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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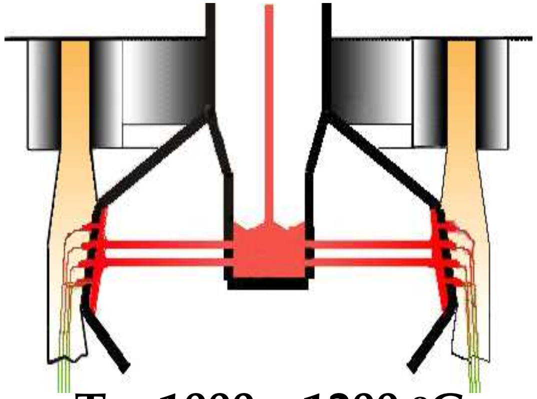
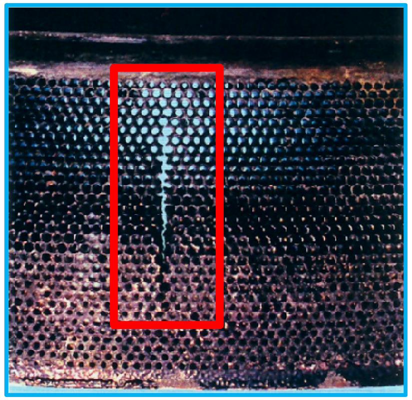
Context

Glass fiberizing

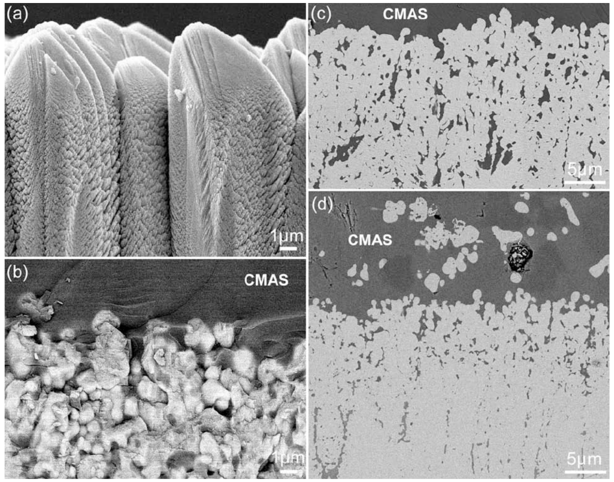




T ~ 1000 – 1200 °C

Rotation ~ 2000 rpm

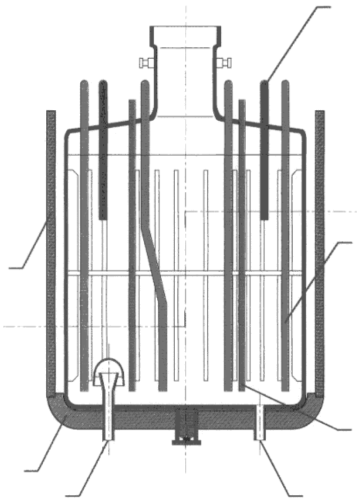
Aeronautical applications: Thermal Barrier Coatings

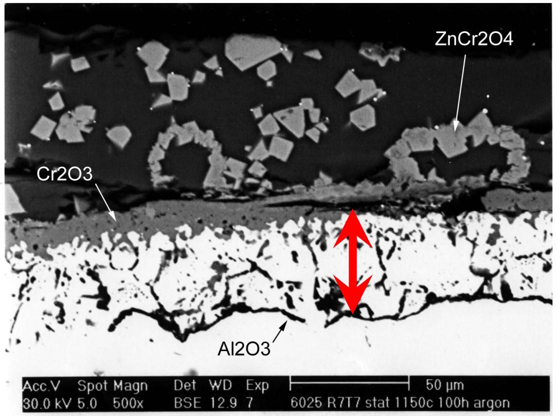


Corrosion by CaO-MgO-Al_2O_3-SiO_2 (CMAS) at 1200°C

Glass = corrosive medium

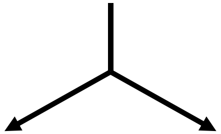
Vitrification of nuclear wastes





Pénétration du verre dans l'alliage

Ni-based superalloys with Al, Cr



Cr_2O_3 Al_2O_3

Outline

1) Corrosion of

   ✓ chromia forming alloy → Ni30Cr (wt.%)

   ✓ alumina forming alloy → Ni8Al28Cr (wt.%)

in soda lime silicate glass (Na_2O-CaO-3SiO_2 = NC3S).

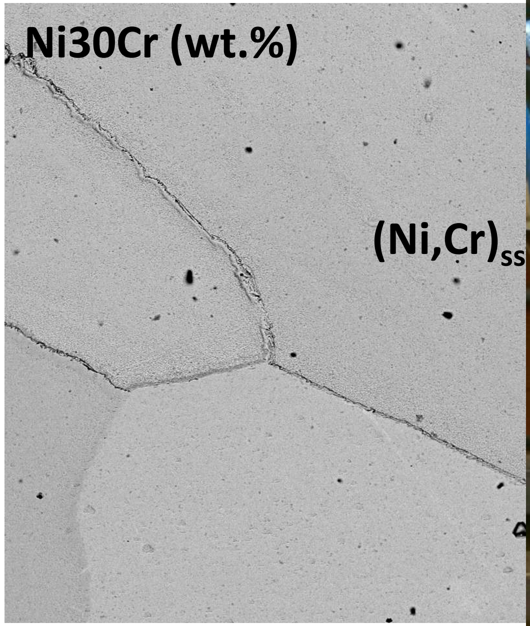
2) Physicochemistry of the protective oxide in the melt. Determination of Cr_2O_3 solubility in soda lime silicate melts as a function of:

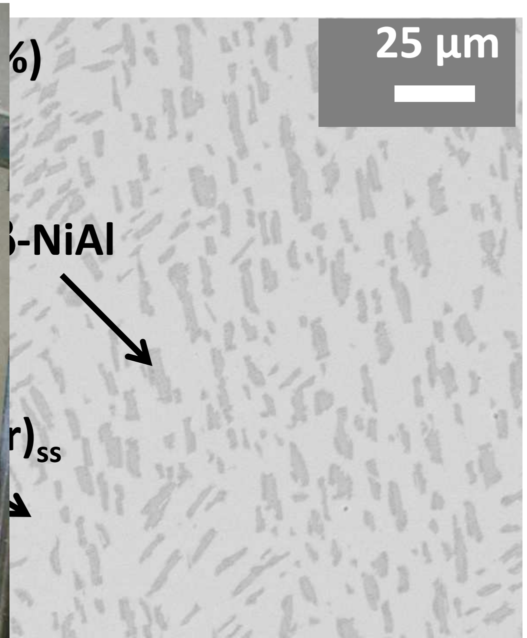
   - oxygen fugacity (fO_2)
   - glass composition
   - temperature

Corrosion of alloys by molten glass

Alloys preparation

- **Induction heating in high frequency furnace**

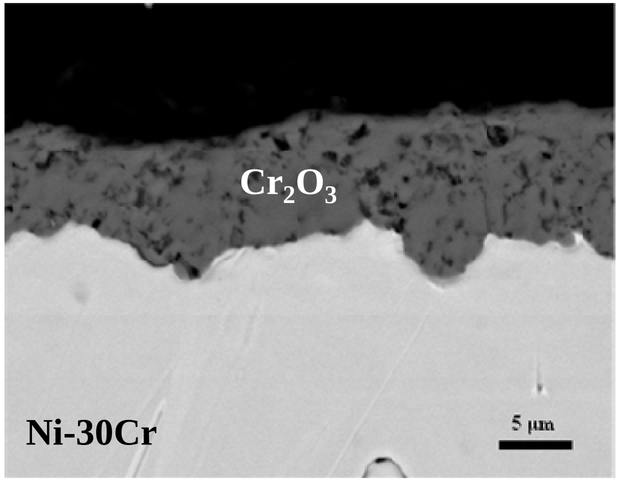




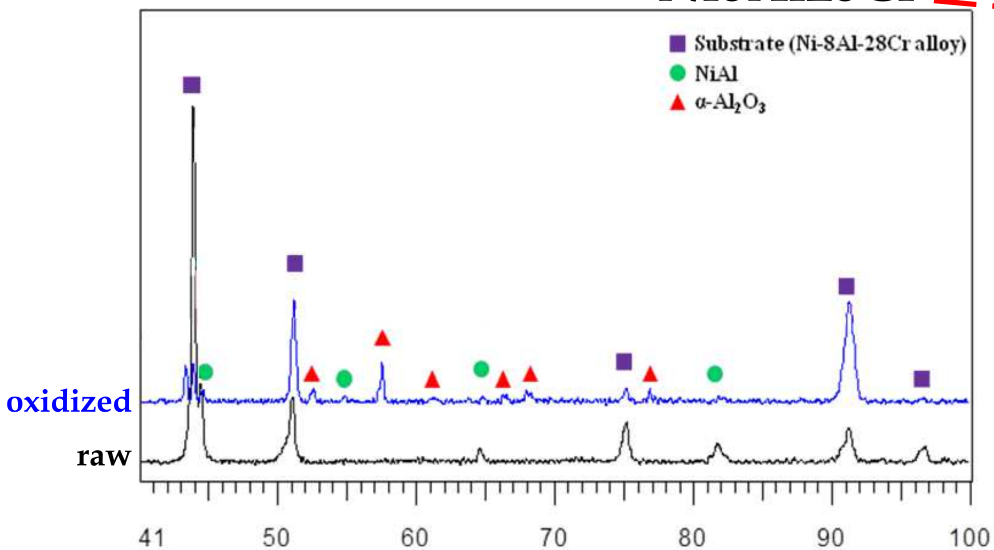
Corrosion of alloys by molten glass

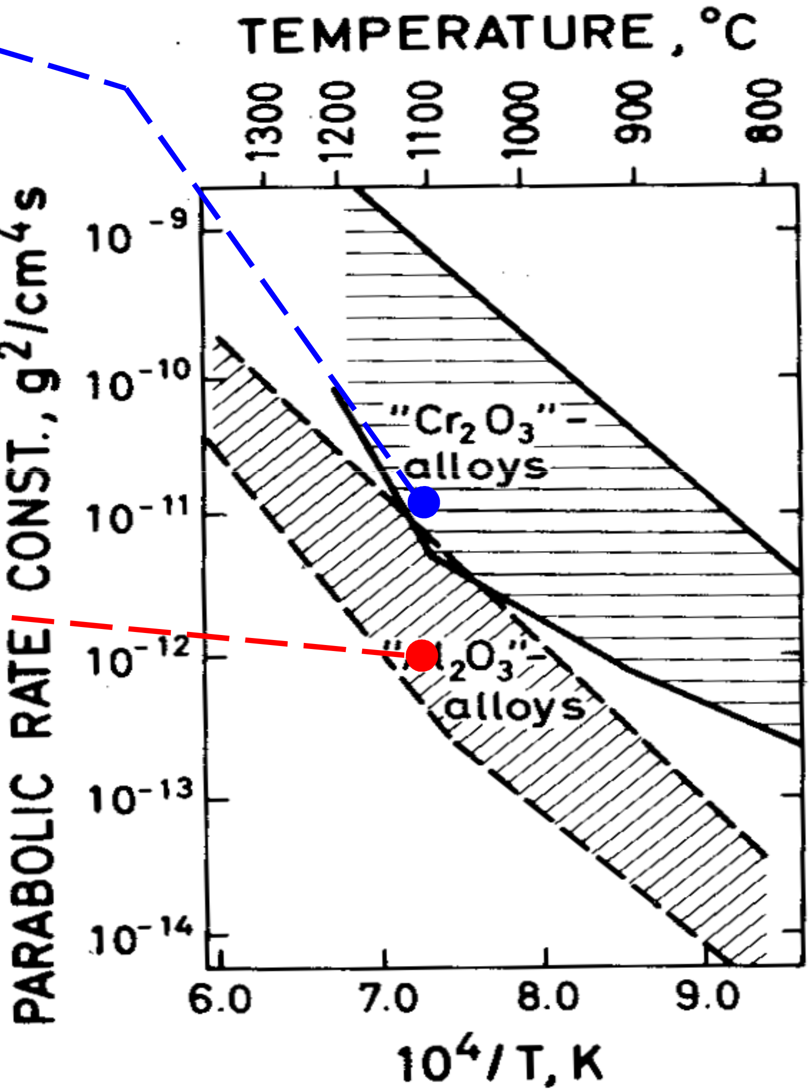
Hot air oxidation of the alloys at 1100°C (100 h)

Ni30Cr



Ni8Al28Cr





Corrosion of alloys by molten glass

Electrochemical measurements

Polarization resistance, free potential, I *vs.* E measurements at high temperature.

3 specific electrodes:

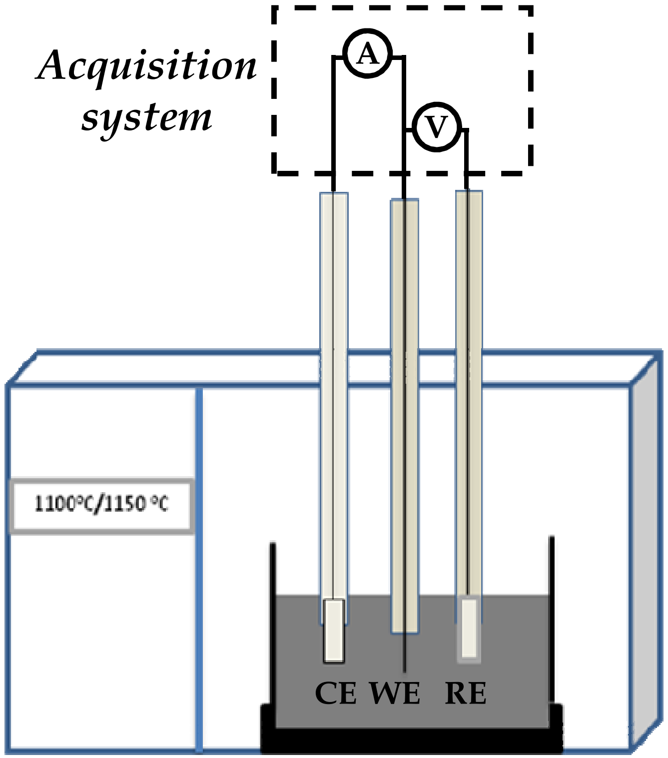
WE = Working Electrode (Pt wire and alloy rods)

RE = Reference Electrode (Yttria Stabilized Zirconia)

CE = Counter Electrode (Pt plate)

Furnace

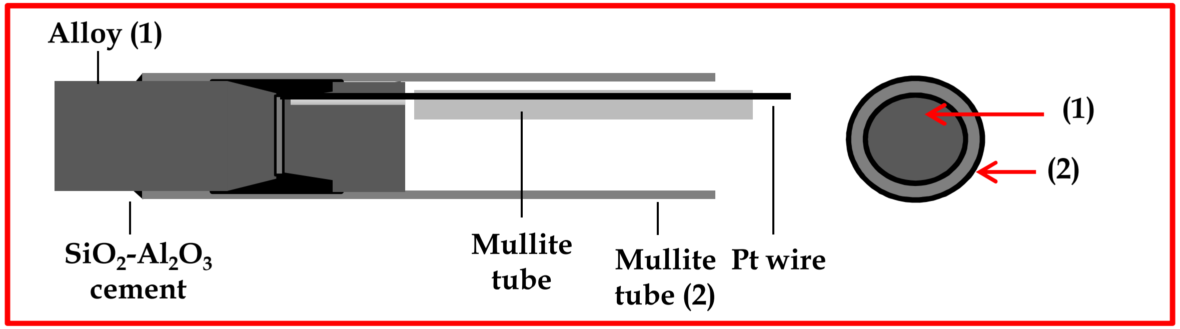
Acquisition system



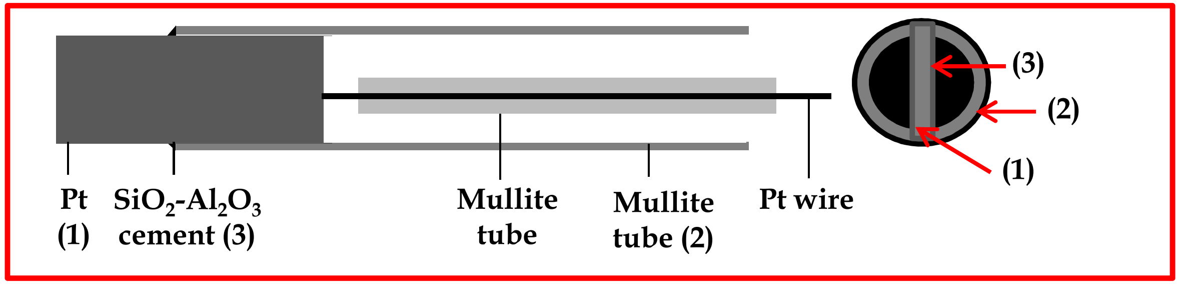
Corrosion of alloys by molten glass

Electrochemical measurements

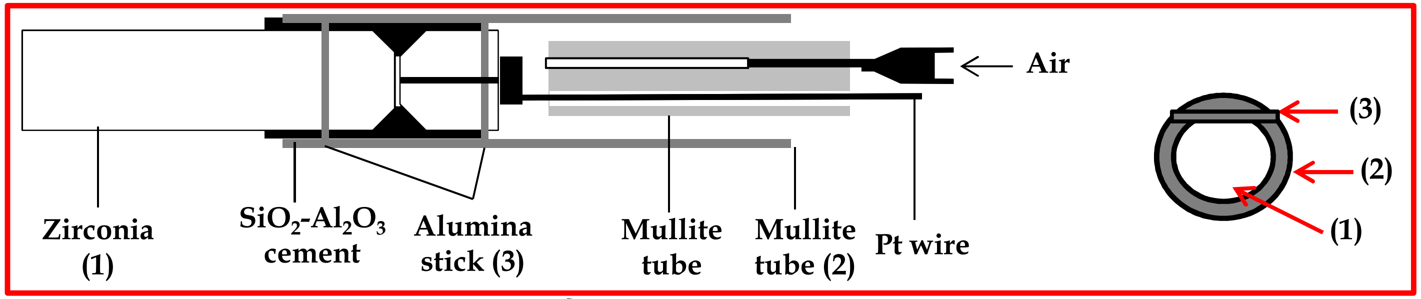
Electrodes:



Working electrode



Counter electrode

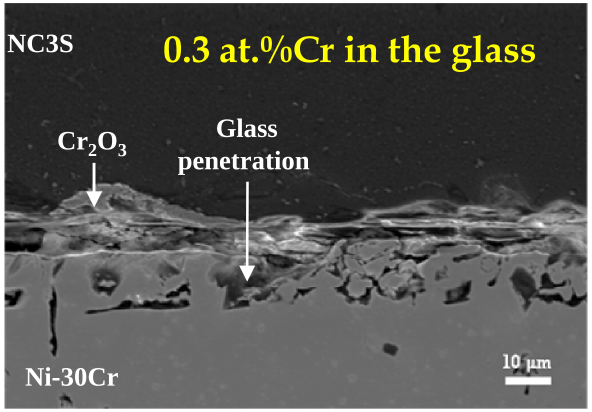


Yttria stabilized zirconia reference electrode (YSZ)

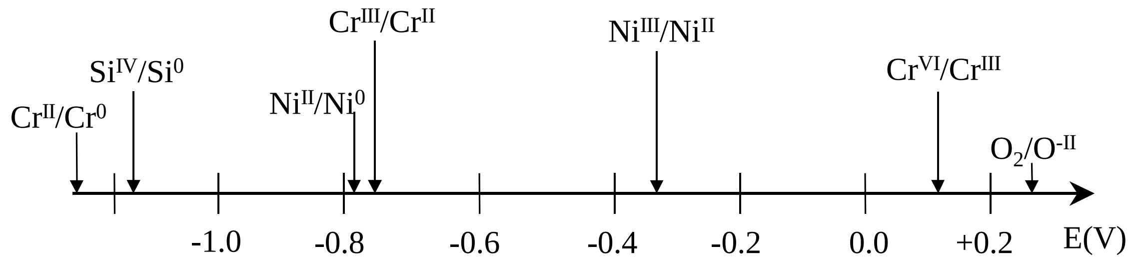
$$\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}$$

Corrosion of Ni30Cr by molten glass

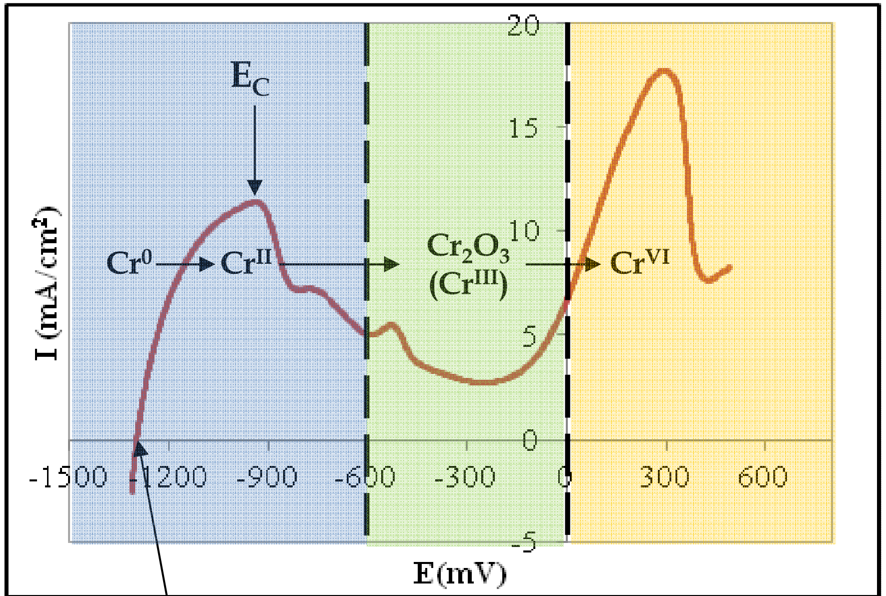
Raw immersion in molten NC3S (1100°C/ 24 h)



CORROSION !



Electrochemical measurements (1100°C)



E_{corr} ~ -1300 mV

R_p ~ 9 Ω.cm² → V_{corr} ~ 5 cm/year !!

$$\left\{\begin{array}{l} Si^{IV}O_4^{4-} + 4e^- \Leftrightarrow Si^0 + 4O^{2-} \\ Cr^0 \Leftrightarrow Cr^{II} + 2e^- \end{array}\right\}$$

active state
I_C > 10 mA.cm^{-2}

$$\left\{\begin{array}{l} O_2 + 4e^- \Leftrightarrow 2O^{2-} \\ Cr^{II} \Leftrightarrow Cr^{III} + e^- \end{array}\right\}$$

leads to passive state
I_P < 5 mA.cm^{-2}

$$\left\{ Cr^{III} \Leftrightarrow Cr^{VI} + 3e^- \right\}$$

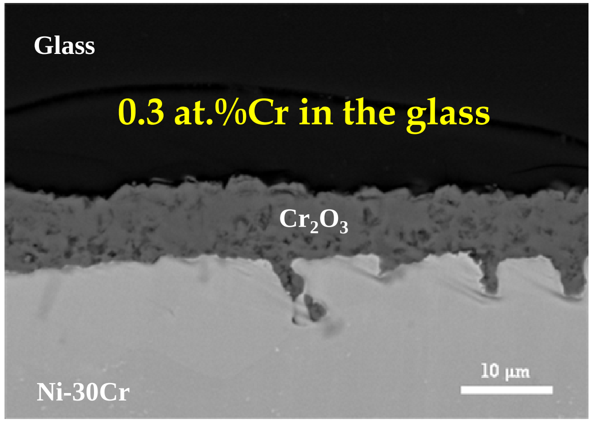
transpassivation
I_T > 15 mA.cm^{-2}

Passivation by preoxidation heat treatment ?

Corrosion of Ni30Cr by molten glass

TGA analysis → preoxidation at 1100°C/2h ~ 5 µm thick Cr_2O_3 layer

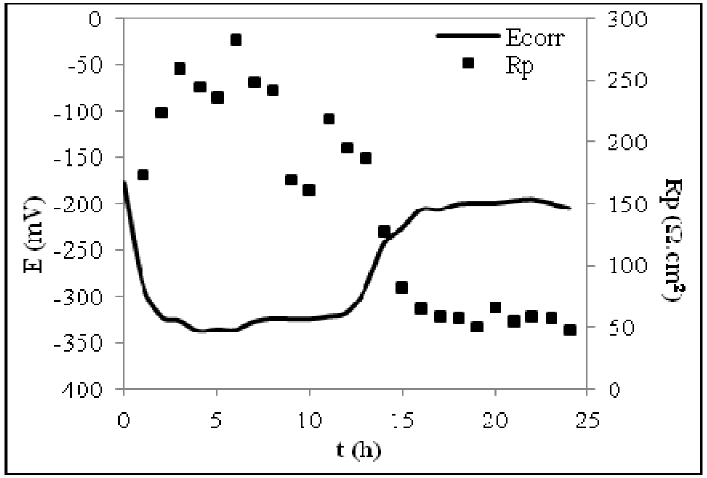
Raw immersion in molten NC3S (1100°C/24 h)



e ~ 6-10 µm

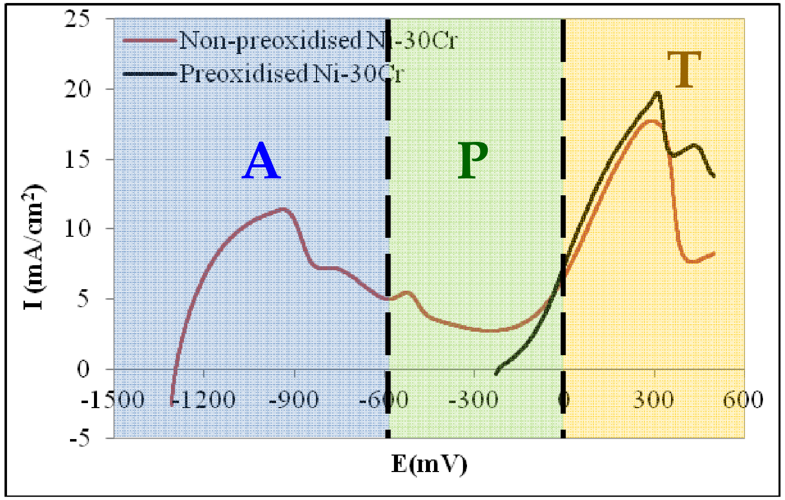
PROTECTION

E_{corr} and R_P measurements (24 h)



-320 mV < E_{corr} < -200 mV   60 Ω.cm² < R_p < 250 Ω.cm²

Linear polarization after 24 h in NC3S



PASSIVE STATE

COMPETITION

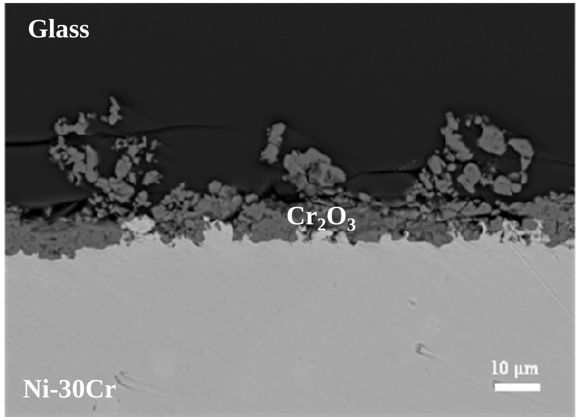
Cr_2O_3 growth ⇔ Cr_2O_3 dissolution

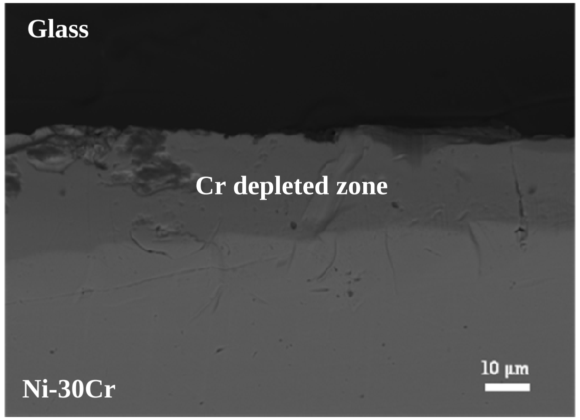
Protection:
Cr_2O_3 growth > Cr_2O_3 dissolution

Corrosion of Ni30Cr by molten glass

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

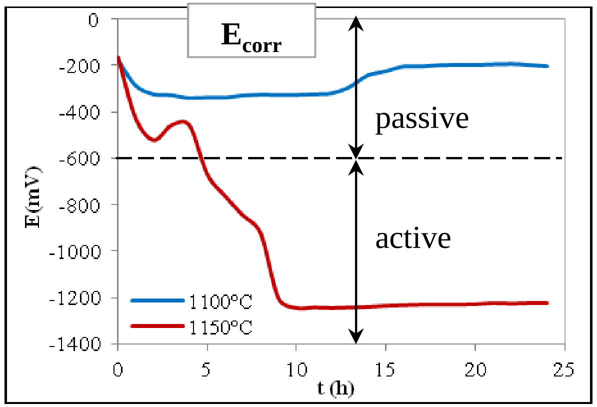
Raw immersion in molten NC3S (1150°C/24 h)

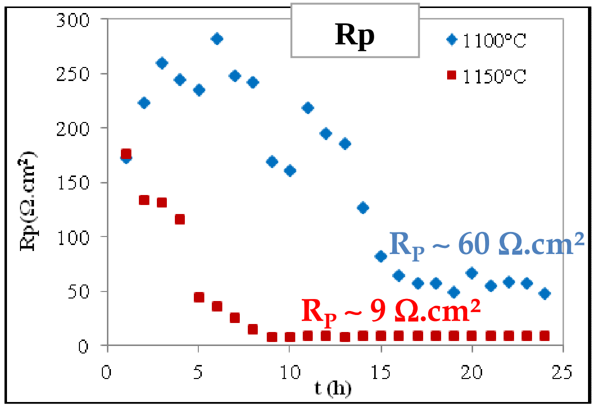




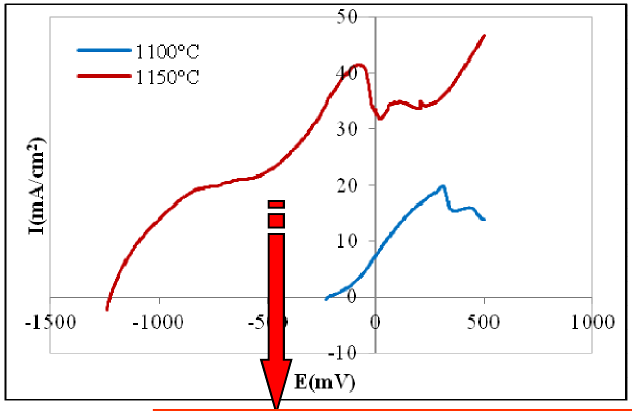
CORROSION !

E_{corr} and R_P measurements (24 h)





Linear polarization after 24 h in NC3S



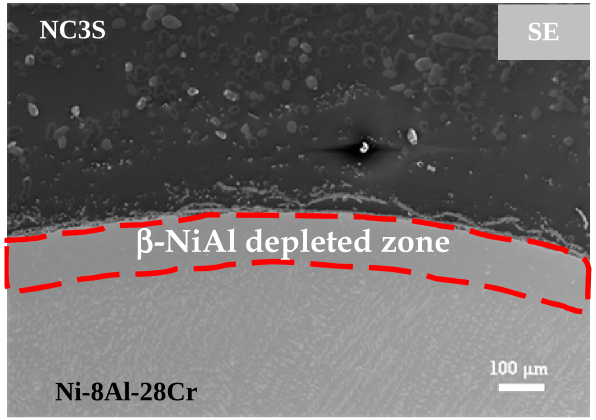
Impossible to obtain passivation at 1150°C

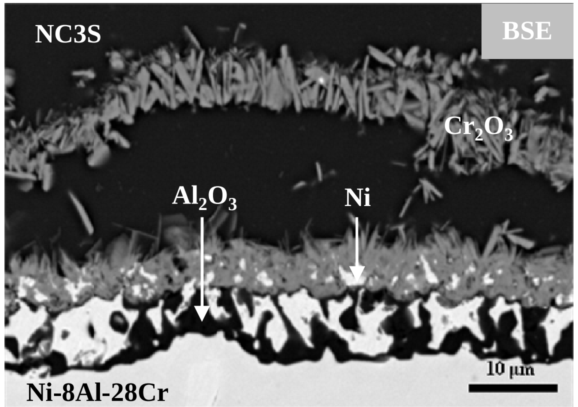
T ↗ ⇒ Cr solubility ↗ ⇒ Cr_2O_3 dissolution > Cr_2O_3 growth

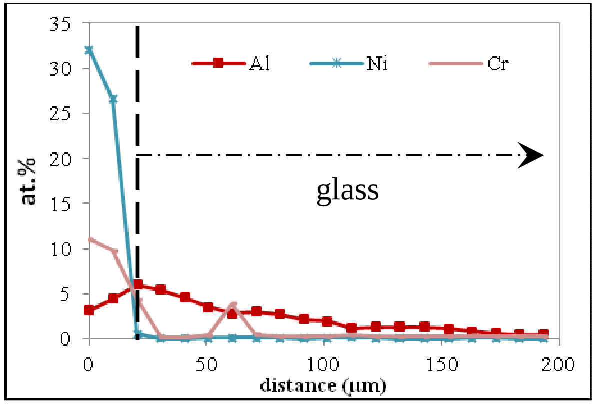
In NC3S, 1100°C < $T_{depassivation}$ < 1150°C

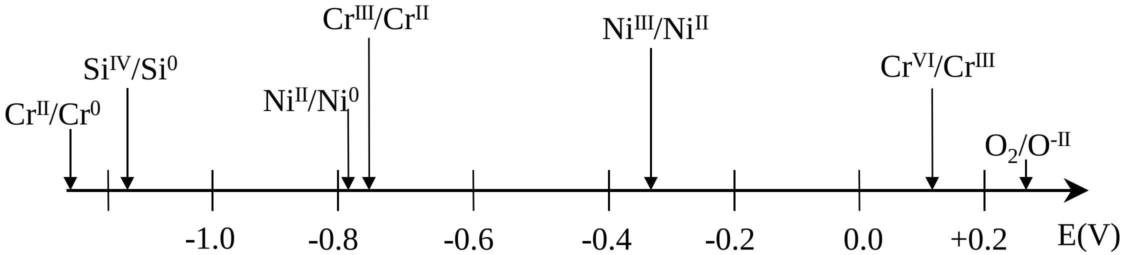
Corrosion of Ni8Al28Cr by molten glass

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





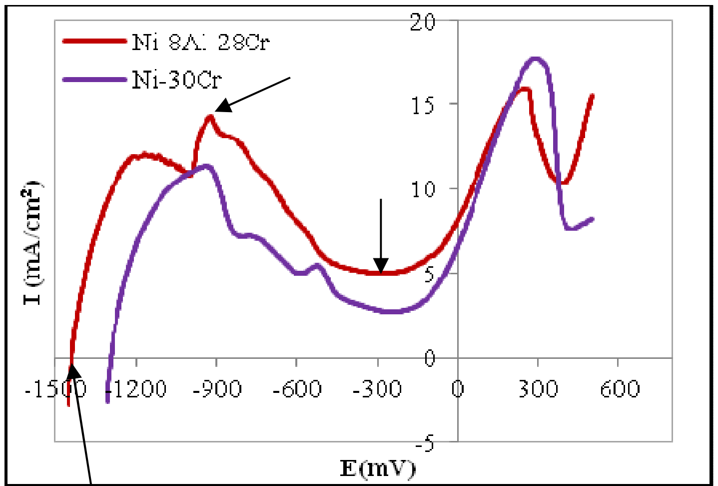




Limit of solubility in soda lime silicates at 1300°C (at.%)[1]	
Cr	**Al**
0.6	21.3

[1] L.J Manfredo *et al.*, J. Am. Ceram. Soc. 67, 155-157 (1984)

Linear polarization after 24 h in NC3S



E_{corr} ~ -1500 mV

R_p ~ 9 Ω.cm²

$$\left\{ \begin{array}{l} Si^{IV}O_4^{4-} + 4e^- \Leftrightarrow Si^0 + 4O^{2-} \\ Al^0 \Leftrightarrow Al^{III} + 3e^- \end{array} \right\}$$

active state

$I_C > 15$ mA.cm^{-2}

Ni8Al28Cr:

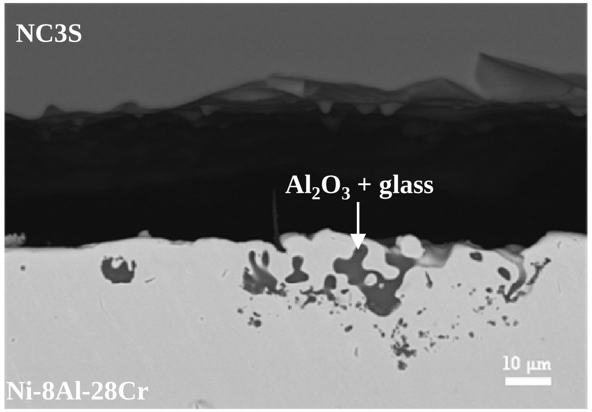
- higher critical current density
- higher current density on the passivation plateau

Protection by Al_2O_3 scale ?

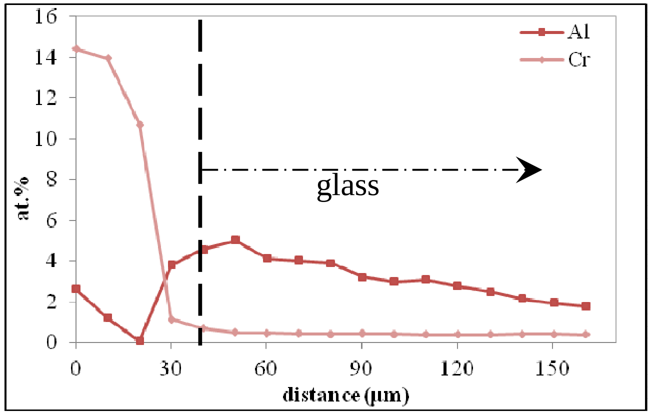
Corrosion of Ni8Al28Cr by molten glass

TGA analysis → preoxidation at 1100°C/24h ~ 2 µm thick Al_2O_3 layer

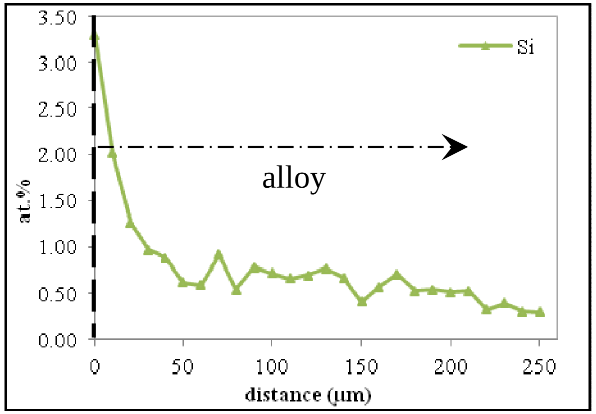
Raw immersion in molten NC3S (1100°C/24 h)



No protective scale

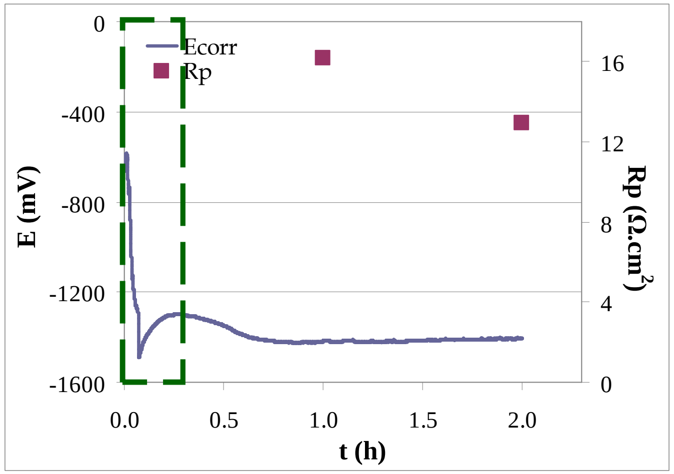


High dissolution of Al in NC3S



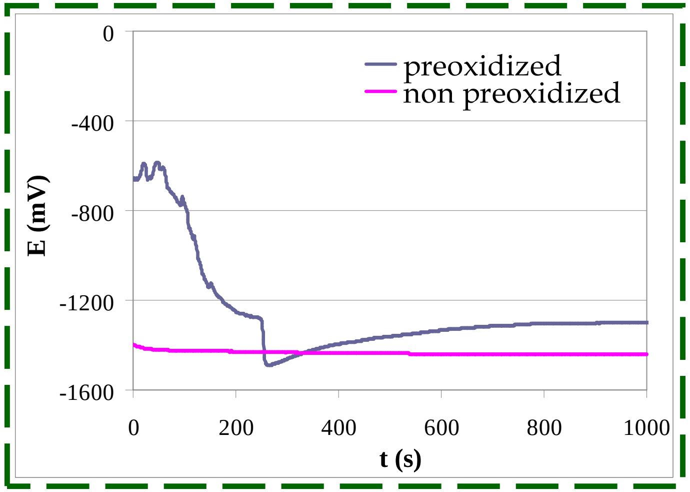
Presence of Si in the alloy

E_{corr} and R_P measurements (2 h)



- t = 0 ; E_{corr} ~ -550 mV
  → **passive state**
- t = 5 min ; E_{corr} ~ -1.3 V
  → **active state**

Dissolution of the Al_2O_3 layer in NC3S in 5 min !



Physico-chemistry of Cr_2O_3 in molten glass

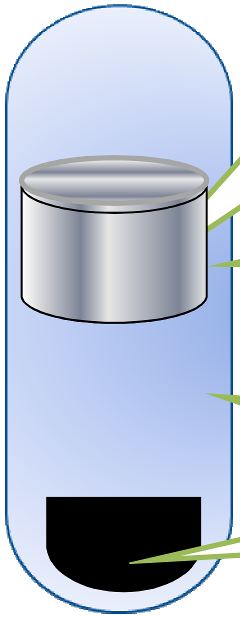
Durability of the protective oxide scale

COMPETITION

Cr_2O_3 growth ⟺ **Cr_2O_3 dissolution**

Limit of solubility ruled by
- ✓ temperature
- ✓ glass composition
- ✓ oxygen fugacity

Experimental device



Glass sample + 5-10 wt.% Cr_2O_3

Glass reservoir
Control Na volatilization

$$NaO_{1/2}(reservoir) \rightarrow Na(g) + \tfrac{1}{4}O_2$$

$$Na(g) + \tfrac{1}{4}O_2 \rightarrow NaO_{1/2}\ (sample)$$

$$aNaO_{1/2}\ (reservoir) = aNaO_{1/2}(sample)$$

Silica tube sealed under secondary vacuum

Buffer M(s)+M_xO_y (s)
Control fO_2

$$2x/yM + O_2 = 2/yM_xO_y$$

(Ellingham diagram)

➡ **Cr solubility at equilibrium**

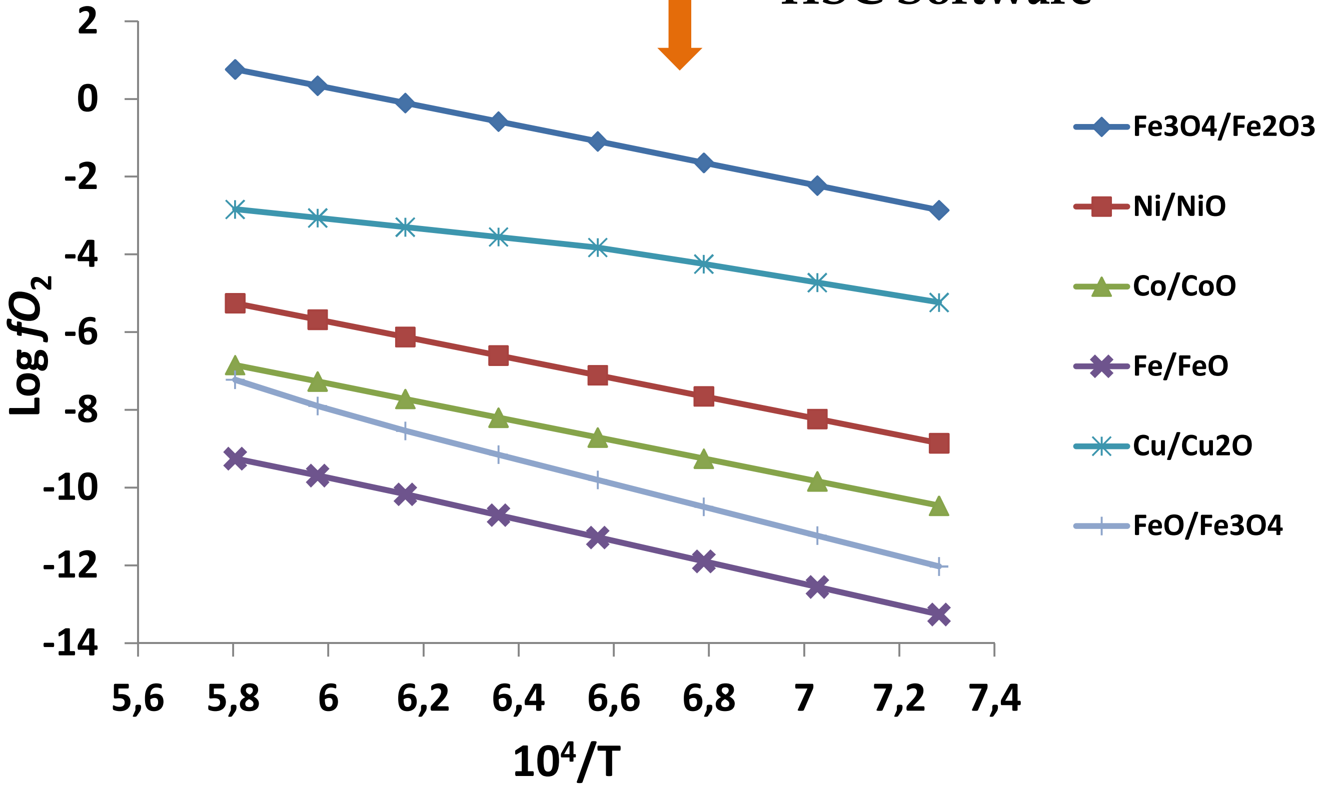
Physico-chemistry of Cr_2O_3 in molten glass

MOx/MO_y buffers

$$\frac{2}{y-x}MO_{x(solid)} + O_{2(g)} \Leftrightarrow \frac{2}{y-x}MO_{y(solid)}$$

$$K = \frac{1}{fO_2}$$

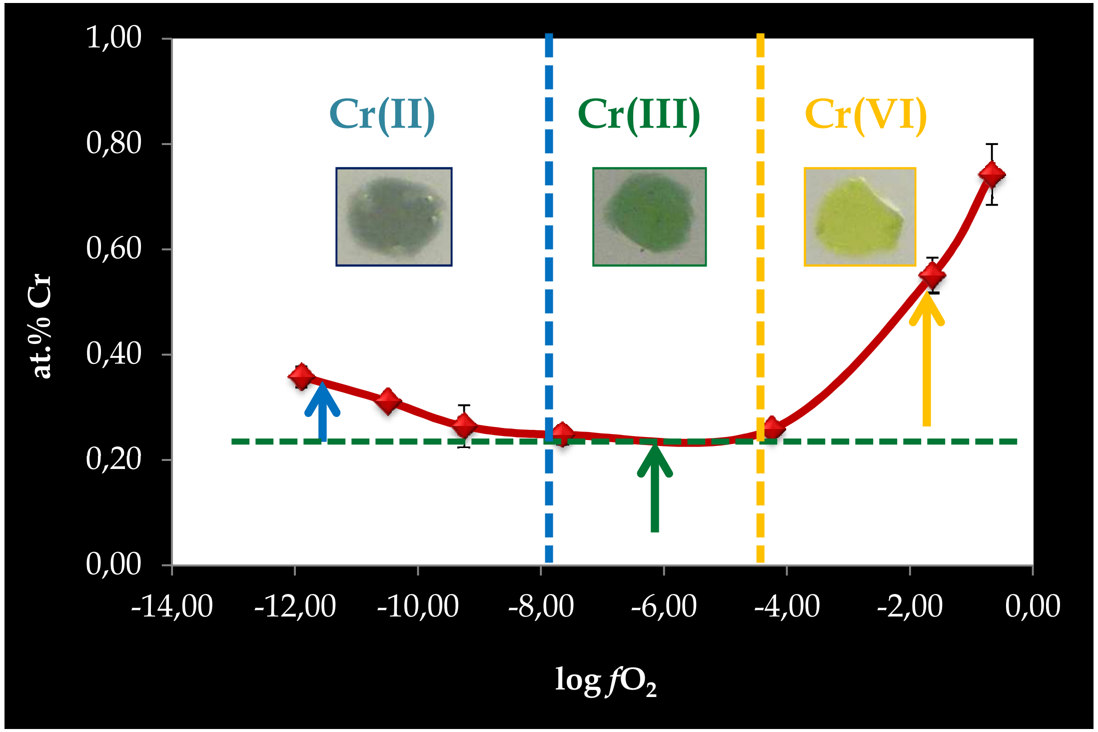
HSC Software



Physico-chemistry of Cr_2O_3 in molten glass

Influence of fO_2

Cr solubility in NC3S (T = 1200°C)



At equilibrium, Cr^{III} is assumed to remain constant with fO_2 at a given T as long as Cr_2O_3 is remaining in the melts

Reducing: $Cr_{(total)} = Cr^{II} + Cr^{III}$

Oxidizing: $Cr_{(total)} = Cr^{III} + Cr^{VI}$

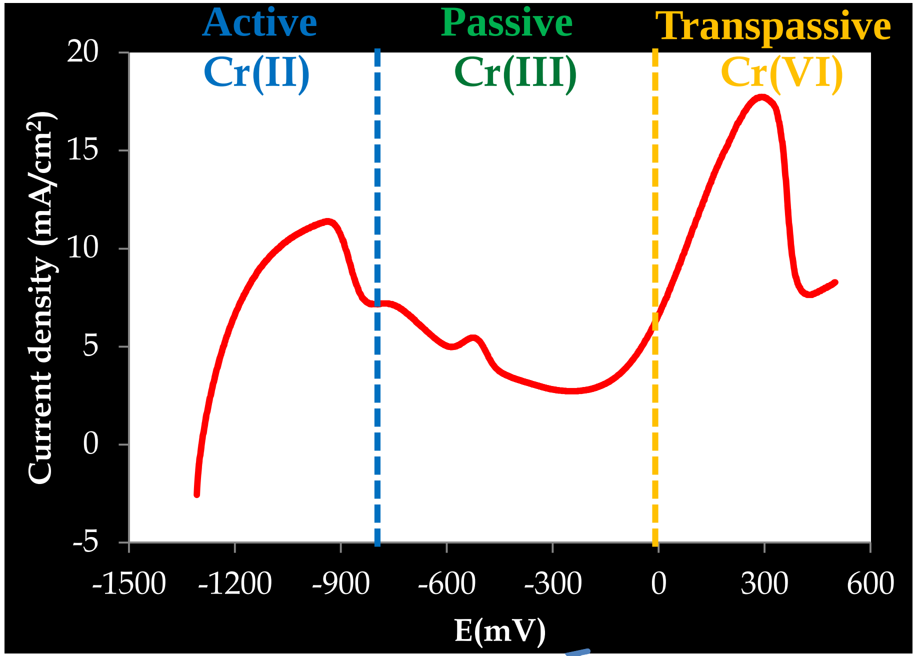
$$\frac{1}{2} Cr_2O_3\,(melt) + \left(x - \frac{3}{2}\right) O^{2-}\,(\text{melt}) \rightarrow Cr^{III} O_x^{(2x-3)-}\,(melt)$$

$Cr_{(total)} = Cr^{II} + Cr^{III} + Cr^{VI}$ (EPMA analysis)

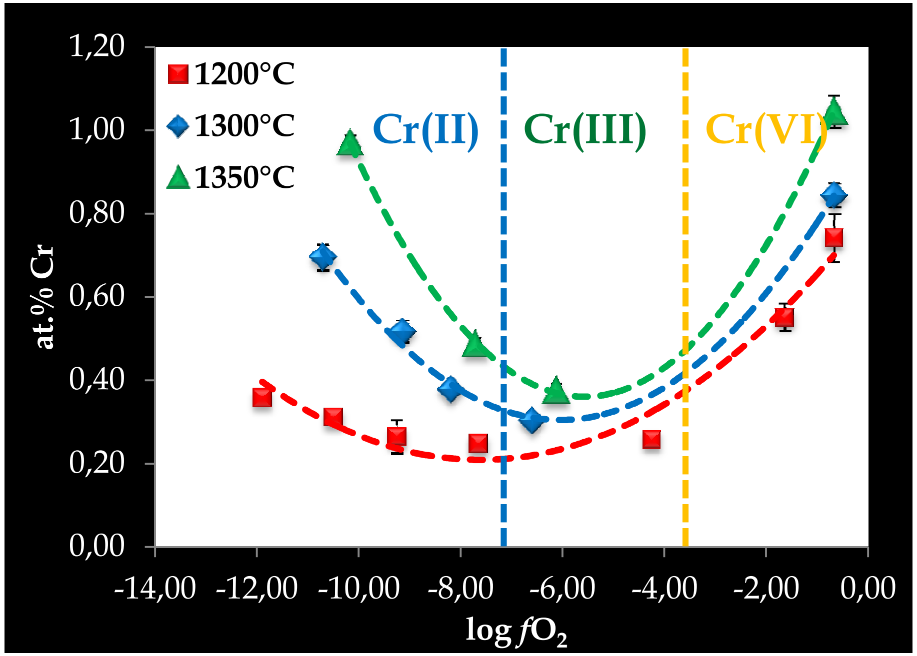
Physico-chemistry of Cr_2O_3 in molten glass

Corrosion-solubility correlation

Corrosion of Ni30Cr rod in NC3S at T =1100°C



Cr solubility in NC3S at 1200°C≤T≤1350°C



Kinetic

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

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_2O_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_2O_3 in the melt

- ✓ The influence of oxygen fugacity (fO_2) on the Cr solubility has been proved:
  → three solubility domains exist by varying the fO_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_2O_3 scale.

→ optimization of the alloy composition (*i.e.* Cr content)

→ optimization of the preoxidation treatment (*i.e.* scale thickness)

✓ Influence of T, fO_2 and melt composition (basicity, viscosity, …) on the Cr solubility at equilibrium

→ correlation with electrochemical measurements

✓ Study of the physico-chemistry of Al_2O_3 in the melts

→ solubility, phase precipitation, …

THANK YOU

TERIMA KASIH

MERCI