Strategy for developing new structural materials for industrial applications in molten silicate glass: fundamental study of the molten glass interaction with model alloys

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**Context**

**Glass fiberizing**
- $T \sim 1000 - 1200 \, ^\circ\text{C}$
- Rotation $\sim 2000$ rpm

**Vitrification of nuclear wastes**

**Industrial aspects**

**Aeronautical applications:**
- **Thermal Barrier Coatings**

  Corrosion by CaO-MgO-Al$_2$O$_3$-SiO$_2$ (CMAS) at $1200^\circ$C

  Glass = corrosive medium

  Ni-based superalloys with $\text{Al, Cr}$

  - $\text{Cr}_2\text{O}_3$
  - $\text{Al}_2\text{O}_3$
Outline

1) Corrosion of
   ✓ chromia forming alloy → Ni30Cr (wt.%)
   ✓ alumina forming alloy → Ni8Al28Cr (wt.%)
   in soda lime silicate glass (Na$_2$O-CaO-3SiO$_2$ = NC3S).

2) Physicochemistry of the protective oxide in the melt. Determination of Cr$_2$O$_3$ solubility in soda lime silicate melts as a function of:
   - oxygen fugacity ($f$O$_2$)
   - glass composition
   - temperature
Corrosion of alloys by molten glass

Alloys preparation

- Induction heating in high frequency furnace
Corrosion of alloys by molten glass

Hot air oxidation of the alloys at 1100°C (100 h)

Ni30Cr

Ni8Al28Cr

**Kp = 1.3 \times 10^{-11} g^2 \cdot cm^{-4} \cdot s^{-1}**

**Cr_2O_3**

**Ni-30Cr**

**Ni-8Al-28Cr**

**TEMPERATURE, °C**

**PARABOLIC RATE CONST., g^2/cm^4s**

**10^{-9}**

**10^{-10}**

**10^{-11}**

**10^{-12}**

**10^{-13}**

**10^{-14}**

**10^4 / T, K**

5
Corrosion of alloys by molten glass

Electrochemical measurements

Polarization resistance, free potential, I \textit{vs.} E measurements at high temperature.

3 specific electrodes:

- **WE** = Working Electrode (Pt wire and alloy rods)
- **RE** = Reference Electrode (Yttria Stabilized Zirconia)
- **CE** = Counter Electrode (Pt plate)

![Diagram showing the setup of furnace and acquisition system with electrodes labeled WE, RE, and CE](image)
Corrosion of alloys by molten glass

Electrochemical measurements

Electrodes:

Working electrode

Counter electrode

Yttria stabilized zirconia reference electrode (YSZ)

\[ \frac{1}{2} O_2 + 2e^- \leftrightarrow O^{2-} \]
Corrosion of Ni$_{30}$Cr by molten glass

Raw immersion in molten NC3S (1100°C/24 h)

Electrochemical measurements (1100°C)

- $E_{corr} \sim -1300$ mV
- $R_p \sim 9 \Omega \cdot cm^2 \Rightarrow V_{corr} \sim 5$ cm/year

PASSIVATION by preoxidation heat treatment?

- Active state: $I_C > 10$ mA.cm$^{-2}$
  - $Si^{IV}O_4^{4-} + 4e^- \leftrightarrow Si^{0} + 4O^{2-}
  - Cr$^{0} \leftrightarrow Cr$^{II} + 2e$^-$

- Passivation: $I_p < 5$ mA.cm$^{-2}$
  - $O_2 + 4e^- \leftrightarrow 2O^{2-}$
  - $Cr$^{II} \leftrightarrow $Cr$^{III} + e$^-$

- Transpassivation: $I_T > 15$ mA.cm$^{-2}$
  - $Cr$^{III} \leftrightarrow $Cr$^{VI} + 3e$^-$
Corrosion of Ni$_{30}$Cr by molten glass

TGA analysis → preoxidation at 1100°C/2h ~ 5 µm thick Cr$_2$O$_3$ layer

Raw immersion in molten NC3S (1100°C/24 h)

0.3 at.%Cr in the glass
e ~ 6-10 µm

**PROTECTION**

Linear polarization after 24 h in NC3S

-320 mV < $E_{corr}$ < -200 mV
60 Ω.cm$^2$ < $R_p$ < 250 Ω.cm$^2$

**PASSIVE STATE**

Cr$_2$O$_3$ growth

**COMPETITION**

Cr$_2$O$_3$ dissolution

Protection: Cr$_2$O$_3$ growth > Cr$_2$O$_3$ dissolution
Corrosion of Ni$_{30}$Cr by molten glass

Influence of the temperature → immersion at 1150°C
After 2 hours of preoxidation

Raw immersion in molten NC3S (1150°C/24 h)

E$_{corr}$ and R$_p$ measurements (24 h)

Linear polarization after 24 h in NC3S

T \nearrow \Rightarrow \text{Cr solubility} \nearrow \Rightarrow \text{Cr}_2\text{O}_3 \text{ dissolution} > \text{Cr}_2\text{O}_3 \text{ growth}

In NC3S, 1100°C < T$_{\text{depassivation}}$ < 1150°C
Corrosion of Ni8Al28Cr by molten glass

Raw immersion in molten NC3S (1100°C/24 h)

Limit of solubility in soda lime silicates at 1300°C (at. %)

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>21.3</td>
<td></td>
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Linear polarization after 24 h in NC3S

Ni8Al28Cr:

- higher critical current density
- higher current density on the passivation plateau

Protection by Al2O3 scale?
Corrosion of Ni8Al28Cr by molten glass

TGA analysis → preoxidation at 1100°C/24h ~ 2 µm thick Al₂O₃ layer

Raw immersion in molten NC3S (1100°C/24 h)

- No protective scale
- High dissolution of Al in NC3S
- Presence of Si in the alloy

$E_{\text{corr}}$ and $R_p$ measurements (2 h)

- $t = 0$ ; $E_{\text{corr}} \sim -550$ mV → passive state
- $t = 5$ min ; $E_{\text{corr}} \sim -1.3$ V → active state

Dissolution of the Al₂O₃ layer in NC3S in 5 min!
Physico-chemistry of $\text{Cr}_2\text{O}_3$ in molten glass

Durability of the protective oxide scale

Limit of solubility ruled by

- temperature
- glass composition
- oxygen fugacity

Experimental device

Glass sample + 5-10 wt.% $\text{Cr}_2\text{O}_3$

- Glass reservoir
  - Control Na volatilization
- Silica tube sealed under secondary vacuum
- Buffer $M(s) + M_xO_y(s)$
  - Control $fO_2$

$\text{NaO}_{1/2}(\text{reservoir}) \rightarrow \text{Na}(g) + \frac{1}{4}\text{O}_2$

$\text{Na}(g) + \frac{1}{4}\text{O}_2 \rightarrow \text{NaO}_{1/2} \ (\text{sample})$

$a\text{NaO}_{1/2} \ (\text{reservoir}) = a\text{NaO}_{1/2} \ (\text{sample})$

$2x/yM + \text{O}_2 = 2/yM_xO_y$ (Ellingham diagram)

Cr solubility at equilibrium
Physico-chemistry of Cr$_2$O$_3$ in molten glass

MO$_x$/MO$_y$ buffers

\[
\frac{2}{y-x} MO_x(solid) + O_2(g) \rightleftharpoons \frac{2}{y-x} MO_y(solid)
\]

\[K = \frac{1}{fO_2}\]

HSC Software

![Graph showing the variation of Log fO$_2$ with 10$^4$/T for different buffers such as Fe$_3$O$_4$/Fe$_2$O$_3$, Ni/NiO, Co/CoO, Fe/FeO, Cu/Cu$_2$O, and FeO/Fe$_3$O$_4$.](image-url)
Physico-chemistry of Cr$_2$O$_3$ in molten glass

Influence of f$_{O_2}$

Cr solubility in NC3S (T = 1200°C)

At equilibrium, Cr$^{III}$ is assumed to remain constant with f$_{O_2}$ at a given T as long as Cr$_2$O$_3$ is remaining in the melts.

\[ \frac{1}{2}Cr_2O_3 \text{(melt)} + \left( x - \frac{3}{2} \right) O^{2-} \text{(melt)} \rightarrow Cr^{III} O_{x}^{(2x-3)-} \text{(melt)} \]

\[ Cr_{(total)} = Cr^{II} + Cr^{III} + Cr^{VI} \text{ (EPMA analysis)} \]
Physico-chemistry of \( \text{Cr}_2\text{O}_3 \) in molten glass

Corrosion-solubility correlation

Corrosion of Ni30Cr rod in NC3S at \( T = 1100^\circ\text{C} \)

Cr solubility in NC3S at \( 1200^\circ\text{C} \leq T \leq 1350^\circ\text{C} \)

\[ E = \frac{RT}{4F} \ln fO_2 + K \]

Kinetic

Thermodynamic
Conclusions

✓ Spontaneous behavior of Ni30Cr and Ni8Al28Cr leads to corrosion of the alloys even for a short run duration.

✓ Preoxidation of Ni30Cr may lead to the growth of a protective Cr$_2$O$_3$ scale.
→ durability of the scale linked to the competition between oxide growth and oxide dissolution

✓ No protection obtained after preoxidation of Ni8Al28Cr:
→ due to the great solubility of Al$_2$O$_3$ in the melt

✓ The influence of oxygen fugacity ($f_{O_2}$) on the Cr solubility has been proved:
→ three solubility domains exist by varying the $f_{O_2}$

✓ Cr content at glass/alloy interface close to equilibrium values:
→ use of the solubility measurements method to evaluate the durability of the materials against glass corrosion
Outlooks

✓ Durability of the protective Cr$_2$O$_3$ scale.
  → optimization of the alloy composition (i.e. Cr content)
  → optimization of the preoxidation treatment (i.e. scale thickness)

✓ Influence of T, $f$O$_2$ and melt composition (basicity, viscosity, …) on the Cr solubility at equilibrium
  → correlation with electrochemical measurements

✓ Study of the physico-chemistry of Al$_2$O$_3$ in the melts
  → solubility, phase precipitation, …
THANK YOU
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MERCI