess of chromium oxide and placed in a closed system (silica tube) sealed under secondary vacuum. A glass buffer is added in order to buffer the atmosphere in sodium and thus to keep a constant composition of the glass sample in limiting the sodium volatilization. The oxygen fugacity is controlled by using solid redox couples M/M_xO_y buffers and determined from Ellingham diagram. The total chromium dissolved in the melts is then determined by Electron Probe Micro Analysis, as described by Khedim *et al.* (2008 and 2010).

3. Results

3.1. Characterization of the glass media

First, the electroactivity potential domain of the glasses has to be determined. The polarization plot I vs. E of a ternary glass $Na_2O-CaO-3SiO_2$ at 1100°C with use of a Pt working electrode is reported in Figure 1, and is representative of the behavior of silicate melts. The curves were obtained by first exploring the anodic field, as a start on the cathodic field could lead to the reduction of some active species which might contaminate the surface of the platinum working electrode.

Globally, the electroactivity domain of a glass extends from -1100 mV to +200 mV as described by Lizarazu *et al.* (1997) and Cabet (1999). The cathodic limit is attributed by Di Martino *et al.* (2004), and Lizarazu *et al.* (1997) to the reduction of the silica network according to the following equation:



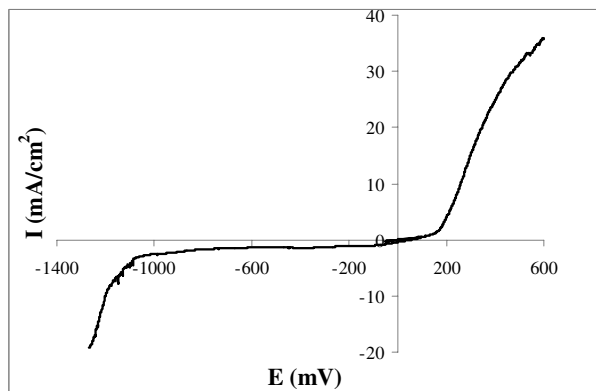


Fig. 1. Electroactivity domain of Na₂O-CaO-3SiO₂ at 1100°C measured on a Pt working electrode with v = 1mV/s. The potentials are reported with respect to the potential of YSZ reference electrode.

The anodic limit corresponds to the oxidation of the O²⁻ ions and to the oxidation of the silica network according to the following equations:



In order to have access to the chemical mechanisms involved in the corrosion of materials, a scale of the formal potentials (*i.e.* potentials in molten silicates at high temperature) of different redox couples including metallic elements has been determined by square wave voltametry methods as described by Gaillard Allemand (2001), Di Martino *et al.* (2004), Lizarazu *et al.* (1997), Rüssel *et al.* (1989), Rüssel (1990), Claussen *et al.* (1996) and Rapin *et al.* (2004). A scale giving the range of these formal potentials at 1050°C is given on Figure 2.

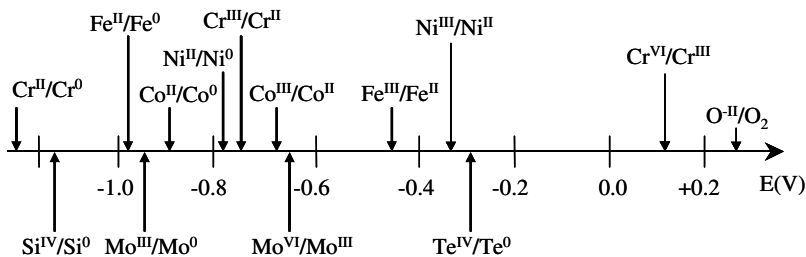


Fig. 2. Scale of formal potential at 1050°C of main redox couples present in glass or constituting the alloys.

The Na_2O activity of different melts has been determined by EMF measurements (C-glass as reference) in the temperature range 1123-1263°C. Figure 3 presents the experimental results versus the optical basicity of the melts calculated from Duffy *et al.* (1976) basicity model.

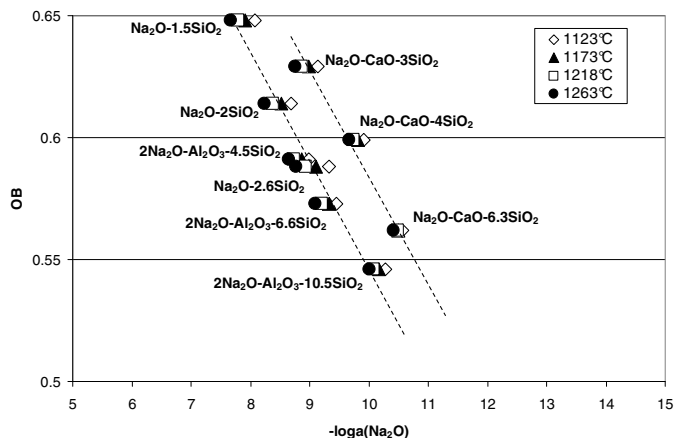


Fig. 3. Optical Basicity (Duffy and Ingram) of different simplified melts vs. Na_2O activity.

Optical basicity is the most used model of basicity amongst several. It can be calculated for a glass according to the following equation:

$$\Lambda = X_{AO_{a/2}} \Lambda_{AO_{a/2}} + X_{BO_{b/2}} \Lambda_{BO_{b/2}} + \dots \quad (8)$$

where X are the fraction of oxygen atoms contributed by each oxide $\text{AO}_{a/2}$, $\text{BO}_{b/2}$, etc..., and Λ are the measured individual optical basicities of these oxides. These individual optical basicities have been determined by absorption spectroscopy measurements and are representative of the ability of the oxides to give oxide ions O^{2-} .

In Figure 3, a linear relation is observed between optical basicity and sodium oxide activity of binary melts $\text{Na}_2\text{O}-x\text{SiO}_2$ and ternary melts $2\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-x\text{SiO}_2$. It can be assumed that in this kind of glasses, the activity of oxide ions is ruled by the activity of the strongest base alkali oxide.

In the case of ternary melts where half of Na_2O are substituted by the CaO base, the linear relation between optical basicity and Na_2O activity is still observed, but the values are shifted to lower sodium oxide activity values. Divalent cation oxides, despite their strong basicity and their network modifier properties, seem to have a specific role once included in a glass structure. If the optical basicity model allows to compare the basicity of glasses of similar types, it is not sufficient when comparing glasses containing different types of network modifiers (*e.g.* alkaline earth oxides).

3.2. Electrochemical study of alloys in glass media

Before studying the corrosion of alloys by electrochemical methods, the anodic polarization of four pure metals classically used in many alloys compositions are presented in Figure 4 by Di Martino *et al.* (2004). These four pure metals have been immersed in an industrial soda-lime glass at 1050°C.

All the metals presented here start from an active state, with an increase of the current density with the imposed potential, due to the oxidation of metallic M to M^{2+} oxidation state. The pure iron sample exhibits a continuous increase of the current density, proving that the attainment of a passive state is impossible. Cobalt and nickel are more noble metals as the corrosion potential is a higher for iron. This is in coherence with the potential scale of Figure 2, which shows that the formal potentials of these metals are in the same ranges as the spontaneous corrosion potentials presented in Figure 4. Both cobalt and nickel exhibit a pseudo passive state with a significant decrease of

the current density after an anodic peak. It is attributed to a modification of the metal surface, as a part of the species generated by the imposed increase of potential (*i.e.* cobalt oxide or nickel oxide) can provide protection and thus limit the current exchange between the glass and the surface of the metal.

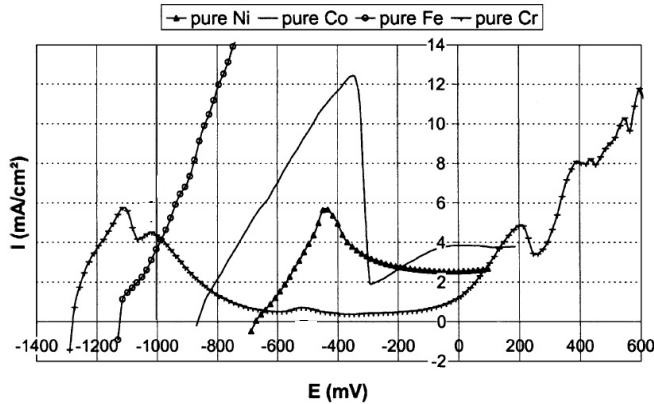


Fig. 4. Anodic polarization of Co, Ni, Fe and Cr in an industrial soda-lime glass at 1050°C.

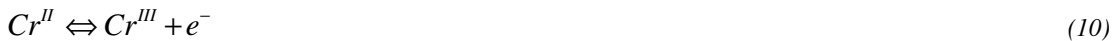
The behaviour of the pure chromium sample can be thoroughly commented by comparison with the potential scale presented in Figure 2. Right after immersion, chromium sample exhibits an active dissolution with a very low potential, the lowest amongst all the pure metals studied here ($E_{\text{corr}} \sim -1300$ mV). Such a low potential can be explained by the chromium oxidation according to:



while the silica network can be reduced according to:



Then, an anodic peak ($E_p \sim -1100$ mV, maximum current density $I_p \sim 6$ mA cm⁻²) is followed by a wide passivation plateau with a very low current density ($I \sim 0.4$ mA cm⁻², about ten times lower than for cobalt or nickel). This means that the corrosion product (*i.e.* Cr₂O₃) is much more protective in the case of chromium. This oxide layer can be formed due to the presence of dissolved O₂ in the melt, according to the simultaneous reactions:



The passivation plateau with low current density extends on a wide potential range, from ~ -700 mV to ~ 0 mV. Beyond 0 mV, the current density increases again, as the protection due to the Cr₂O₃ layer cannot be provided anymore. Indeed, for high potentials, Cr^{III} can be oxidized to the soluble Cr^{VI} specie according to:



This is known as the transpassivation domain.

This electrochemical behavior of chromium has been described by Carton *et al.* (2006) and Abdelouhab (2007) in model glass.

In order to get closer to real corrosion cases, the same kind of study has been performed on a simplified model alloy with chromium content optimized at 30 wt.%, which can provide chromia forming properties to the alloy (Abdullah *et al.* (2013)). Figure 5 reports SEM pictures of the cross surface after 24 hours of immersion in a soda-lime silicate at 1100°C and the anodic polarization of Ni-30Cr in the same conditions (glass, T).

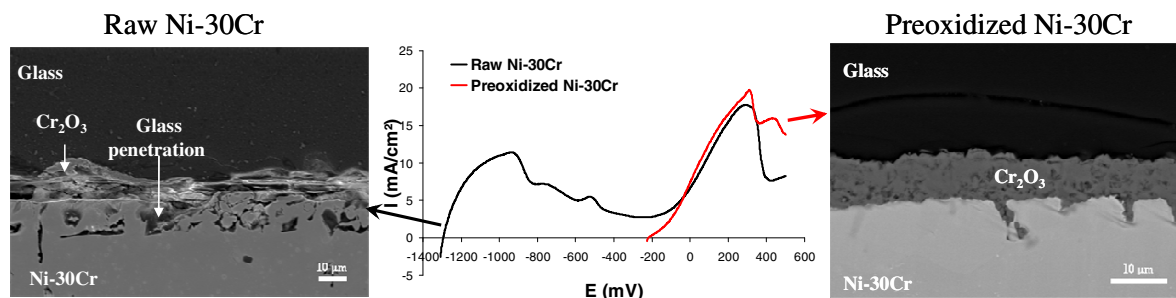


Fig. 5. Anodic polarization of raw and preoxidized Ni-30 Cr at 1100°C after 40 minutes of immersion in $\text{Na}_2\text{O-CaO-3SiO}_2$ melt, and SEM pictures of raw and preoxidized Ni-30Cr after 24 hours of raw immersion in the same glass at the same temperature 1100°C.

The behaviour of the raw sample is very close to the one described above for pure chromium. The spontaneous corrosion potential is also very low in the case of the alloy, as it is in active state. The SEM picture of the surface of the alloy in Figure 5 clearly shows that it is corroded with glass penetration on more than 10 μm from the surface after 24 hours of contact with the molten glass. The passivation domain extends from ~ -600 mV to ~ 0 mV with a low current density around 3 mA cm^{-2} .

The existence of the passivation domain with low current density proves the efficiency of Cr_2O_3 for providing protection against corrosion by molten glass. As a consequence, a preoxidation heat treatment has been performed at 1100°C for 2 hours just before immersion in the melt. According to previous thermogravimetric analysis, a 5 μm thick chromia layer is supposed to grow after such a heat treatment. On the anodic polarization plotted after a few minutes of immersion in soda-lime glass, the corrosion potential is quite high (~ -200 mV), and exactly in the passivation domain defined above. The SEM picture of a preoxidized sample after 24 hours of immersion exhibits a compact, adherent and homogeneous Cr_2O_3 layer with thickness comprised between 6 and 10 μm , avoiding contacts between the metallic surface of the alloy and the molten glass. In these conditions (potential in the passivation domain), the alloy is perfectly protected against corrosion.

It must be noticed here that in all cases of corrosion studies concerning contact between molten glass and a chromia forming alloy, some chromium dissolved in the melt has been detected and could be measured by Electron Probe Micro Analysis. So, even if chromia is well known to be an oxide with one of the lowest solubility as described by Manfredo *et al.* (1984), among many other oxides there is a perpetual competition between the growth of the protective chromia layer and its dissolution in the corrosive media, *i.e.* molten glass. As a consequence, the durability of the protection of the chromia layer is completely depending on its solubility in the molten glass, and thus strongly linked to the properties of the melt.

3.3. Stability of the passive state: correlation electrochemical behavior of chromia forming alloys and the solubility of chromia in molten glass

The solubility of chromium oxide can be studied in molten glass by considering the influence of temperature, glass composition and oxygen fugacity. Many previous studies report general aspects about the kinetics and mechanisms of dissolution of chromia in binary soda silicate melts $\text{Na}_2\text{O-xSiO}_2$ and in ternary soda-lime silicate melts $\text{Na}_2\text{O-CaO-xSiO}_2$. The main studies are performed by Khedim *et al.* (2008 and 2010), and Abdullah *et al.*

(2013). The oxygen fugacity is of first importance in the case of a multivalent element such as chromium, and the influence of this parameter on the total chromium solubility at equilibrium in a soda-lime silicate melt at different temperatures is reported in Figure 6.

The typical evolution of the Cr solubility with $\log fO_2$ has been previously described by Khedim *et al.* (2008) and Abdullah (2013) is the same for the three temperatures presented here. At equilibrium, the total dissolved Cr in the glass ($Cr(tot)$) is considered as the sum of all Cr species:

$$Cr(tot) = Cr^{II} + Cr^{III} + Cr^{VI} \quad (13)$$

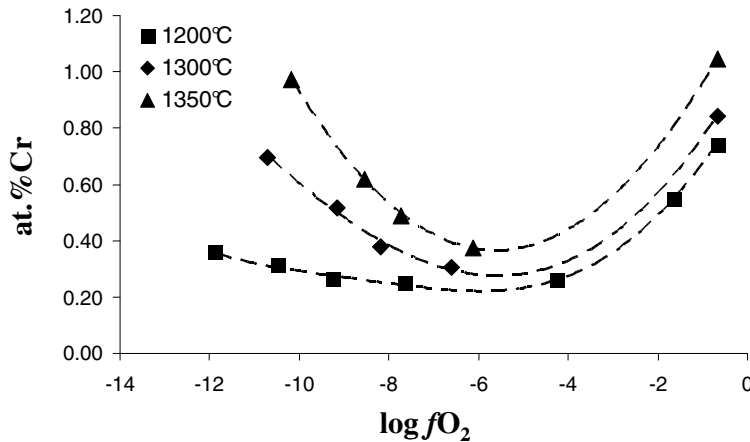
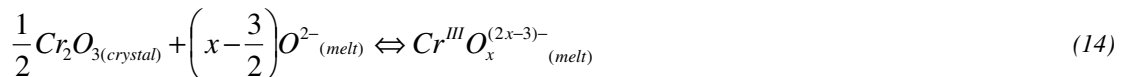


Fig. 6. Cr solubility in $Na_2O-CaO-3SiO_2$ versus oxygen fugacity fO_2 at 1200°C, 1300°C and 1350°C.

Cr^{III} content in the melt is assumed to remain constant with fO_2 for a given temperature, as long as chromia grains are remaining in the melt: this is attributed to the fact that the Cr^{III} contribution corresponds to the direct dissolution of Cr_2O_3 by following an acid-base reaction only depending on the composition of the glass.



Therefore, the minimum of solubility of each plot presented in Figure 6 is considered as the sole contribution of the Cr^{III} specie. Under reducing and oxidizing conditions, an increase of the solubility is observed. This increase is attributed to the reduction of Cr^{III} to Cr^{II} in reducing conditions (Cr^{VI} is neglected) and to the oxidation of Cr^{III} to Cr^{VI} in oxidizing conditions (Cr^{II} is neglected). Furthermore, the observation from the glass balls coloration, which are bluish (typical color of Cr^{II}), greenish (typical color of Cr^{III}) and yellowish (typical color of Cr^{VI}) in reducing, intermediate and oxidizing atmospheres respectively, proves the speciation of chromium according to the imposed oxygen fugacity.

The influence of the basicity of the glass is illustrated in Figure 7, which reports the evolution of the chromium solubility with the oxygen fugacity at 1200°C for two melts with different silica contents: $Na_2O-CaO-3SiO_2$ and $Na_2O-CaO-5SiO_2$ (*i.e.* NC3S and NC5S respectively). According to the model proposed by Duffy *et al.* (1976), the optical basicities of NC3S and NC5S are 0.63 and 0.58 respectively. It is noteworthy that, in oxidizing conditions ($\log fO_2 > -4$), the Cr solubility is higher in more basic melt (NC3S), whereas the inverse phenomenon occurs in lower fO_2 ($\log fO_2 < -8$). This fact highlights that increasing the basicity favors the stabilization of upper oxidation states, which means that Cr^{VI} is more stabilized in the basic melt. The phenomena occurring in reducing conditions can be explained in the same way, as Cr^{II} is more stabilized in the acidic melt.

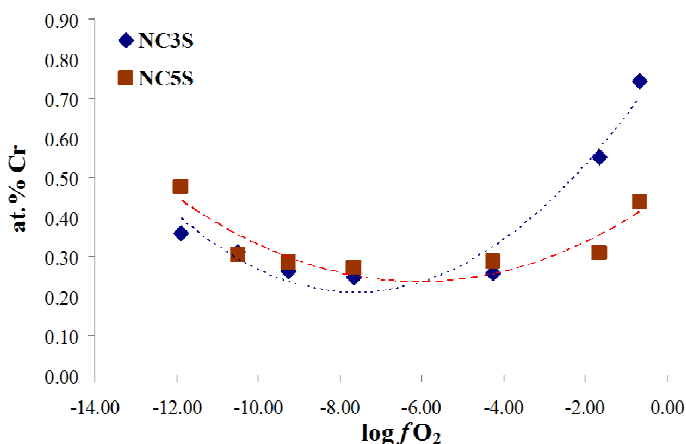


Fig. 7. Cr solubility in $Na_2O-CaO-3SiO_2$ (i.e. NC3S) and in $Na_2O-CaO-5SiO_2$ (i.e. NC5S) versus oxygen fugacity fO_2 at $1200^\circ C$.

It is possible to correlate the thermodynamic solubility data obtained here to the kinetic data collected during the corrosion study through electrochemical characterization. The oxygen fugacity imposed for the solubility measurements in a given glass can be translated to a potential value according to the Nernst's law:

$$E = \frac{RT}{4F} \ln fO_2 + K \quad (15)$$

where E is a potential, R the ideal gas constant, T the absolute temperature, F the Faraday's constant, fO_2 the oxygen fugacity and K a constant. Considering this, it is interesting to correlate the high solubility domains, corresponding to the lowest and highest oxygen fugacities, to the potential domains exhibiting high current densities, corresponding to the active and transpassive states for the lowest and highest potentials respectively. High solubility and high current density domains correspond to the stability domains of Cr^{II} and Cr^{VI} species respectively. In the same way, the lowest solubility values, measured for intermediate oxygen fugacities, correspond to the Cr^{III} specie and can be correlated to the large passivation plateau with low current densities. The relative stability of the Cr_2O_3 layer is thus emphasized by the coherence between the low current density and solubility domains.

4. Conclusion

Molten glass media have been proved to be corrosive against metallic and ceramic materials, due to their acido-basic and oxido-reducing properties. As these media are excellent electrolytes, the development of a specific device devoted to the electrochemical characterization at high temperature was necessary.

The experimental characterization of the basicity through the *in situ* measurement of the strong base Na_2O activity has been performed. A correlation with different theoretical models, as the Duffy and Ingram's optical basicity, has shown that such models could be used to predict the basicity of simple glasses. Nevertheless, the specific behavior of basic species as alkaline-earth oxides (i.e. CaO) has to be clarified as their contribution to the global basicity is lower than expected.

Through the years, it has been possible to build a scale of the formal potentials of many couples in molten glass. These data are precious to give access to the complex mechanisms potentially leading to the corrosion of many alloys. The study of the immersion in molten glass of pure metals classically used in the composition of glass industry alloys, and of a chromia forming model alloy clearly showed that chromium is a very important element.

Indeed, by using an appropriate preoxidation treatment, it is possible to build a protection chromium oxide scale. However, despite the very low solubility of Cr_2O_3 in molten glass, it is necessary to control it as the durability of the protection directly depends on the competition between the oxide growth and its dissolution in the corrosive medium.

As a consequence, thorough studies of the parameters controlling the solubility of a multivalent element as chromium have been performed, through the development of a specific device giving access to equilibrium values of solubility as a function of temperature, glass composition (*i.e.* basicity) and oxygen fugacity. The results presented here show the correlation between the high solubility of Cr^{II} and Cr^{VI} species and the active and transpassive domains of chromia forming alloys exhibiting high current densities, as the low solubility of the Cr^{III} specie can be linked to the passivation state with low current densities.

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