Use of electrochemical techniques for the characterization of alloys corrosion in molten glasses

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Electrochemical methods have been used for the characterization of alloys corrosion in molten glasses : corrosion potential, polarization resistance, polarization curve. Numerous alloys have been studied in a borosilicate glass at 1050°C, with rotating working electrodes. A minimum chromium level is required to obtain a passivable alloy. On the one hand, active state is characterized by a rapid dissolution of constitutive elements of the alloy in the glass melt (corrosion rate up to a few cm/year). On the other hand, a passive state involves the presence of a thin protective chromia scale (corrosion rate lower close to 1 mm/year). The passive state can be obtained by preoxidation or anodic polarization of the alloy. The addition of an oxidizing agent to the glass is also effective.

Introduction

In glass industry, superalloys are widely used where Platinum is too expensive or too soft and refractory oxides are too fragile. In dynamic processes, the contact between molten glass and alloys leads to corrosion and erosion phenomena. Electrochemical methods adapted from aqueous corrosion studies, used in a dedicated experimental apparatus, are precious tools by the fact that an in situ recording is easy. By this way, determination of corrosion rates and mechanisms are possible. The efficiency of protection methods is also assessable.

1) Electrochemical determination of alloys' corrosion rates

1.1) Experimental apparatus

The usual experimental apparatus consists in a furnace in which a Pt-10%Rh crucible is placed in air atmosphere. As for classical aqueous measures, three electrodes are needed. The electrodes' tip are immersed in the glass melt (figure 1).

1 : Working electrode 2 : Counter electrode 3 : Comparison electrode (Yttria stabilized electrode) 4 : Furnace (16 litters) 5 : Pt-10Rh crucible (ϕ=110mm, h=130mm) 6 : Glass 7 : Engine 8 : Rubber belt

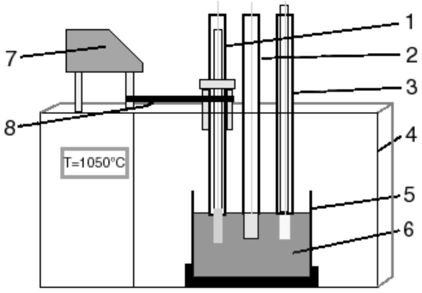

Figure 1 : Experimental equipment used for the electrochemical study of the corrosion by molten glasses

A second furnace is air proof to allow experiments in other atmospheres (Ar, Air/Ar…). The working temperature is generally between 1000°C and 1300°C. The working electrode is a 5.5 mm diameter alloy rod polished to the 1200 grid SiC paper. Counter electrode is a Platinum plate (25*2*10 mm). All potentials are given versus self constructed Yttria

Stabilized Comparison Electrode. These high temperature adapted electrodes are extensively detailed in ref. (1), (2), (3) and (4). The working electrode is linked by a rubber belt to an engine, allowing an axial rotation, up to 300 rpm. In this study, 60 rpm is the only applied rotating speed. It corresponds to a linear speed of about 1 m/min in rod's periphery. Parc M273 and M263A potentiostats were used to perform the electrochemical measurements.

1.2) The glass

The results presented here have been performed in an industrial borosilicate glass (64.5%SiO_2 -0.15%Fe_2O_3 -3.40%Al_2O_3 -7.2%CaO -16.0%Na_2O -1.20%K_2O -4.5%B_2O_3 in weight %) at 1050°C. The solvent's electroactivity domain extends approximately from -1.2 to +0.1 V (Figure 2). It is limited in the negative potentials by the reduction of the silicate network in accordance with $SiO_4^{4-} + 4\ e^- \rightarrow Si + 4\ O^{2-}$ (4). The oxidation anodic limit of the solvent corresponds to oxygen gas formation, due to the oxidation of the O^{2-} ions ($O^{2-} \rightarrow \frac{1}{2}\ O_{2\,(g)} + 2\ e^-$), then of the silicates network ($SiO_4^{4-} \rightarrow SiO_3^{2-} + \frac{1}{2}\ O_{2\,(g)} + 2\ e^-$).

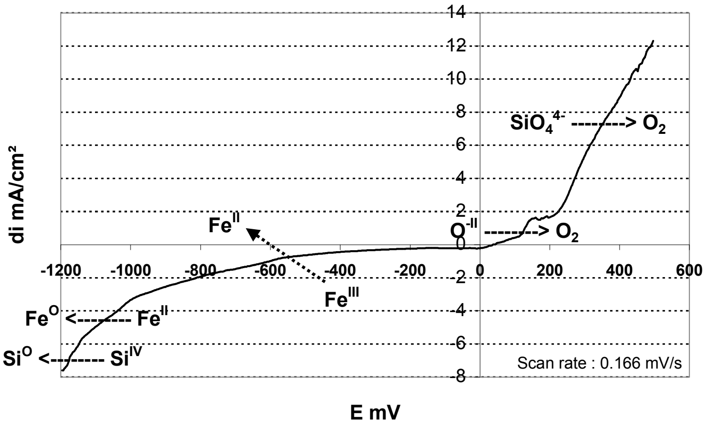

Figure 2 : Electroactivity domain of the glass on a Pt electrode. T = 1050°C.

Even if numerous species are present in this glass, only Si^{IV}/Si^0, Fe^{III}/Fe^{II}, Fe^{II}/Fe^0 and O_2/O^{2-} couples are electroactive. Figure 3 shows the formal potentials of these couples, and those of Co^{III}/Co^{II}, Co^{II}/Co^0, Cr^{VI}/Cr^{III} and Cr^{III}/Cr^{II}. Square Wave Voltammetry methods have been used as developed in ref (5), (6) to determine them (formal potentials of chromium couples are taken from ref (7)).The potential scale is useful to assign the anodic and cathodic reactions of a corroding alloy.

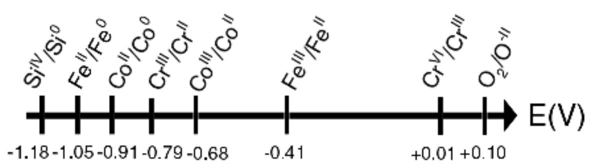

Figure 3 : Formal potentials of redox couples in the glass.

1.3) Alloys' corrosion rates measurements

Corrosion potential values point out the oxidizing agent involved in corrosion reactions (e.g. Si^{IV} if $E_{corr} \approx -1.3$ V, or Fe^{III} if $-1.05V < E_{corr} < -0.41V$ …). The polarization resistance (Rp) measurement gives the current density (I_{corr} = constant/Rp). The higher the Rp values are, the less the current densities are. By using Faraday's law, corrosion rate in cm/year can be estimated from I_{corr} values.

2) Characterization of the passive state. Methods to reduce corrosion rates.

2.1) Passive versus active state

As shown by Lizarazu (4) on Ni-Cr alloys, a 25-35 % chromium content is necessary to expect a chromia forming alloy. The corrosion resistance of Ni base-25Cr, Co base-30Cr and Ni base ODS-31Cr alloys have been tested by electrochemical techniques. Figure 4 shows typical polarization curves of these alloys. Two distinct behaviors appear : the curve n°1 is characteristic of an active alloy whereas n°2 is characteristic of a passive alloy. For an alloy in active state, the initial potential is low (≈ -1.2 V, oxidant being Si^{IV}) and an anodic peak (here I = 2.9 mA/cm²) is followed by a wide passivation plateau with relatively low current densities (≈ 0.5 mA/cm²). Rp values are close to 20 Ω.cm², which corresponds to a corrosion rate from 1.5 to 3.5 cm/year (Table 1).

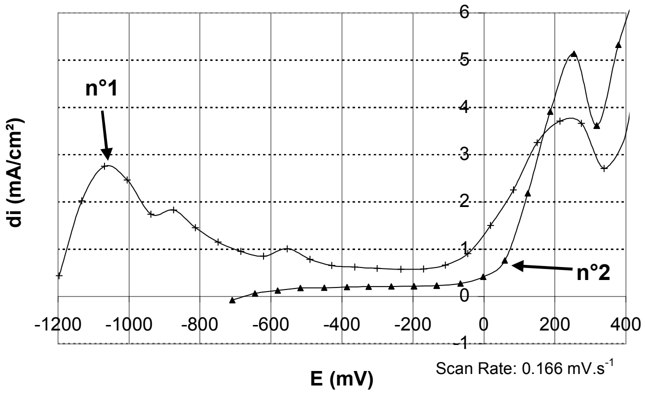

Figure 4 : Polarization curves of an active alloy (n°1), and of a passive one (n°2). E is imposed from E_{corr} - 20 mV to + 0.4 V.

Figure 5 (a) shows a section of the Ni-30Cr alloy in active state after 2 hrs of free immersion in glass at 1050°C. In addition to the generalized corrosion of the entire surface, a glass penetration on an approximate 40 µm depth can be noted at grain boundaries.

The second curve of figure 4 is characteristic of a passive alloy. It exhibits no anodic peak and a high corrosion potential located in the passivation plateau (oxidant are Fe^{III} and dissolved O_2). Rp values are then usually from 200 to 400 Ω.cm² corresponding to a corrosion rate near of 2 mm/year (Table 1), that is to say one magnitude lower than for the active alloy. The glass/alloy interface of a passive Ni-30Cr alloy after 14 hrs of free immersion in glass at 1050°C is shown in Figure 4 (b). A 3-5 µm chromia layer present on the surface is responsible for the passivation, protecting the alloy from glass penetration and reducing the corrosion rate.

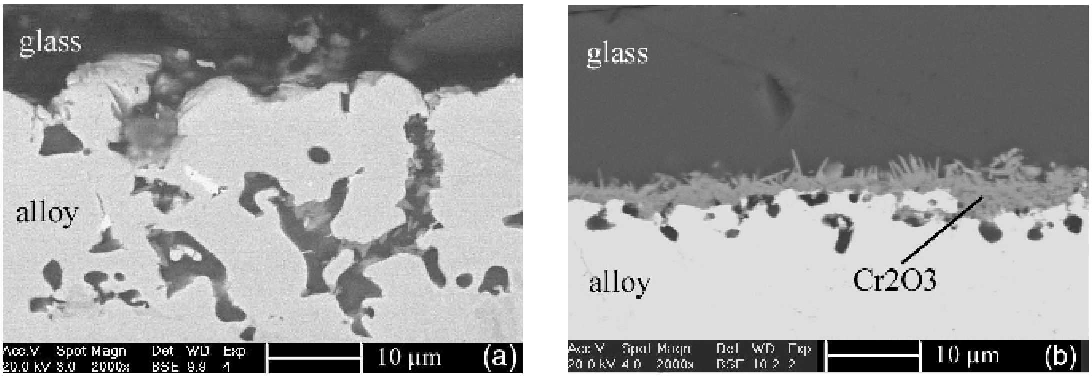

Figure 5 : (a) Section of the Ni-30Cr alloy after 2 hrs of free immersion in glass at 1050°C. The separation of alloy and glass happens during cooling). (b) Section of the passive Ni-30Cr alloy after 14 hrs of free immersion in glass at 1050°C. Back scattered electrons.

2.2) Efficient protective methods

Passivity for alloys implies the formation of a protective scale. In our case of high chromium alloys, chromia should play this role but as-polished alloys release Cr^{II} ions instead of spontaneously forming chromia. The working glass of this study is not oxidant enough. Three efficient methods have been developed to reach a passive state.

(1) The addition of oxidizing species to the glass (Mn^{IV}, Fe^{III}…) increases its potential, resulting in Cr_2O_3 formation at the alloy/glass interface. If modification of glass composition is not suitable, two other ways are left.

(2) A temporary anodic protection is possible, by imposing a potential located in the passivation plateau ($-0.7<E<-0.1V$) during one hour. It also leads to chromia formation at the alloy/glass interface. Yet, this method can be difficult to use in dynamic industrial processes. The last one is easier.

(3) The formation of a chromia protective layer before glass contact can be obtained by hot air oxidation of the alloy. Classically, one hour in furnace just above the crucible (called "preoxidation") is efficient.

These methods have been applied on numerous Cobalt base and Nickel base alloys, including ODS Ni base alloy, having in common a high chromium content (25-30%). 100 hrs testing have shown that the reached passive state is reproducible and long lasting. The thickness losses of a Cobalt base industrial component (1000 hrs life time, same temperature, same glass) gave a corresponding Rp value of about 400 $\Omega.cm^2$. It is in very good accordance with the electrochemically measured values (table 1).

Conclusion

Classical electrochemical methods with adapted experimental apparatus are suitable for the characterization of alloys corrosion in molten glasses. The electrochemically measured corrosion rates are in good accordance with the thickness losses of an industrial component. Few hours electrochemical testing gives a good estimation of the long time behavior of alloys. In the glass of this study, all the tested high chromium alloys are spontaneously in an active state, corresponding to a corrosion rate of a few cm/year. In the passive state, these alloys can be protected by the presence of a thin chromia layer on their surface. Chromia protection allows at least a one magnitude decrease in corrosion rates. The three following methods are efficient to reach a passive state : addition of oxidizing agents to the glass, temporary anodic protection and preoxidation.

Table 1 : E_{corr} and Rp of active and passive alloys. 60 rpm rotating electrodes. T=1050°C.

	Active state				**Passive state**			
Alloy	**Ecorr (V)**	**Rp $(\Omega.cm^2)$**	**Oxidizing species**	**Corrosion rate in cm/year**	**Ecorr (V)**	**Rp $(\Omega.cm^2)$**	**Oxidizing species**	**Corrosion rate in cm/year**
Co base-30Cr-6W	-1.15	20	Si^{IV}	2.3	-0.25	300	O_2	0.15
Co base-30Cr-0W	-1.20	27		1.6	-0.60	240	Fe^{III}, O_2	0.18
Co base-30Cr-2Al	-1.20	12		3.5	-0.13	180	O_2	0.24
Ni base-25Cr	-1.20	20		2.2	-0.20	400	O_2	0.11
ODS Ni base-31Cr	-1.20	16		2.6	-0.15	230	O_2	0.18

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