



Corrosion of superalloys in molten glass - Electrochemical characterization of the passive state

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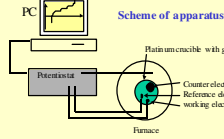
Introduction

In the glass industry, the lifetime of many metallic parts in contact with molten glass is mainly controlled by high temperature corrosion. The degradation of the alloys immersed in the molten glass is governed by oxido-reduction reactions. Then electrochemical techniques were developed for the characterization of the alloys corrosion. The aim of this paper is to describe the corrosion behavior of superalloys containing about 30% of chromium in a soda-lime molten glass at 1050°C and to determine the mechanism of passivation.

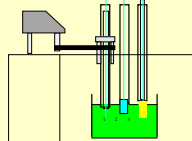
Experimental

This study was performed in an industrial soda-lime glass (64.5%SiO₂ - 0.15%Fe₂O₃ - 3.40%Al₂O₃ - 0.1%SO₃ - 7.2%CaO - 16.0%Na₂O - 1.20%K₂O - 4.5%B₂O₃ - 3% MgO in weight %) at T = 1050°C. The studied alloys are high chromium cast Ni-base (base Ni, 28wt% Cr, 0.7wt%W, 7.5wt%Fe) and Co-base commercial superalloys, containing Fe, Ta, W and C as additional elements (base Co, 30wt%Cr, 0.4wt%C, 3wt%Ta, 6wt%W, 8.5wt%Ni). These alloys are classical high temperature superalloys, mechanically strengthened by intergranular carbide (MC or M₂₃C₆ type).

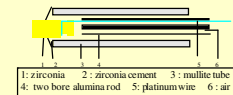
Electrochemical study in molten glass



Scheme of the furnace with glass crucible



Reference electrode : zirconia stabilized electrode



Princeton interface (a/b) / Zirconia/zirconia/glass interface

Air/argon interface

$$M \rightarrow M^{n+} + n e^-$$

glass/argon interface

$$E = E^0 + E' = E^0 - \frac{RT}{4F} \ln(P_{O_2}) - \frac{RT}{2F} \ln(a_{O^{2-}})$$

Scheme of electrodes

Platinum electrode : glass study

Alloy electrode : corrosion study

1 - platinum wire 2 - Al₂O₃-SiO₂ cement 3 - mullite tube 4 - platinum wire

1 - alloy studied 2 - Al₂O₃-SiO₂ cement 3 - mullite tube 4 - platinum wire

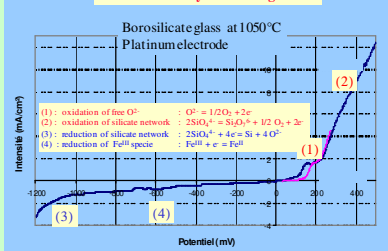
Working electrode

Counter electrode

1 - platinum plate 2 - Al₂O₃-SiO₂ cement 3 - mullite tube 4 - platinum wire

Glass Study

Electroactivity domain of glass

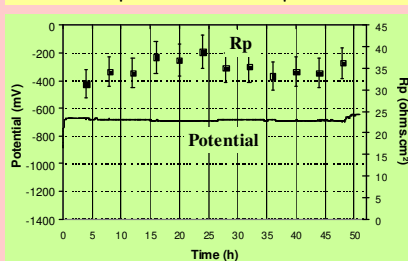


Potential scale used in molten glass to assign corrosion reaction

Corrosion of pure metals and alloys

Alloys /metals	Active state				Passive state			
	E _{corr} (V)	R _p (Ω.cm²)	Oxidant	Corrosion rate (cm/y)	E _{corr} (V)	R _p (Ω.cm²)	Oxidant	Corrosion rate (cm/y)
Fe	-1.10	14	Si ^{IV}	3.2	-	-	-	-
Co	-0.85	15	Fe ^{III} , O ₂	3.0	-	-	-	-
Ni	-0.65	35	Fe ^{III} , O ₂	1.3	-	-	-	-
Cr	-1.30	9	-	5.0	-0.1	80	-	0.4
Co base 30Cr-6W	-1.10	25	-	1.8	-0.55	200	Fe ^{III}	0.2
Co base 30Cr	-	-	Si ^{IV}	-	-0.60	400	-	0.1
Co base 30Cr-2Al	-1.20	12	-	3.9	-0.25	250	O ₂	0.2
Ni base 25 Cr	-1.20	20	-	2.3	-0.65	800	-	0.05

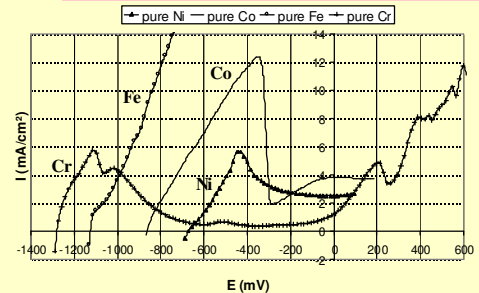
Electrochemical parameters recorded on pure metals and alloys in molten glass



Corrosion potential versus time and polarization resistance measurement. Case of pure nickel. Borosilicate glass, T = 1050°C

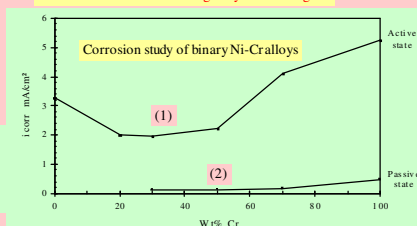
Stability of recorded parameters

Polarization curves of pure metals in molten glass at 1050°C

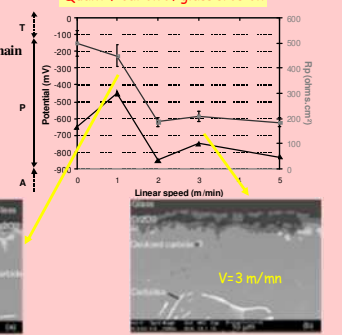


Only chromium exhibits a passivation plateau

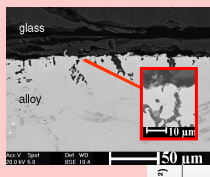
Utilisation of chromia forming alloys in molten glass



Quantification of glass erosion

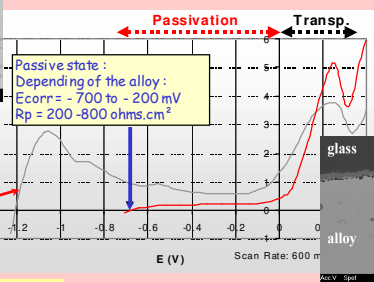


Corrosion study of chromia forming alloys Example Ni-30% Cr in borosilicate glass at 1050°C

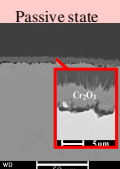


Active State

Active state :
Depending of the alloy :
E_{corr} = -1200 mV
Rp = 15-30 ohms.cm²



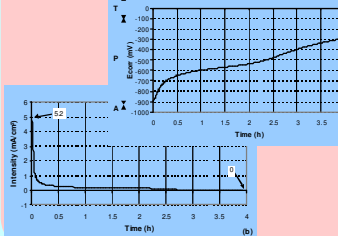
Passive state :
Depending of the alloy :
E_{corr} = -700 to -200 mV
Rp = 200-800 ohms.cm²



Passive state

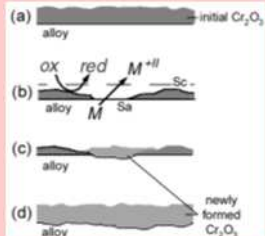
Determination of passivation mechanisms

Galvanic couplings were realised between an active electrode and a passive one. First, an electrode (Ni base alloy) was preoxidized. After immersion, it stayed in a passive state (E_{corr} = -430 mV and Rp = 800 Ω.cm²). Secondly, this electrode was coupled with a half surface as-polished immersed electrode (active state). The current quickly decreases from 5.2 mA/cm² to 0 mA/cm² in 4 hours. Correlatively, the potential of the active electrode increases from the activation domain (-900 mV) to the passivation domain (-300 mV).



Mechanisms of stabilisation of the passive state

If a part of the Cr₂O₃ protective layer is damaged, a galvanic coupling can lead to the restoration of the layer. A cathodic surface over anodic surface ratio Sc/Sa of 2 is favourable, while Sc/Sa = 1 is not. These experiments allow to partially understand the role of the preoxidation.
(a) After air oxidation, the sample is covered with a Cr₂O₃ layer.
(b) Some parts of the alloy may become active (unavoidable solubility of Cr₂O₃).
(c) With a favourable Sc/Sa ratio, the galvanic coupling leads to the restoration of the passive state.
(d) Finally, after a long time of immersion, the whole surface of the alloy is covered with Cr₂O₃ generated in the glass.



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. 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. The erosion phenomena has been shown on a rotating electrode. In the case of a passive scale damage, a favourable galvanic coupling allows a restoration of the protective layer