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Electrochemical Study of Metal and Alloys Corrosion by Molten Glasses

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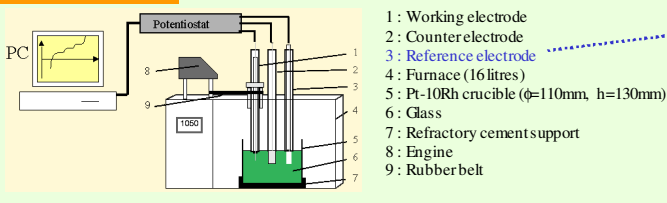
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In the glass industry, the lifetime of many metallic parts in contact with molten glass is mainly controlled by high temperature corrosion. The damages caused to alloys are governed by oxido-reduction reactions. Preliminary studies have demonstrated that electrochemical methods can be used for the characterization of alloys corrosion in molten glasses. A typical experimental apparatus was developed to work in the 950-1200°C temperature range. It allows studies under controlled atmosphere, using static or rotating working electrodes.

EXPERIMENTAL EQUIPMENT

Adapted for high temperature and molten glass contact



Yttria stabilized reference electrode

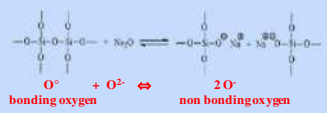


ELECTROCHEMICAL STUDY OF GLASSES

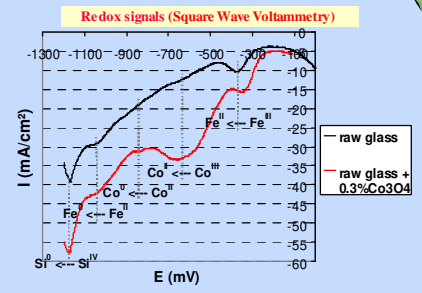
A few industrial glasses

| Oxide wt% | Soda-lime TC 22 | CE57 vit heat zinc | E glass | C3 glass | Basaltic glass |
|--------------------------------|-----------------|--------------------|---------|----------|----------------|
| SiO ₂ | 73.76 | 60.8 | 54.5 | 68 | 45.7 |
| Al ₂ O ₃ | 0.86 | 4.4 | 14 | 3.1 | 14.3 |
| Fe ₂ O ₃ | 0.16 | 0.31 | 0.13 | 11.4 | |
| TiO ₂ | | | 0 | 2.6 | |
| CaO | 8.75 | 5.4 | 22.2 | 7.5 | 9.65 |
| MgO | 2.71 | | 0.35 | 3.5 | 8.5 |
| Na ₂ O | 13.66 | 7.2 | 0.6 | 15.7 | 2.9 |
| MnO | | | 0.4 | 1.25 | 1.25 |
| K ₂ O | | | 0 | 0 | 0.22 |
| B ₂ O ₃ | 18.8 | 7.4 | 4.1 | 0 | 0 |
| Li ₂ O | 2.7 | | | | |
| ZnO | 0.7 | | | | |
| P ₂ O ₅ | | | 0 | 0 | 0 |
| Temperature (°C) | 1100 | 1150 | 1250 | 1050 | 1300 |

A molten glass is a good electrolyte, by the way of the O²⁻ ions exchange :

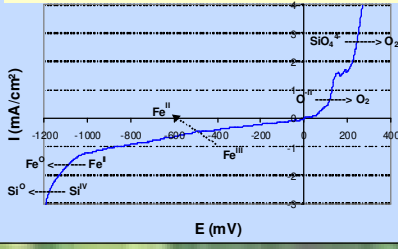


The use of Cyclic and Square Wave voltmetries allows the determination of redox couples potentials (addition of electroactive elements in the glass) :



Classical electrochemistry techniques are then possible in situ in a molten glass :

Electroactivity domain of the C glass (Linear polarization curve)

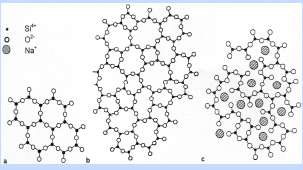


Formal and half waves potentials (C glass, 1050°C)



These information are needed to identify the corrosion reactions of metals and alloys.

Structure of a simple SiO₂-Na₂O glass



PURE METALS AND ALLOYS CORROSION BY MOLTEN GLASS

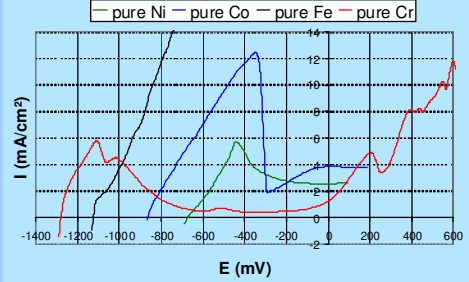
Pure metals

| | Cr | Fe | Co | Ni |
|--|--|--|--|--|
| E _{corr} (mV) | -1300 | -1100 | -850 | -650 |
| Anodic reaction | Cr → Cr ^{III} + 2 e ⁻ | Fe → Fe ^{II} + 2 e ⁻ | Co → Co ^{II} + 2 e ⁻ | Ni → Ni ^{II} + 2 e ⁻ |
| Main cathodic reaction | Si ^{IV} + 4e ⁻ → Si ⁰ | Fe ^{III} + 1e ⁻ → Fe ^{II} | Fe ^{III} + 1e ⁻ → Fe ^{II} | Fe ^{III} + 1e ⁻ → Fe ^{II} |
| R _p (Ω.cm ²) | 9 | 14 | 15 | 35 |
| I _{corr} (mA.cm ⁻²) | 4.2 | 5.4 | 5.1 | 2.2 |
| State | Active | Active | Active | Active |

The comparison of E_{corr} with the redox potential values allows the assignment of the anodic and cathodic reactions.

The R_p values are low and characteristic of both material in the activation state and high corrosion rates.

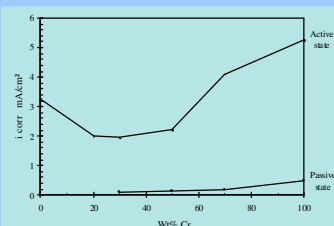
Linear polarization curves



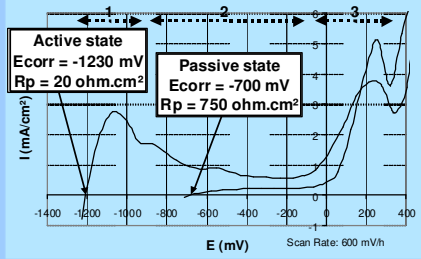
Only Cr curve exhibits an interesting passivation domain (wide plateau with low currents).

⇒ High chromium superalloys could be tested in molten glasses.

Ni-Cr alloys



⇒ Minimum I_{corr} for Cr = 30%.
⇒ One magnitude corrosion rate gain when the alloy is in the passive state.



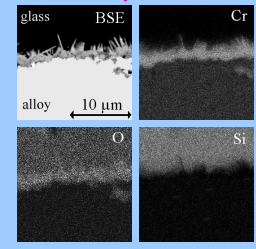
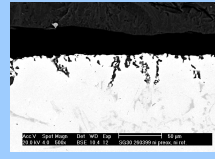
⇒ When the alloy is passivated, E_{corr} and R_p are higher and the polarization curve begins in the passivation domain.

Passive alloy after 14h in a C glass at 1050°C:

⇒ No glass penetration, due to the presence of a Cr₂O₃ protective layer.

Active alloy after 2h in a C glass at 1050°C:

⇒ Glass penetration at the grain boundaries.



The electrochemical methods allow the identification of the reaction involved in the corrosion of metals and superalloys in a molten glass. As in aqueous solution, the corrosion rate of high chromium superalloys is decreased when a protective Cr₂O₃ layer is present at the glass/alloy interface. The passive state can be reached by the use of anodic polarization or preoxidation.