Les processus de corrosion à haute température

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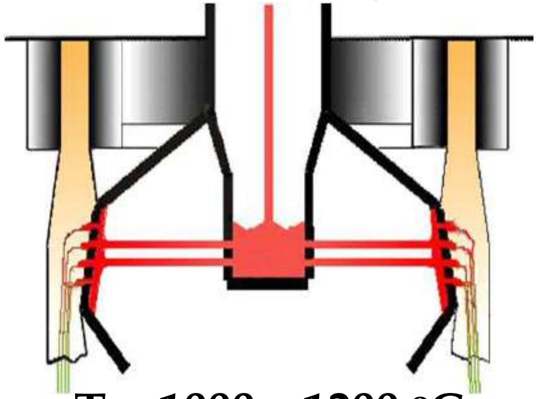
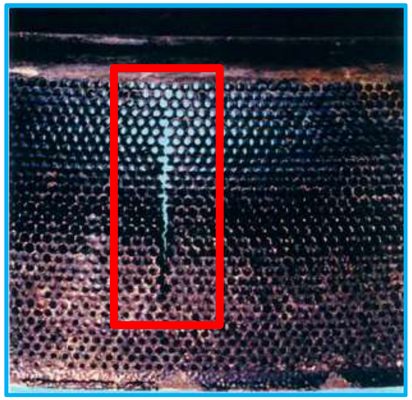
Contexte : corrosion par les verres fondus
Aspects applicatifs

Fibrage du verre



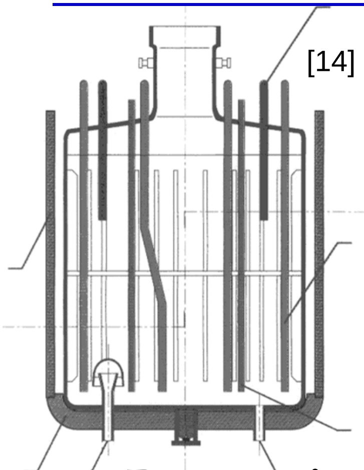


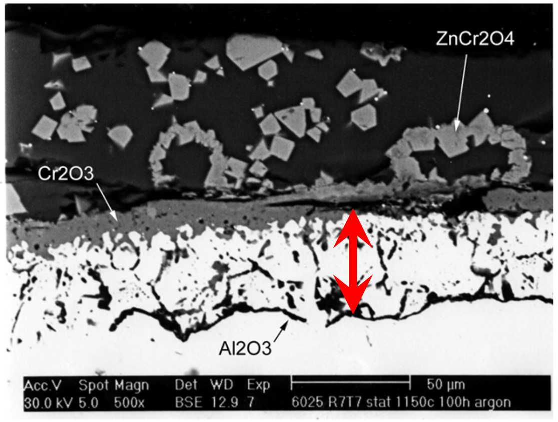
T ~ 1000 – 1200 °C

Rotation ~ 2000 rpm

[15]

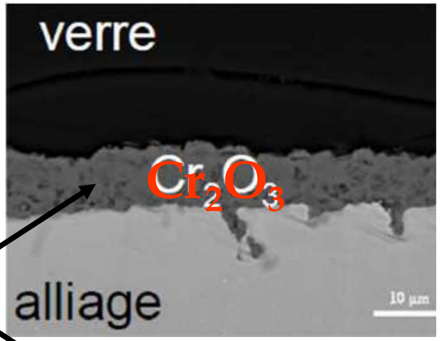
Vitrification des déchets nucléaires





Pénétration du verre dans l'alliage

⇨ **Corrosion des superalliages en conditions sévères**



Propriétés des matériaux:

Meilleure tenue au fluage, à l'oxydation et à la corrosion par les gaz et les milieux fondus

Superalliages base Ni avec Al, Cr

Air HT corrosion

Protection par une couche d'oxyde

Al_2O_3

[7]

Contexte : corrosion par les verres fondus Aspects fondamentaux

A. Aspects thermodynamiques de la corrosion

=> prévision de la réactivité chimique

- ✓ Réaction d'oxydo-réduction à haute température

  => formation potentielle d'une couche d'oxyde protectrice

- ✓ Réaction acido-basique

  => dissolution potentielle de la couche d'oxyde

B. Aspects cinétiques de la corrosion

=> détermination des vitesses de réaction

- ✓ Vitesse d'oxydation par les gaz

=> Compétition formation - "Desquamation" et/ou vaporisation

- ✓ Vitesse d'oxydation électrochimique en milieu liquide

  => Compétition formation – dissolution

A. et B. : Modèle prédictif de la durée de vie

Plan de la présentation

- ➢ Comportement des alliages métalliques dans les environnements gazeux à Haute Température

Aspects thermodynamique et cinétique de l'oxydation "sèche"

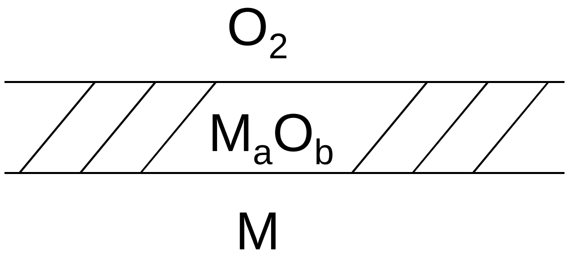
- ➢ Comportement des alliages métalliques dans les silicates fondus

Dissolution – précipitation
Oxydation électrochimique

- Comportement des alliages métalliques dans les environnements gazeux à Haute Température

Aspects thermodynamique et cinétique de l’oxydation “sèche”

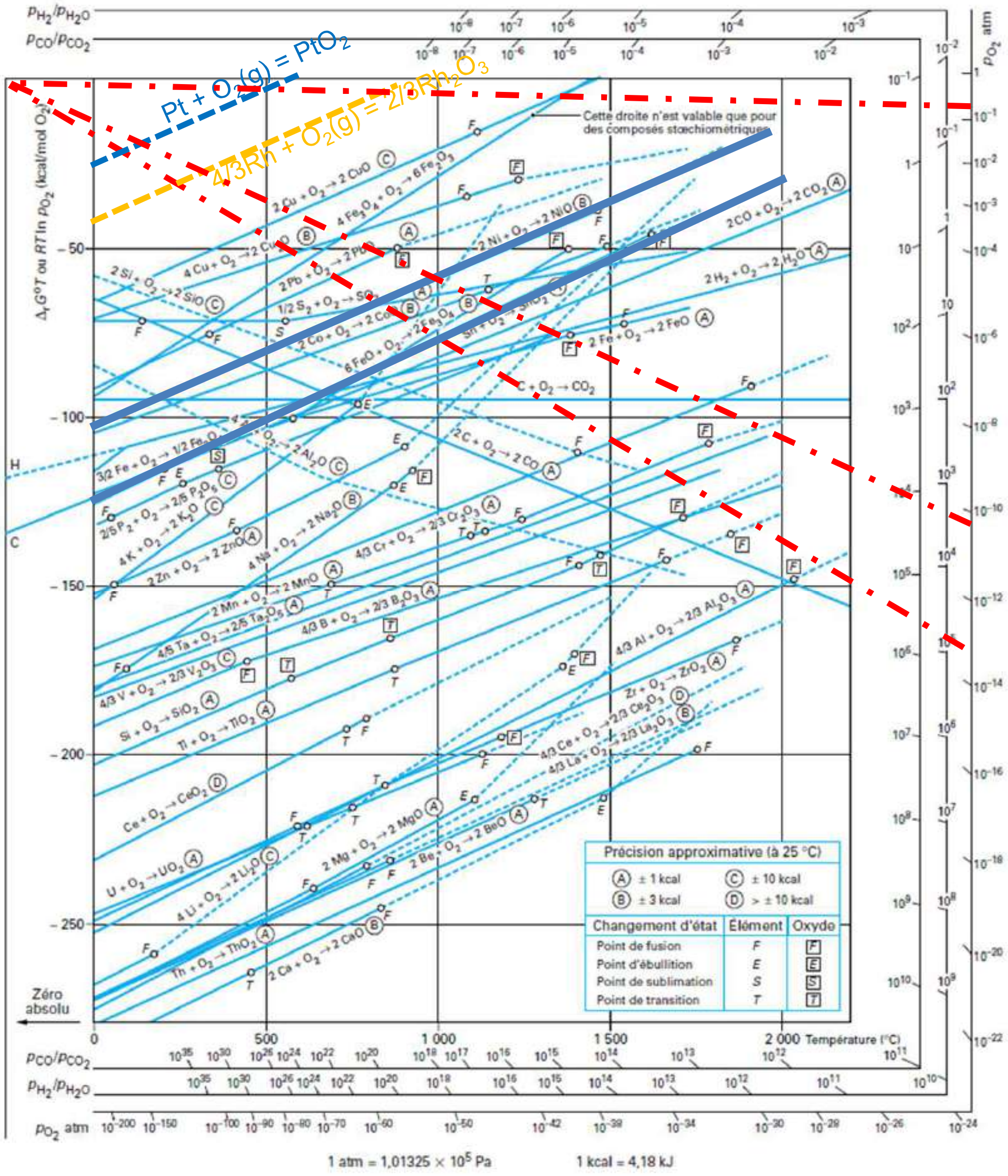
Approche Thermodynamique



$$2a_{/b}\,M\,(s) + 1\,O_2\,(g) \Leftrightarrow 2_{/b}\,M_aO_b\,(s)$$

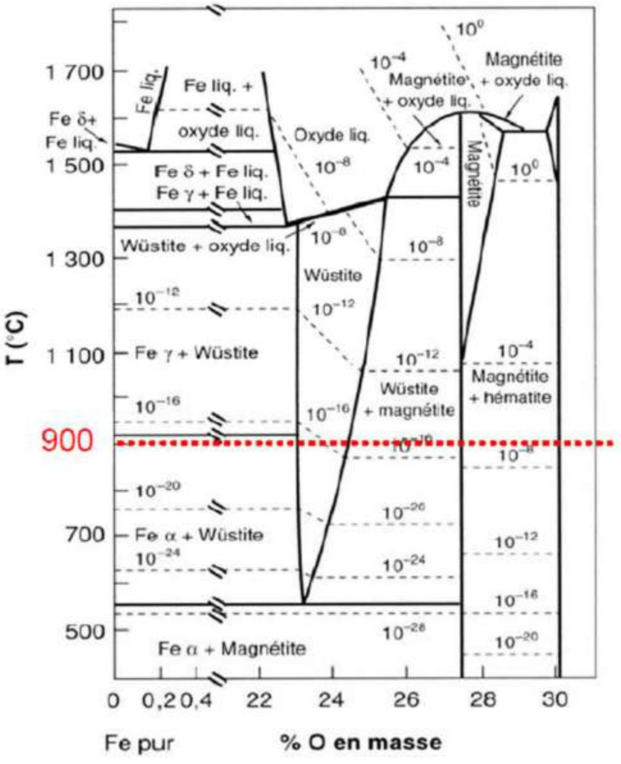
$$\Delta G°_T = \Delta H°_T - T\Delta S°_T$$

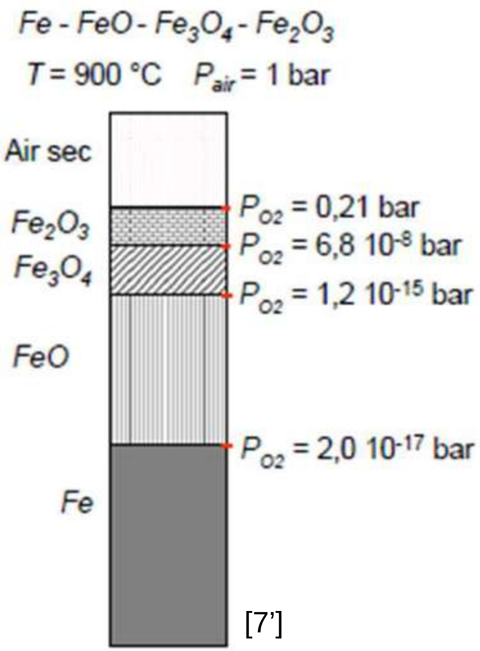
$$\Delta G°_T = RT\ln P_{O_2}$$



[3]

➢ Oxydation des métaux purs





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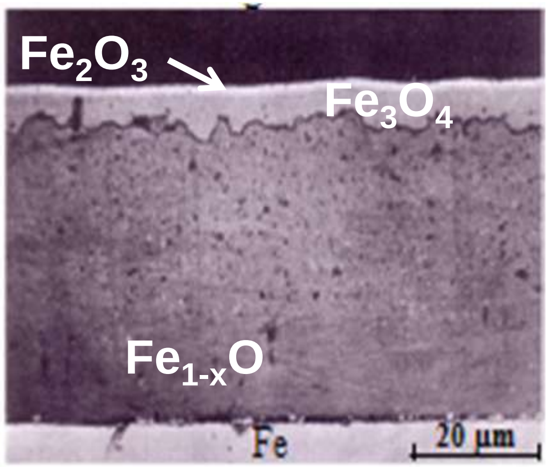
✓ **Oxydation 100H à 700°C sous Air**



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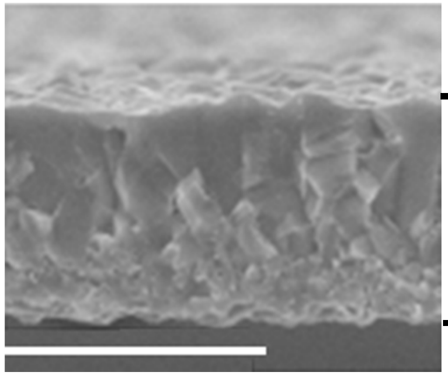


O_2

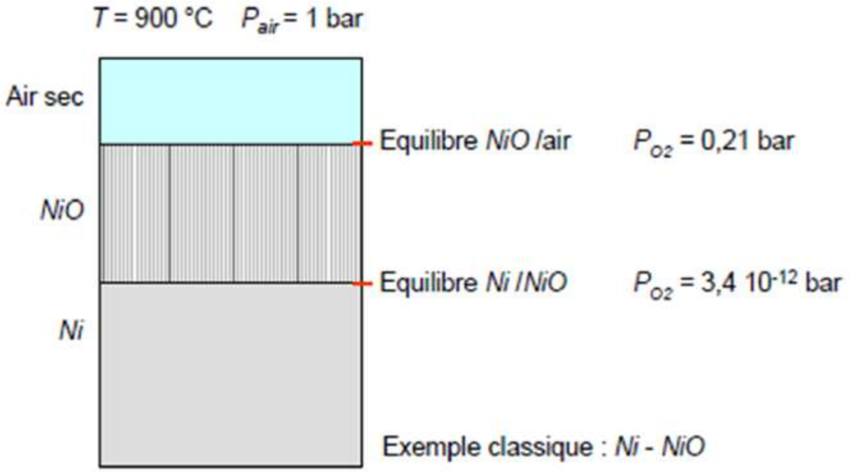
$P_{O2} = 0{,}21$ bar

NiO

$P_{O2} = 3{,}4\ 10^{-12}$ bar

Ni

✓ **Oxydation 15H à 800°C sous O_2**



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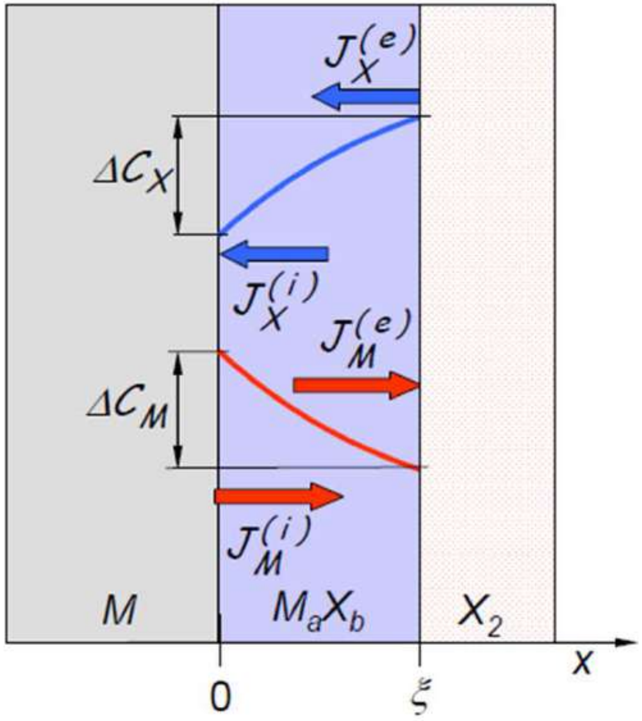
➢ Mécanisme d’oxydation à Haute Température

Les oxydes « protecteurs » sont des composés ioniques non stoechiométriques

✓Mécanisme de croissance [7’]

2. Diffusion au sein de MO

- Contrôle par le défaut prépondérant



3. Interface MO/ Métal

- Oxydation du métal et transfert dans MO
- Création/annihilation des défauts

1. Interface gaz/MO

- Adsorption
- Transfert de l'oxydant du gaz à la couche d'oxydation
- Création/annihilation des défauts

✓Exemple : Cas de NiO

- 1 : *Réactions à l'interface externe*

$$O_2 + 2s \rightarrow 2O - s$$

(Chimie sorption dissociative)

$$z\,O - s \rightarrow z\,O_O^X + 2V_M^{z'} + 2z\,h^{\circ} + z\,s$$

-2 : *Diffusion au sein de la couche d'oxyde*

Généralement contrôlée par un défaut majoritaire

- 3 : *Réactions à l'interface interne*

$$\underline{M}_M + V_M^{z.'} + z\,h^{\circ} \rightarrow M_M^X$$

(Semi-conducteur de type p)

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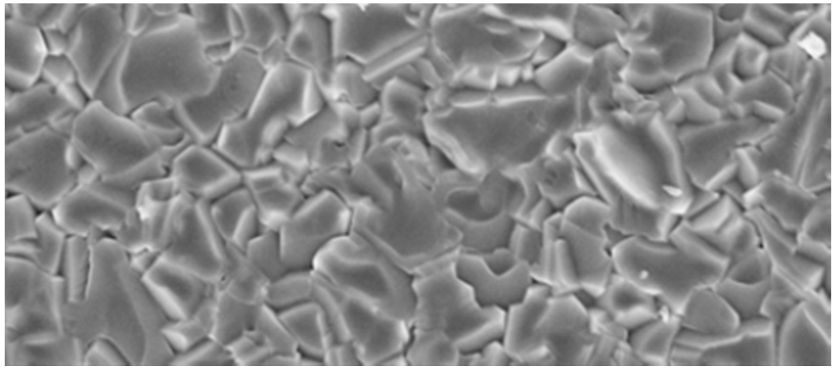


Ni pur oxydé 1H à 1100°C (P_{O2}= 1bar)

- La morphologie et la microstructure des couches d'oxyde sont peu influencées par la microstructure du métal sous-jacent.
  => Il n'y a plus de trace de l'état de surface initial

✓Exemple : Cas de Cr_2O_3

- 1 : *Réactions à l'interface externe*

$$O_2 + 2s \rightarrow 2O - s$$

(Chimie sorption dissociative)

$$z\,O - s + 2\,M_i^{z\circ} + 2z\,e' \rightarrow z\,O_O^X + 2\,M_M^X + z\,s$$

-2 : *Diffusion au sein de la couche d'oxyde*

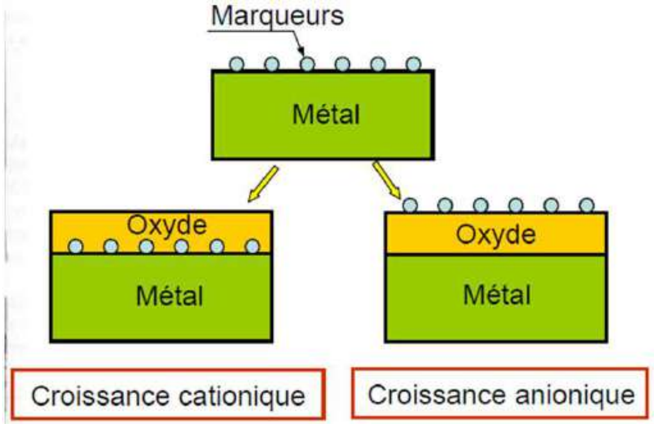
Généralement contrôlé par un défaut majoritaire

- 3 : *Réactions à l'interface interne*

$$\underline{M}_M \rightarrow M_i^{z\circ} + z\,e'$$

(**Semi-conducteur de type n**)

- Mise en évidence : emploi de marqueurs inertes et caractérisation de sections métallographiques



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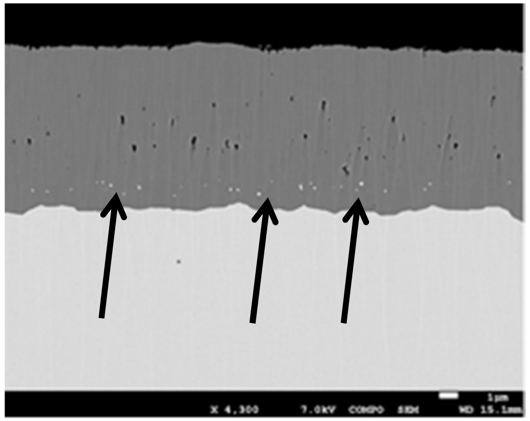
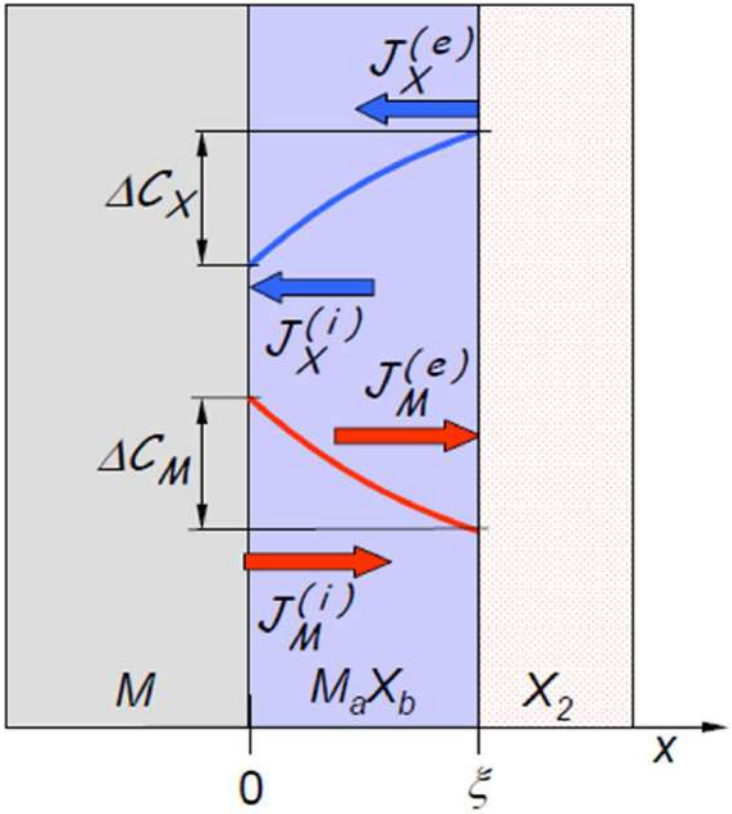


Ni30Cr oxydé 9H sous P_{O2} = $2,8.10^{-13}$ atm
E. Schmucker – IJL 2015

Cinétique d’oxydation Haute Température

✓Modèle de Wagner simplifié

- Couche de MX compacte et adhérente
- Interfaces M/MX et MX/X_2 à l'équilibre
- Croissance contrôlée par la diffusion au travers de la couche
- Etat quasi-stationnaire : $J_j^{(e)} = J_j^{(i)} \quad (j = M, X)$



ξ : épaisseur de la couche (cm)
t : temps (s)
k'_p: constante parabolique de vitesse ($cm^2.s^{-1}$)

$$J_j = -\tilde{D}_j \frac{\Delta C_j}{\xi} \quad (j = M, X)$$

$$\frac{d\xi}{dt} = \Omega_{M_aX_b}\left(aJ_M^{(e)} + bJ_X^{(i)}\right)$$

$$\frac{d\xi}{dt} = \Omega_{M_aX_b}\frac{a\left|\tilde{D}_M\Delta C_M\right| + b\left|\tilde{D}_X\Delta C_X\right|}{\xi}$$

Cinétique d'oxydation Haute Température

$$\frac{d\xi}{dt} = \Omega_{M_aX_b}\,\frac{a\left|\widetilde{D}_M \Delta C_M\right| + b\left|\widetilde{D}_X \Delta C_X\right|}{\xi}$$

Cationique MAJ.

$$\frac{d\xi}{dt} = \Omega_{M_aX_b}\,\frac{a\left|\widetilde{D}_M \Delta C_M\right|}{\xi} = \frac{k'_p}{2\xi}$$

$$\boxed{k'_p = 2a\,\Omega_{M_aX_b}\left|\Delta C_M\right|\,\widetilde{D}_M = k\widetilde{D}_M}$$

Anionique MAJ.

$$\frac{d\xi}{dt} = \Omega_{M_aX_b}\,\frac{b\left|\widetilde{D}_X \Delta C_X\right|}{\xi} = \frac{k'_p}{2\xi}$$

$$\boxed{k'_p = 2b\,\Omega_{M_aX_b}\left|\Delta C_X\right|\,\widetilde{D}_X = k\widetilde{D}_X}$$

Variation de masse in-situ

$$\boxed{\frac{d\Delta m}{dt} = \frac{k_p}{2\,\Delta m} \quad \Leftarrow \quad k_p = \frac{M_X^2}{\Omega_{MX}^2}\,k'_p}$$

Mesure d'épaisseur ex-situ

Cinétique d'oxydation Haute Température

- Oxydation à l'air à 1000°C

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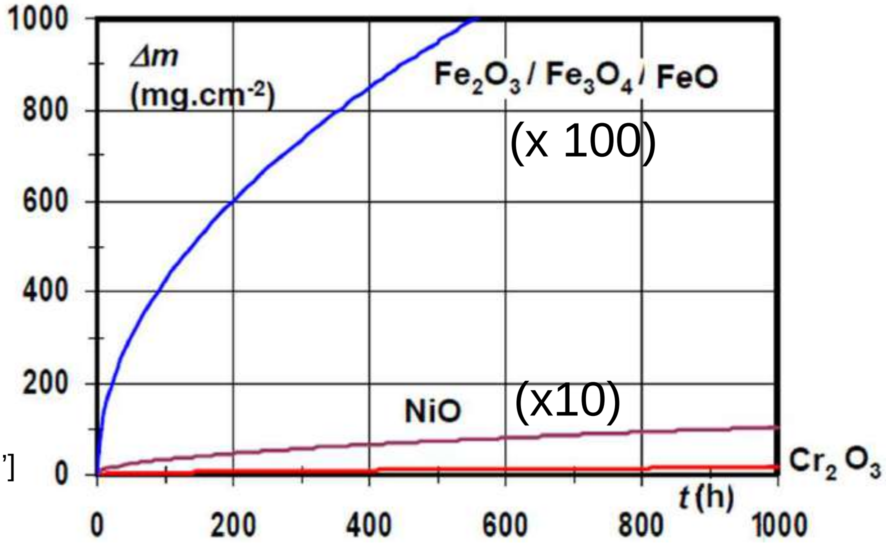

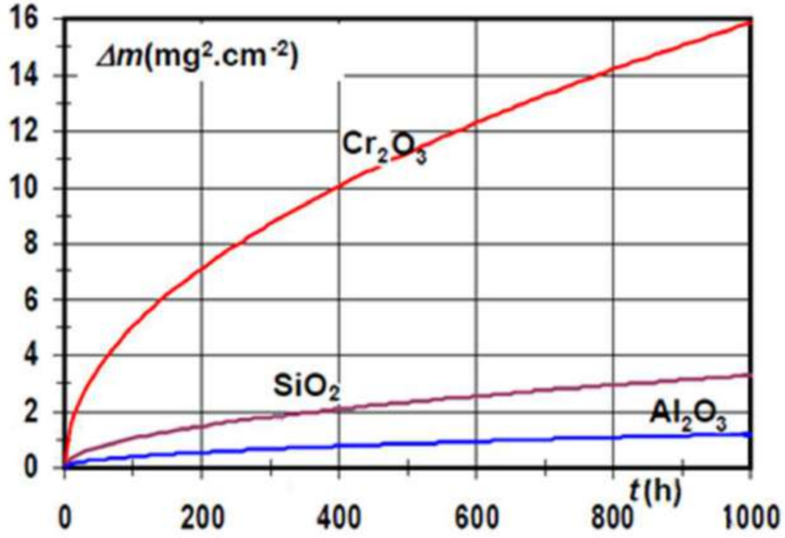

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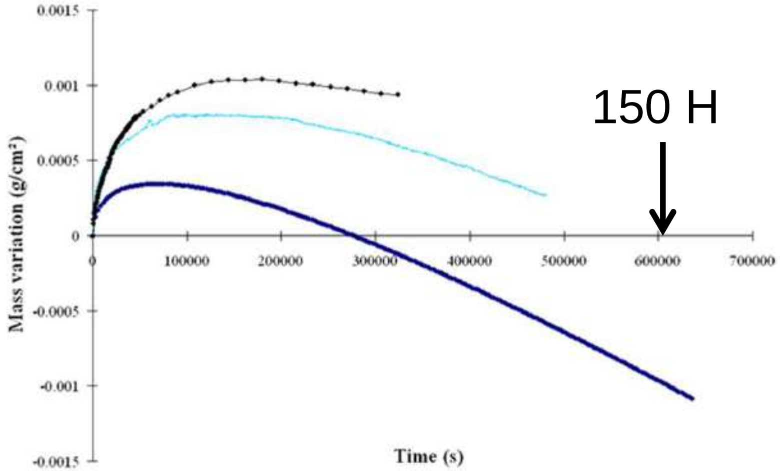
- Oxydation à l'air à T=1300°C



[14, 18]

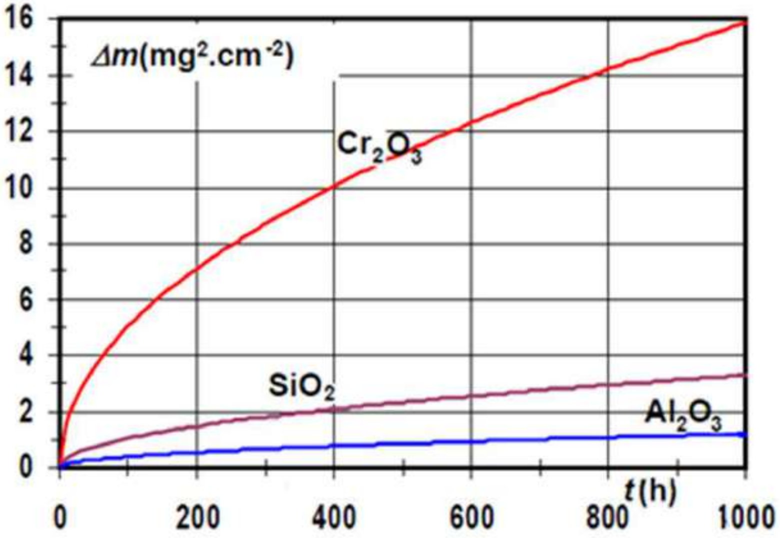
Formation de Cr_2O_3

$$\frac{d\,\frac{\Delta m_{oxide}}{S}}{dt} = \frac{k_p'}{\frac{\Delta m_{oxide}}{S}} - k_l'$$

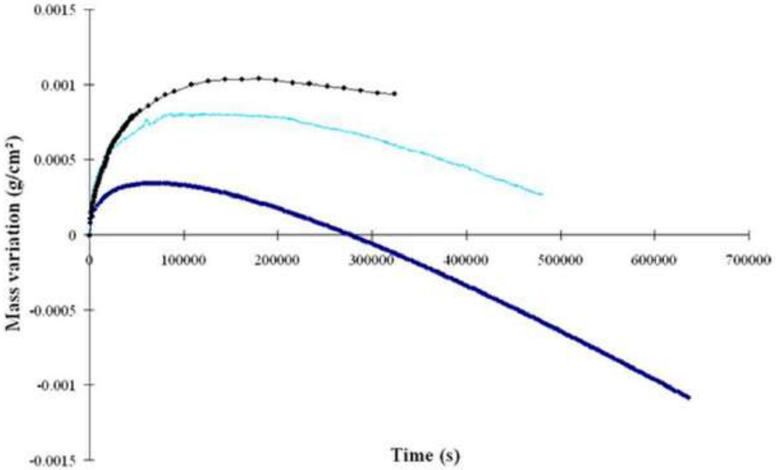
Vaporisation de CrO_3

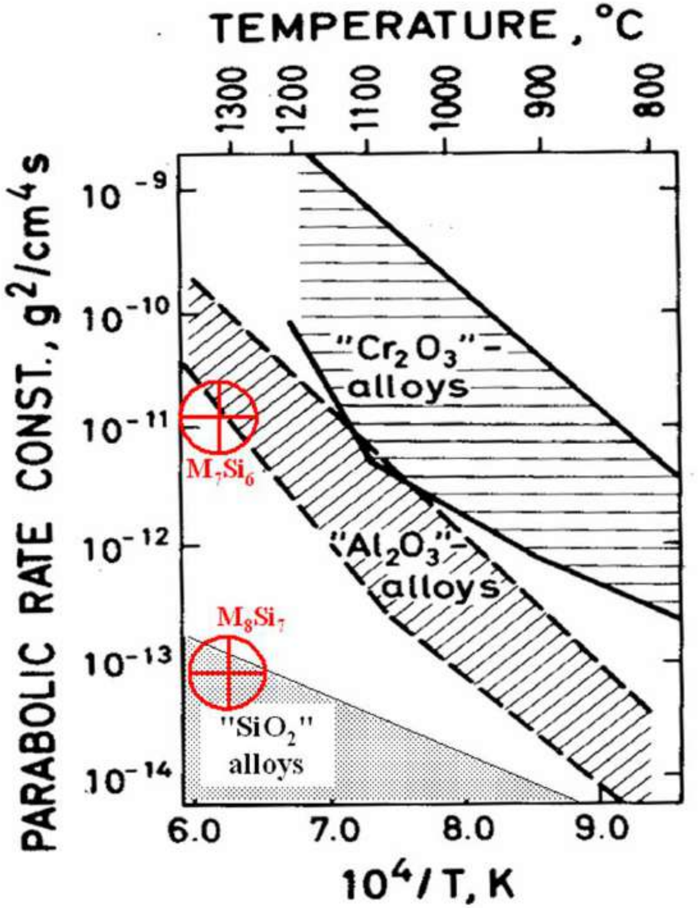
Cinétique d’oxydation Haute Température

- Oxydation à l’air à 1000°C



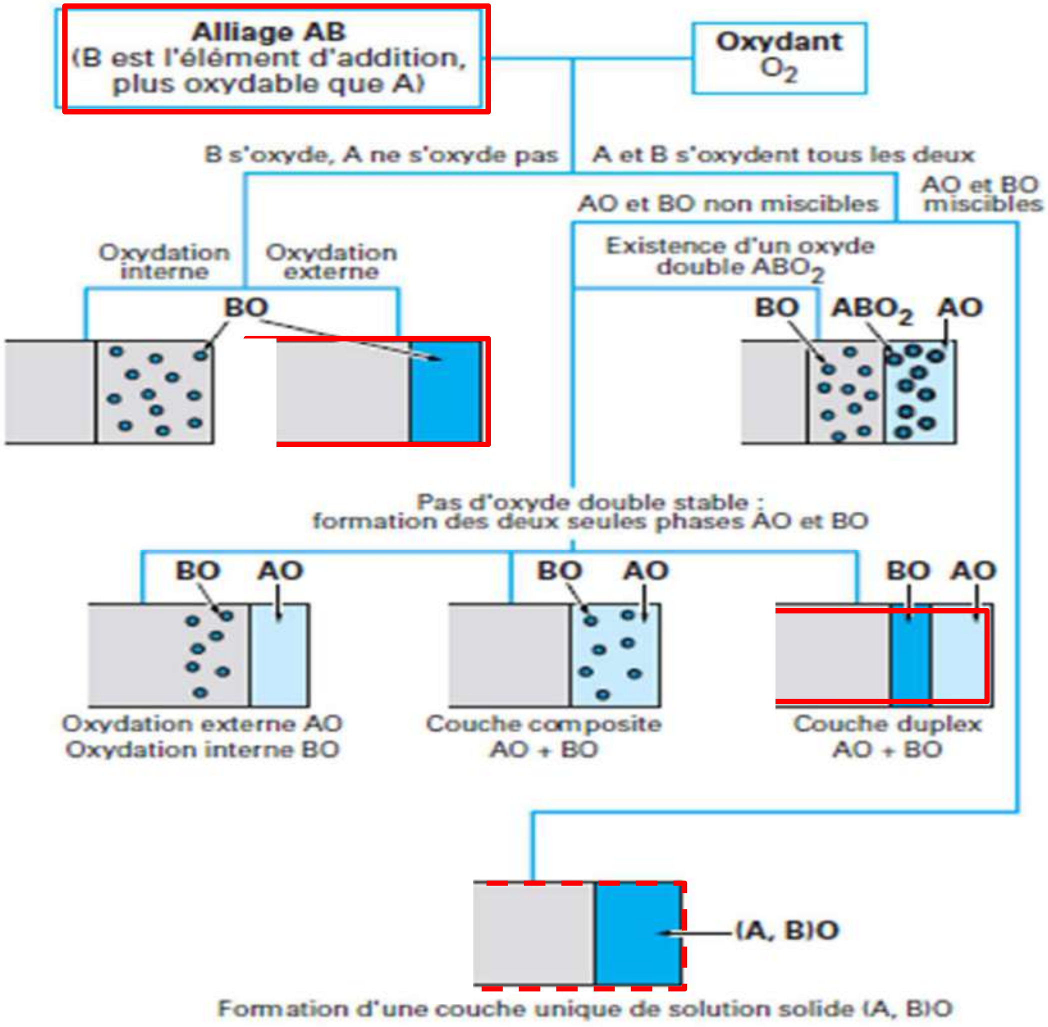
- Oxydation à l’air à T=1300°C





*Hindam, Whittle *Oxidation of Metals* **18,** 5-6 (1982)

Morphologie et microstructure des couches d'oxyde



Alliage AB
(B est l'élément d'addition, plus oxydable que A)

Oxydant
O_2

B s'oxyde, A ne s'oxyde pas

A et B s'oxydent tous les deux

AO et BO non miscibles

AO et BO miscibles

Oxydation interne

Oxydation externe

BO

Existence d'un oxyde double ABO_2

BO **ABO_2** **AO**

Pas d'oxyde double stable : formation des deux seules phases AO et BO

BO **AO**

Oxydation externe AO
Oxydation interne BO

BO **AO**

Couche composite
AO + BO

BO **AO**

Couche duplex
AO + BO

(A, B)O

Formation d'une couche unique de solution solide (A, B)O

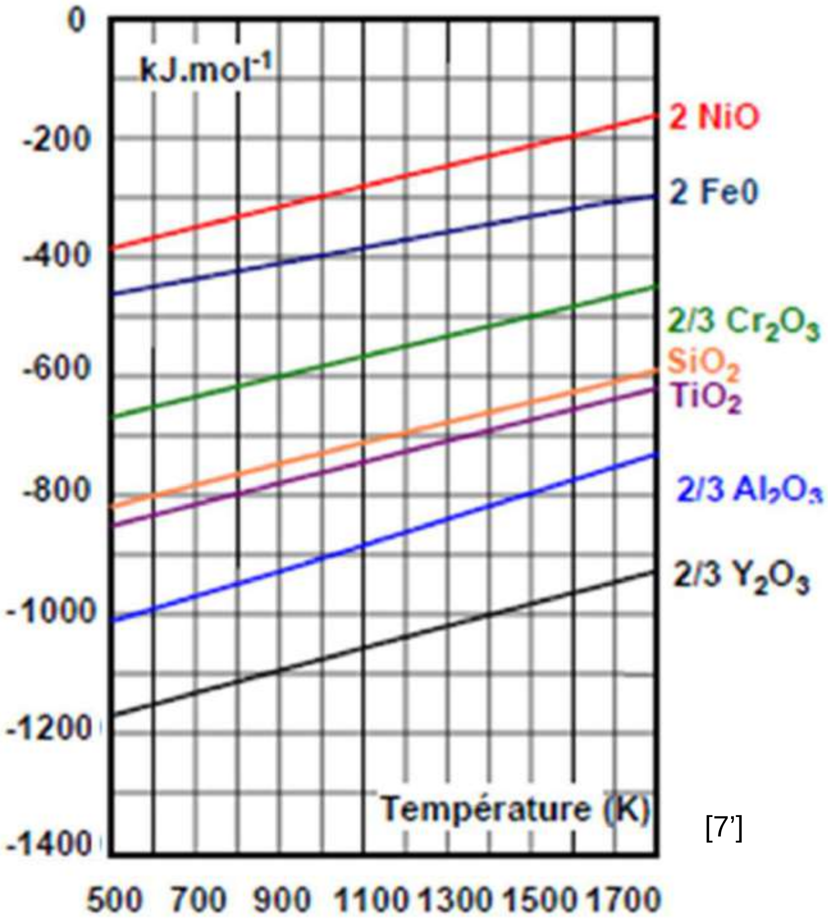
[3]

A élément constituant de l'alliage
B élément d'addition

Morphologie et microstructure des couches d'oxyde

Possible Utilisation à H.T.

- Oxydation sélective de B : Thermodynamique



[7']

Les seuls éléments pouvant être utilisés dans des alliages industriels pour induire la formation de couches d'oxyde stables et protectrices à haute température sont *Al*, *Ti*, *Si* et *Cr*.

Si : parfois néfaste du point de vue des caractéristiques mécaniques.
Ti : problème lié à la dissolution de l'oxygène dans les alliages de Ti. Non-protection de TiO_2.

Deux familles d'alliages métalliques résistants à l'oxydation :
- alumino-formeurs,
- chromino-formeurs

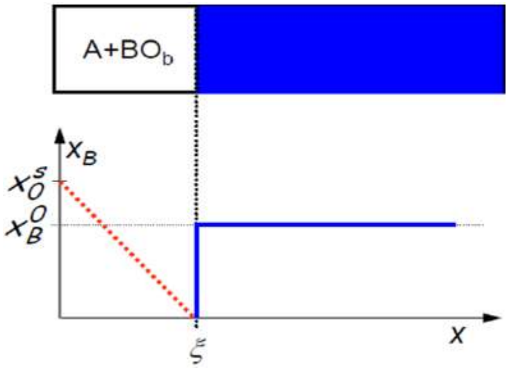
[7']

Morphologie et microstructure des couches d'oxyde

Possible Utilisation à H.T.

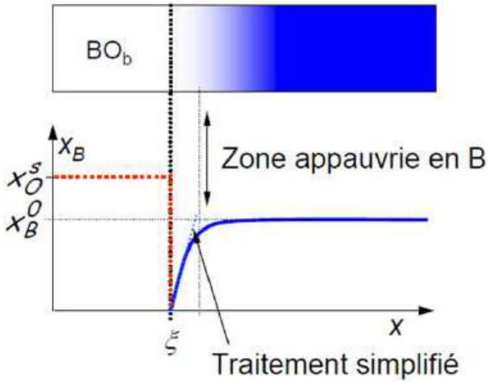
- Formation d'une couche externe de BO_b : modèle de Wagner [8]

Oxydation INTERNE



$$\boxed{\xi^2_{int.} = 2D_O \frac{\Omega_{all}\, x_O^s}{b\, \Omega_{ox}\, x_B^0} t}$$

Oxydation EXTERNE



$$\boxed{\xi'^2_{ext} = 4D_B t}$$

Transition

Teneur critique de l'élément B

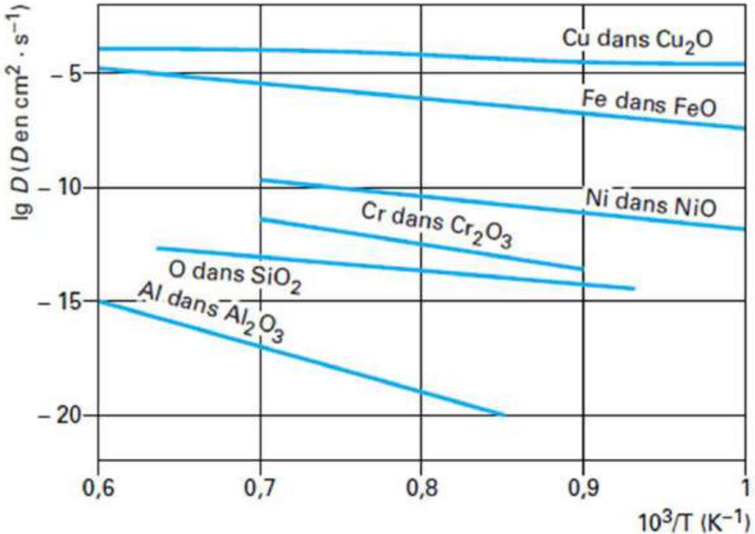
$$\gamma = \frac{\zeta_{ext}}{\zeta_{int}} > 1 \Rightarrow \boxed{\left(2b\frac{D_B \Omega_{ox} X_B^O}{D_O \Omega_{all} X_O^S}\right)^{1/2} > 1} \Rightarrow \boxed{\left(\frac{D_O X_O^S}{\Omega_{ox}}\right)}$$

Perméabilité à O_2 de l'alliage

Possible Utilisation à H.T.

- Caractère protecteur

[3]



1. Faible écart à la stoechiométrie et faible valeur de $D_{\text{défaut}}$: Al_2O_3, Cr_2O_3, SiO_2

Expl : $D_o^{vol}/D_{Cr}^{vol} = 10^{-6}$

2. Paramètres microstructuraux à considérer :

$$D_x^{vol} < D_x^{disloc} < D_x^{jdg} < D_x^{surf}$$

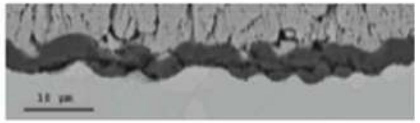
=> Rapport de Pilling et Bedworth :

$$PBR = \frac{V_{MaOb}}{aV_M}$$

PBR <1 : oxyde non couvrant, poreux
1<PBR<1,5 : oxyde couvrant et compact Al_2O_3
PBR >1,5 : « *oxyde devient fissuré et poreux* » *(sens de croissance)*

3. Effet du $3^{\text{ème}}$ élément : oxydabilité intermédiaire entre A_{matrice} et $B_{\text{élém.alliag.}}$

A.



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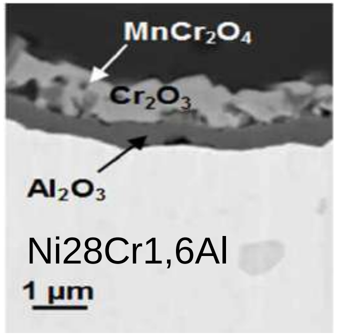
Ni(15-25)Al

Ni5Al25Cr(X,Z,…)

B.



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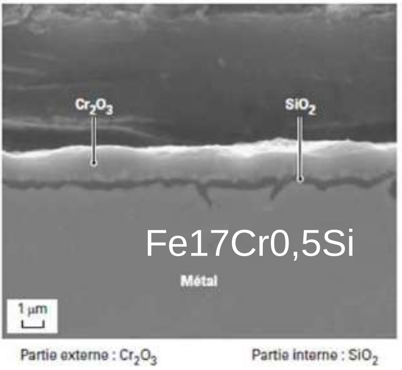
C.



[3]

- Comportement des alliages métalliques dans les silicates fondus

Dissolution – précipitation
Oxydation électrochimique

➢ Physico-chimical characteristics of molten glasses

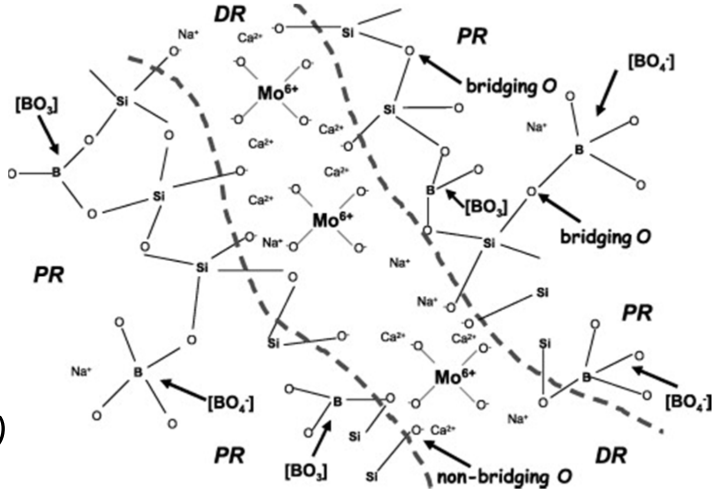
Acido-basic properties allowing the exchange of O^{2-} :

$Na_4SiO_4 \Leftrightarrow 4\ Na^+ + 2O^{2-} + SiO_2$ $K_T^{ionisation}$?

$K_{298}^{H_2O} = 10^{-14}$

Oxo-complexing properties: formation of octa-, tétrahedra

Hydrine$Al(H_2O)_6^{3+}$

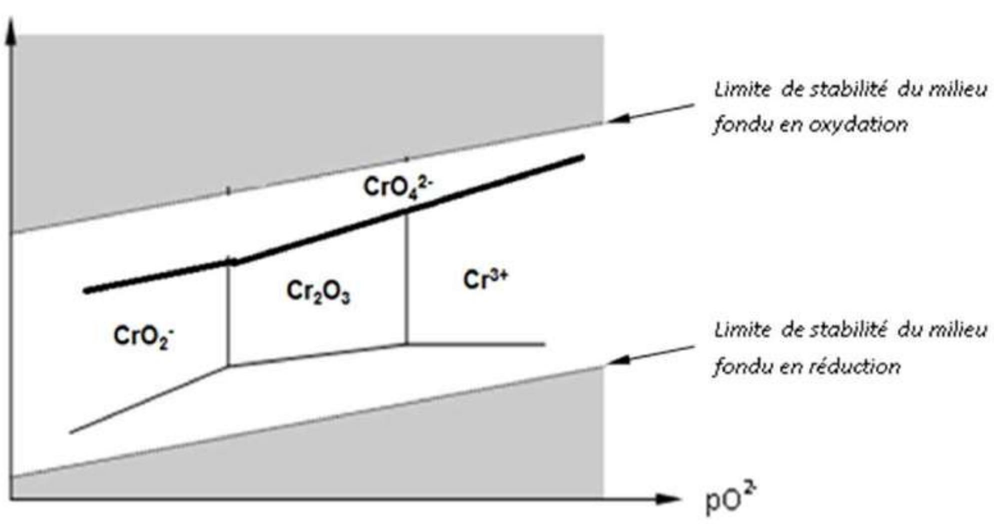


D. Caurant et al (2010)

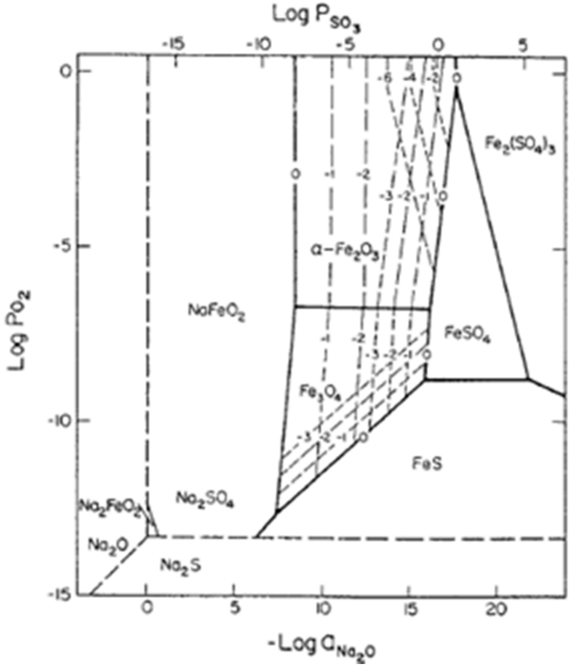
- ➢ Comme l’eau : les verres fondus sont des électrolytes qui ont des propriétés solvatantes et complexantes
- ➢ A la différence de l’eau : le milieu est très polymérisé

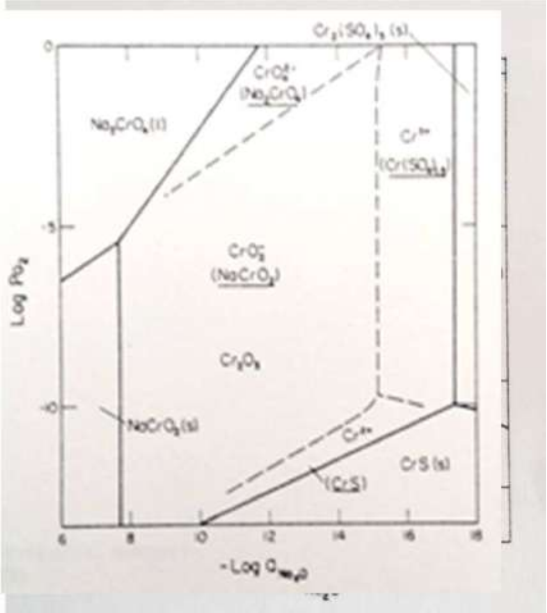
  => les solutés et complexes sont inclus dans le réseau et deviennent indiscernables du solvant

Probablement illusoire =>



$Na_2SO_4 \Leftrightarrow Na_2O(l) + SO_3\ (g) \Rightarrow K_{1200} = 10^{-17}$





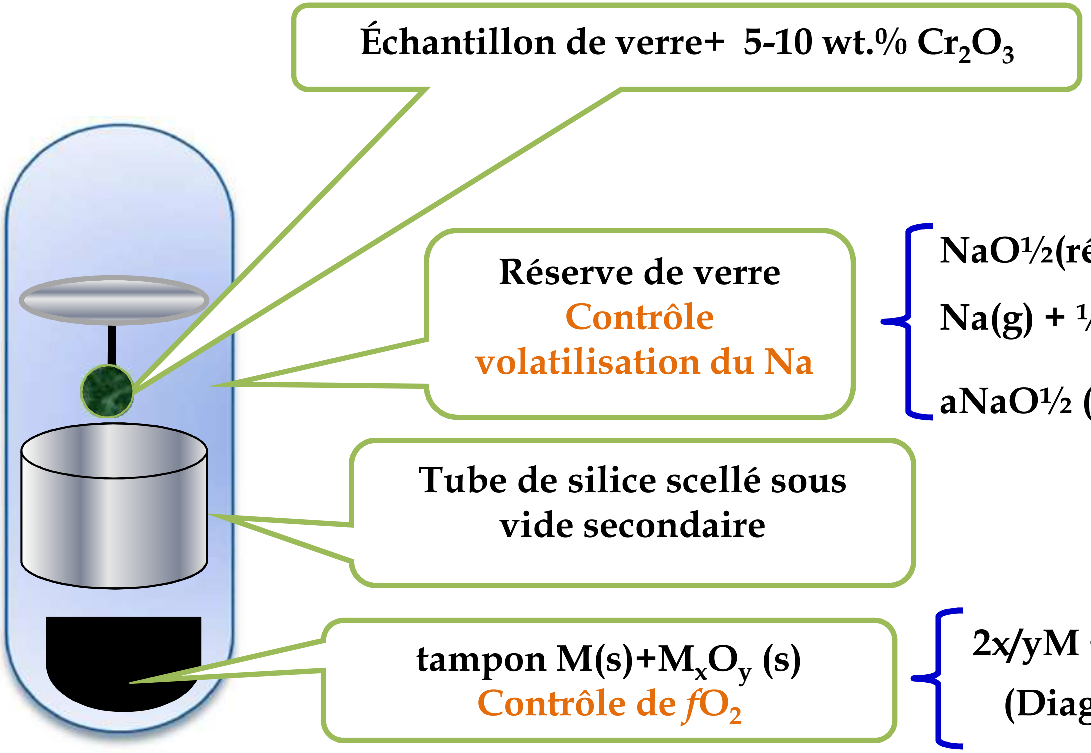
R.A. Rapp et al. Electrchem. Sic. Vol132 10 (1985)

➢ Mesure de la solubilité de Cr_2O_3 : oxyde à cation multivalent

Limite de solubilité fonction
- ✓ température
- ✓ composition du verre
- ✓ fugacité en oxygène

➡ **Mesure solubilité de Cr_2O_3 à l'équilibre**

Montage expérimental



Échantillon de verre+ 5-10 wt.% Cr_2O_3

Réserve de verre
Contrôle volatilisation du Na

Tube de silice scellé sous vide secondaire

tampon M(s)+M_xO_y (s)
Contrôle de fO_2

[6]

$\mathrm{NaO}\frac{1}{2}$(réservoir) $\rightarrow$ Na(g) + $\frac{1}{4}$O2

Na(g) + $\frac{1}{4}$O2 $\rightarrow$ $\mathrm{NaO}\frac{1}{2}$ (échantillon)

$a\mathrm{NaO}\frac{1}{2}$ (réservoir) = $a\mathrm{NaO}\frac{1}{2}$(sample)

$2x/yM + O_2 = 2/yM_xO_y$
(Diagramme Ellingham)

➢ Mesure de la solubilité de Cr_2O_3 : oxyde à cation multivalent

Limite de solubilité fonction
- ✓ température
- ✓ composition du verre
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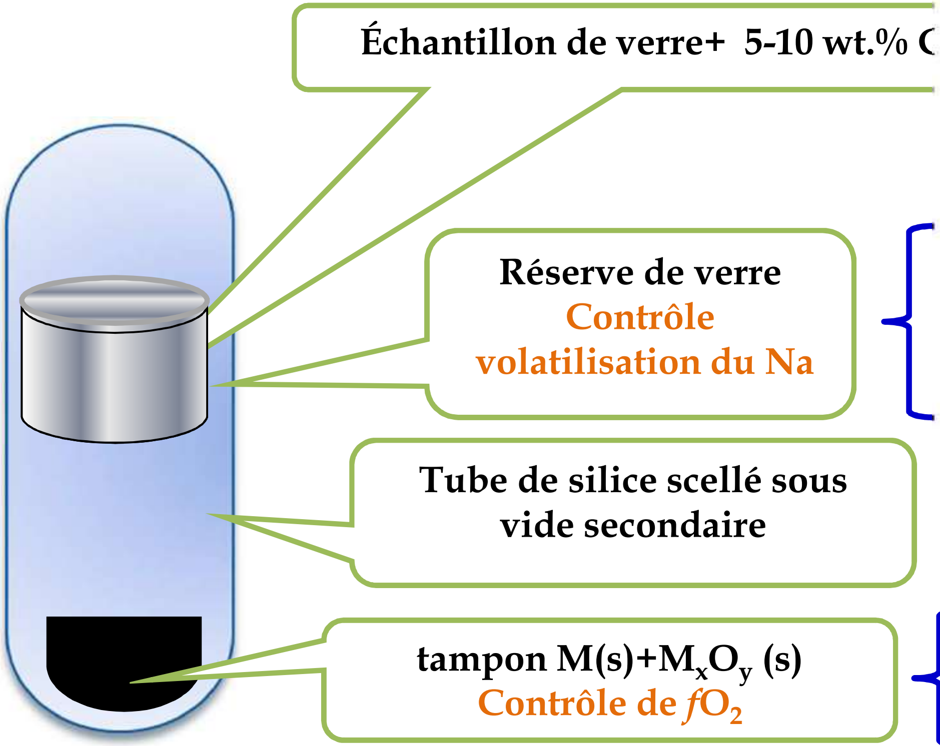
➡ **Mesure solubilité de Cr_2O_3 à l'équilibre**

Montage expérimental

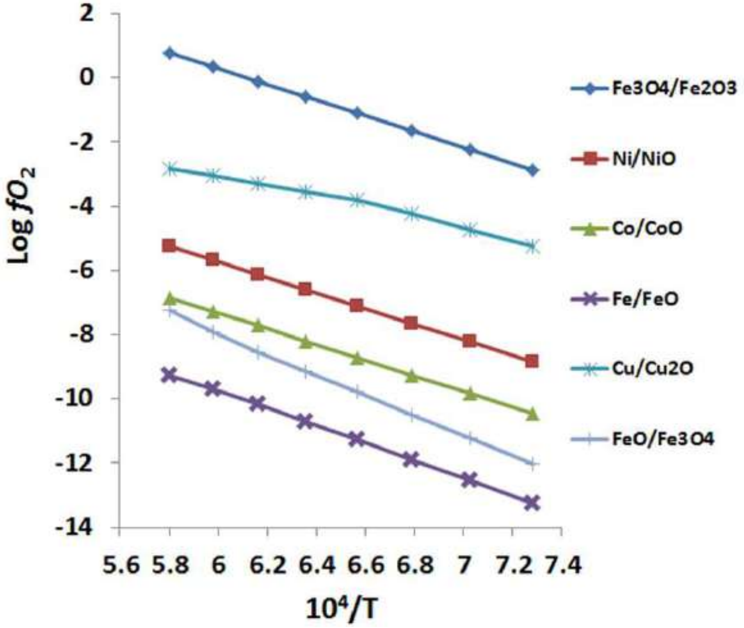


Échantillon de verre+ 5-10 wt.% C

Réserve de verre
Contrôle volatilisation du Na

Tube de silice scellé sous vide secondaire

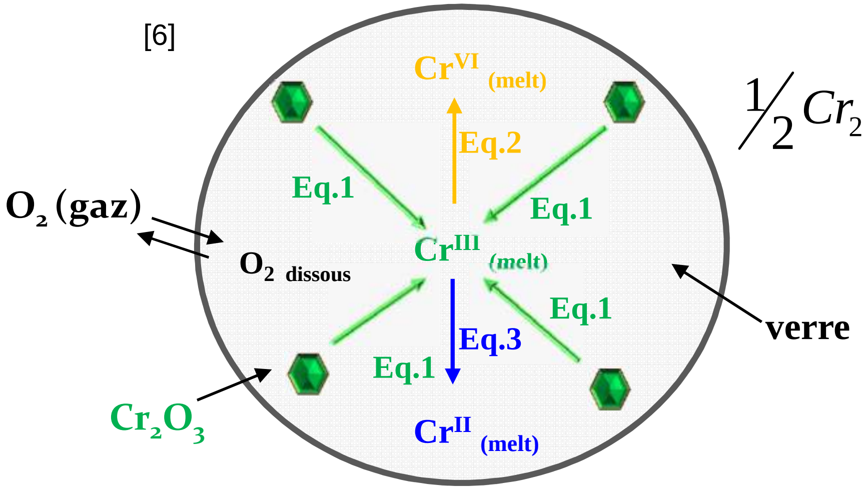
tampon $M(s)+M_xO_y$ (s)
Contrôle de fO_2



$2x/yM + O_2 = 2/yM_xO_y$
(Diagramme Ellingham)

Physicochimie de Cr_2O_3 dans les verres fondus

[6]



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

Eq.1 : Réaction acide/base

$$Cr^{III}O_x^{(2x-3)-}(melt) + \tfrac{3}{4}\,O_2(gas) \rightarrow Cr^{VI}O_z^{(2z-6)-}(melt) + (x-z+\tfrac{3}{2})O^{2-}(melt)$$

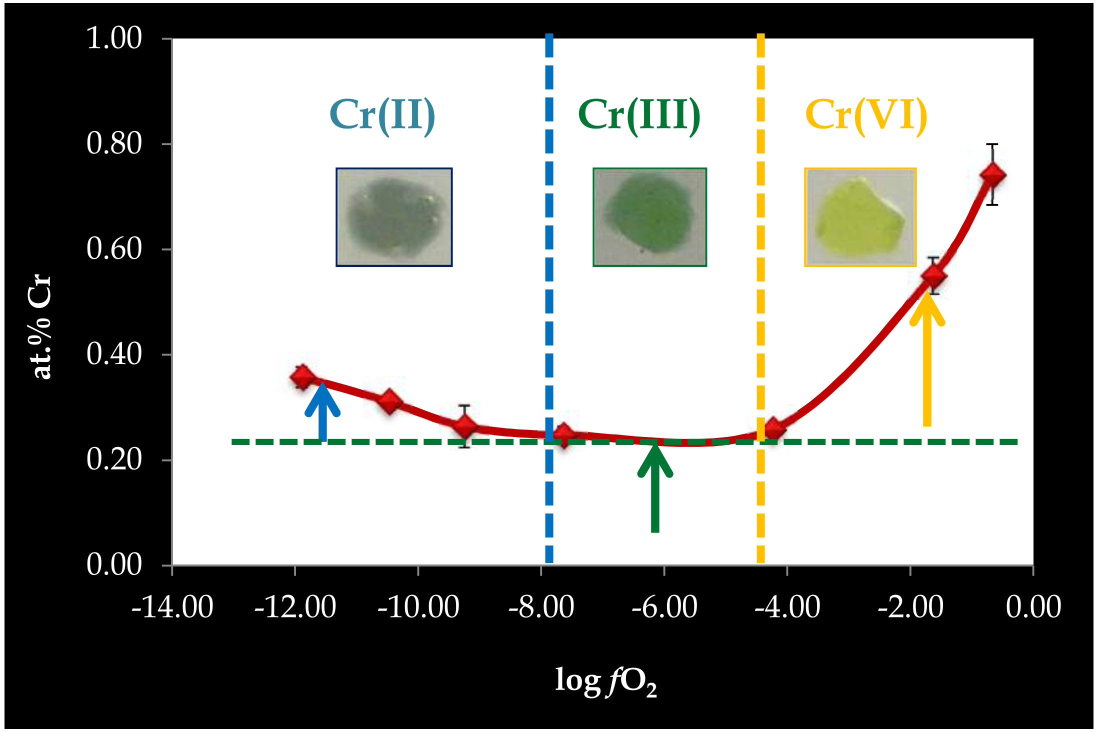
Eq.2 : Réaction d'oxydation

$$Cr^{III}O_x^{(2x-3)-}(melt) + (y-x+\tfrac{1}{2})O^{2-}(melt) \rightarrow Cr^{II}O_y^{(2y-2)-} + \tfrac{1}{4}\,O_2(gas)$$

Eq.3 : Réaction de réduction

Solubilité de Cr_2O_3 dans NC3S (T = 1200°C)

[7]

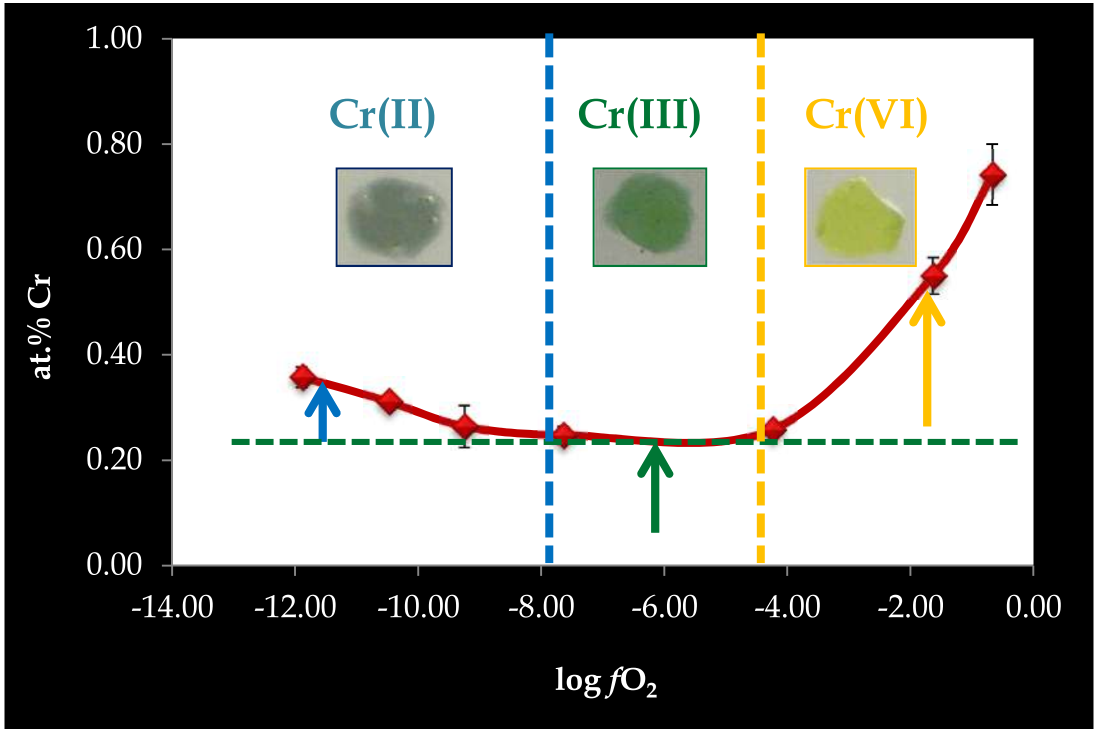


A l'équilibre, T=cte et fO_2 quelconque, la teneur en Cr^{III} est considérée constante tant que Cr_2O_3 solide persiste : saturation

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

$$\boxed{Cr_{(total)} = Cr^{II} + Cr^{III} + Cr^{VI}\ \text{(Analyses microsonde)}}$$

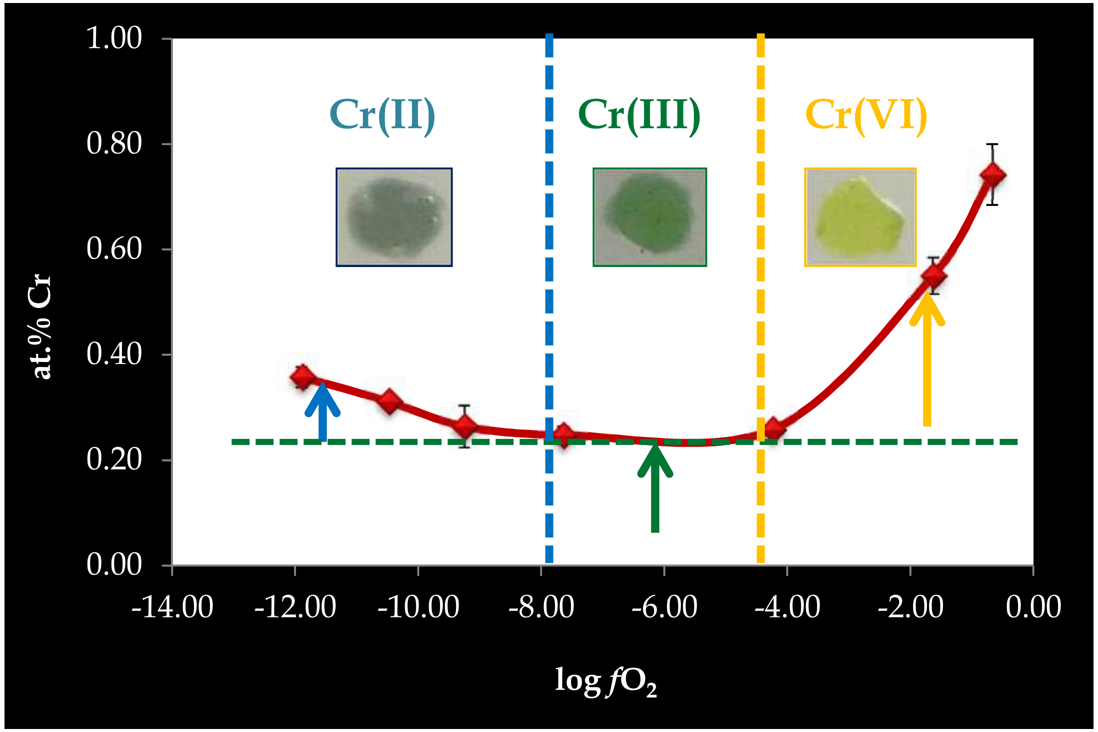
Solubilité de Cr_2O_3 dans NC3S (T = 1200°C)



[7]

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

Solubilité de Cr_2O_3 dans NC3S (T = 1200°C)

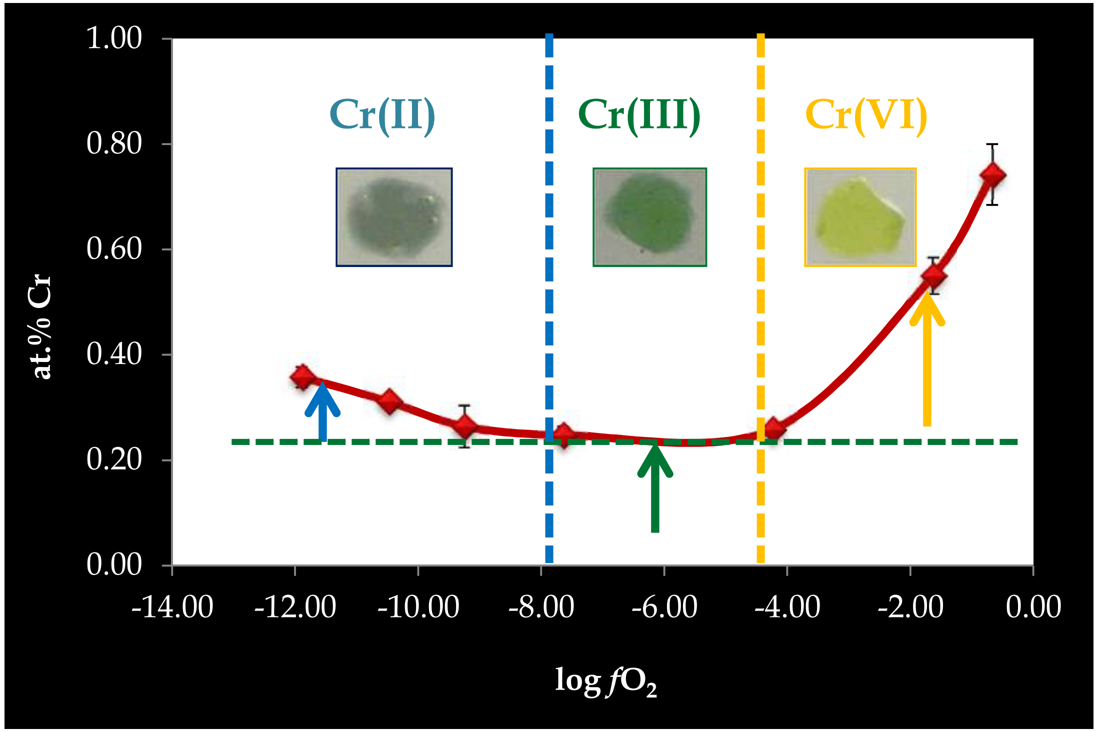


[7]

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

Solubilité de Cr_2O_3 dans NC3S (T = 1200°C)

[7]



A l'équilibre, T=cte et fO_2 quelconque, la teneur en Cr^{III} est considérée constante tant que Cr_2O_3 solide persiste : saturation

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

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

$Cr_{(total)} = Cr^{II} + Cr^{III} + Cr^{VI}$ (Analyses microsonde)

Chimie du chrome dans le verre

Equilibres RédOx associés à des réactions acide/base dans les verres

- **Oxydation ($Cr^{III} \rightarrow Cr^{VI}$)**

$$Cr^{III}O_x^{(2x-3)-} + \frac{3}{4}O_2 = Cr^{VI}O_y^{(2y-6)-} + \left(x - y + \frac{3}{2}\right)O^{2-}$$

$$\boxed{\log\frac{a[CrO_y^{(2y-6)-}]}{a[CrO_x^{(2x-3)-}]}} = +\frac{3}{4}\,\boxed{\log fO_2} + \boxed{\text{Constante}}$$

- **Réduction ($Cr^{III} \rightarrow Cr^{II}$)**

$$Cr^{III}O_x^{(2x-3)-} + \left(z - x + \frac{1}{2}\right)O^{2-} = Cr^{II}O_z^{(2z-2)-} + \frac{1}{4}O_2$$

$$\boxed{\log\frac{a[CrO_z^{(2z-2)-}]}{a[CrO_x^{(2x-3)-}]}} = -\frac{1}{4}\,\boxed{\log fO_2} + \boxed{\text{Constante}}$$

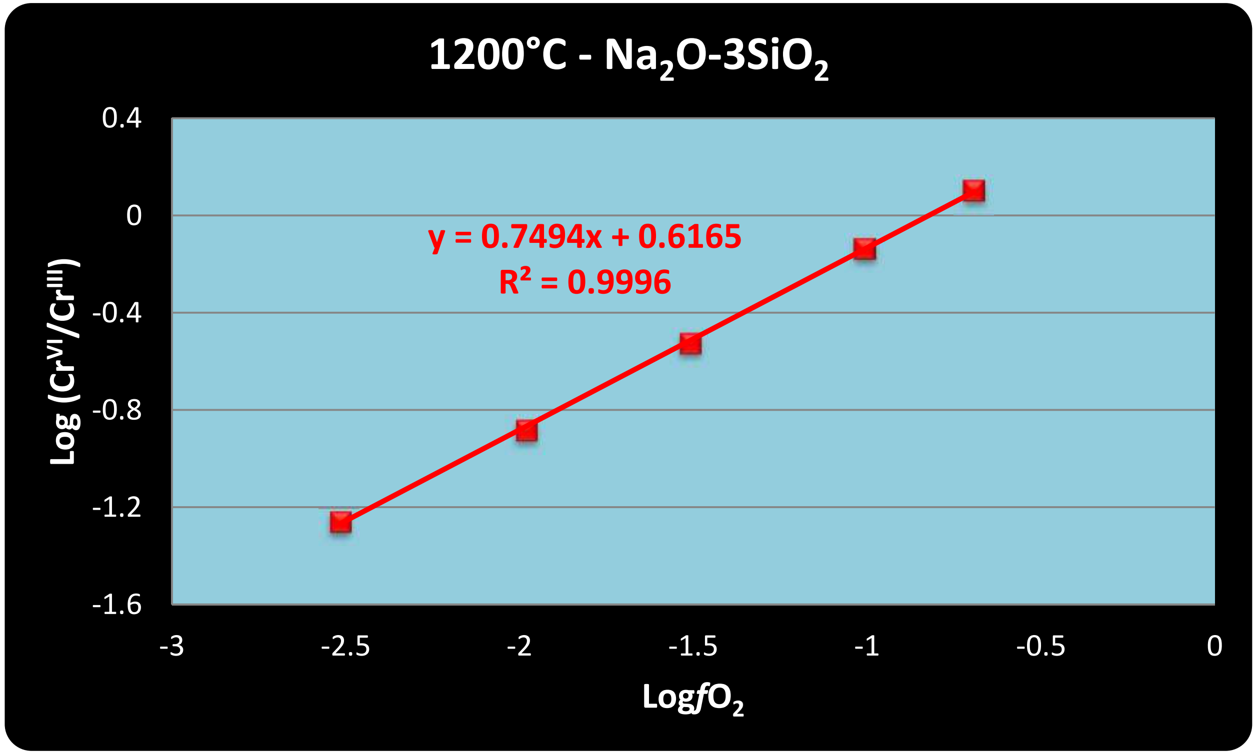
Chimie du chrome dans le verre

$\log(Cr^{VI}/Cr^{III})$ est tracé en fonction de $\log fO_2$

$$\log\frac{[CrO_y^{(2y-6)-}]}{[CrO_x^{(2x-3)-}]} = +\frac{3}{4}\log fO_2 + A_{ox}$$

$$\boxed{A_{ox} = \left(y - x - \frac{3}{2}\right)\log a[O^{2-}] + \log K_{Ox}}$$

[7]

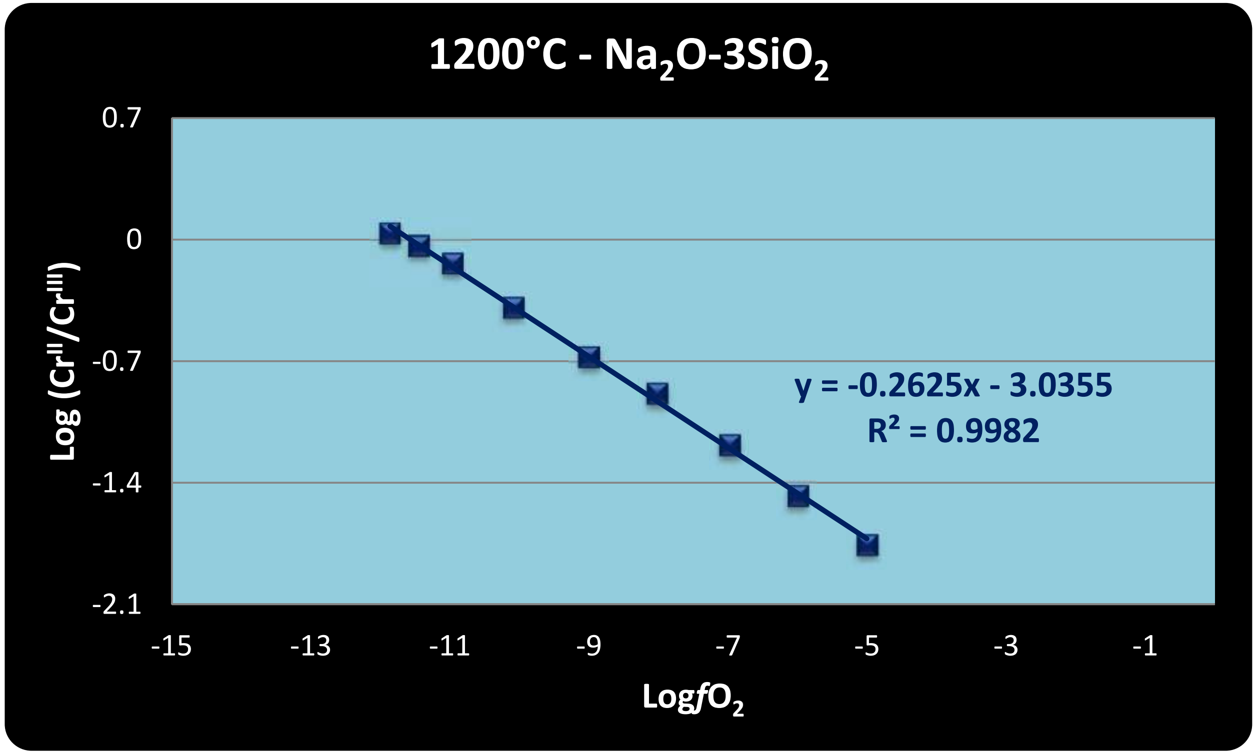


Chimie du chrome dans le verre

$\log(Cr^{II}/Cr^{III})$ est tracé en fonction de $\log fO_2$

$$\log\frac{[CrO_z^{(2z-2)-}]}{[CrO_x^{(2x-3)-}]} = \boxed{-\frac{1}{4}}\log fO_2 + A_{red}$$

$$\boxed{A_{red} = \left(z - x + \frac{1}{2}\right)\log a[O^{2-}] + \log K_{Red}}$$



[7]

Influence de la basicité sur la solubilité de Cr_2O_3

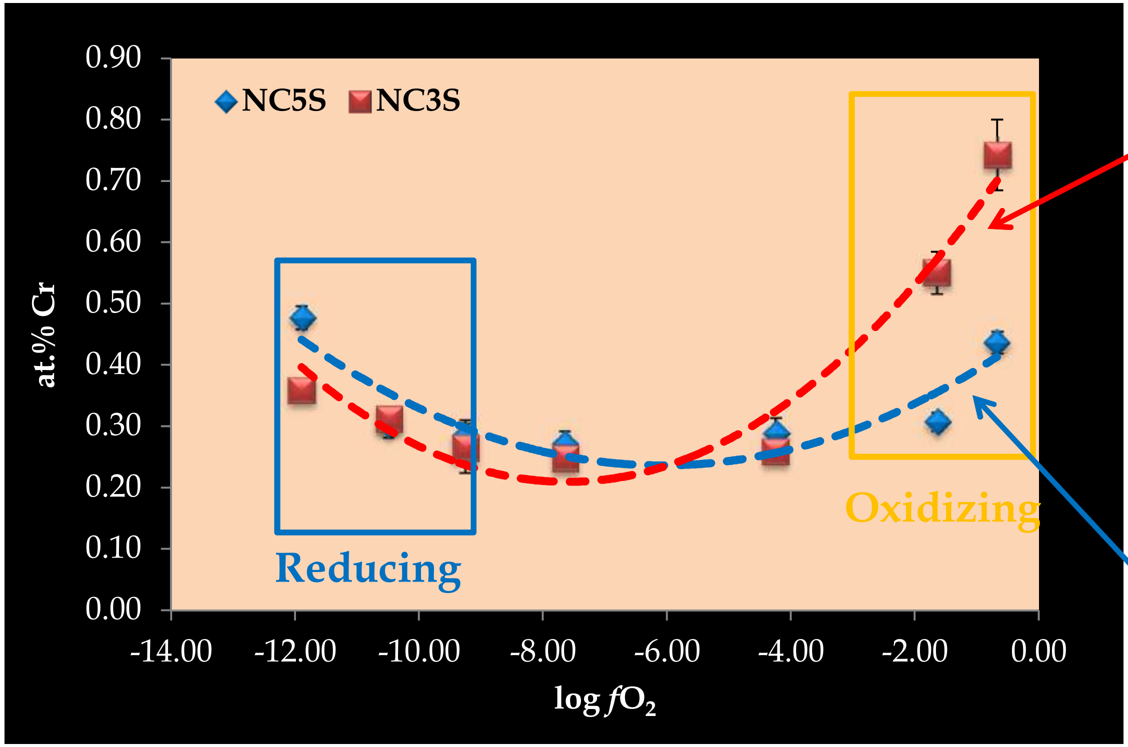
La solubilité de Cr dans NC3S et dans NC5S à T = 1200°C

Cr^{III} + Cr^{II}

-Cr^{II} is less stabilized in more basic melt

Cr solubility decreases with increasing basicity

[6]



Higher basicity

Cr^{III} + Cr^{VI}

-Cr^{VI} is stabilized in more basic melt

Cr solubility increases with increasing basicity

Lower basicity

L'augmentation de basicité favorise la forme la plus oxydée de Cr

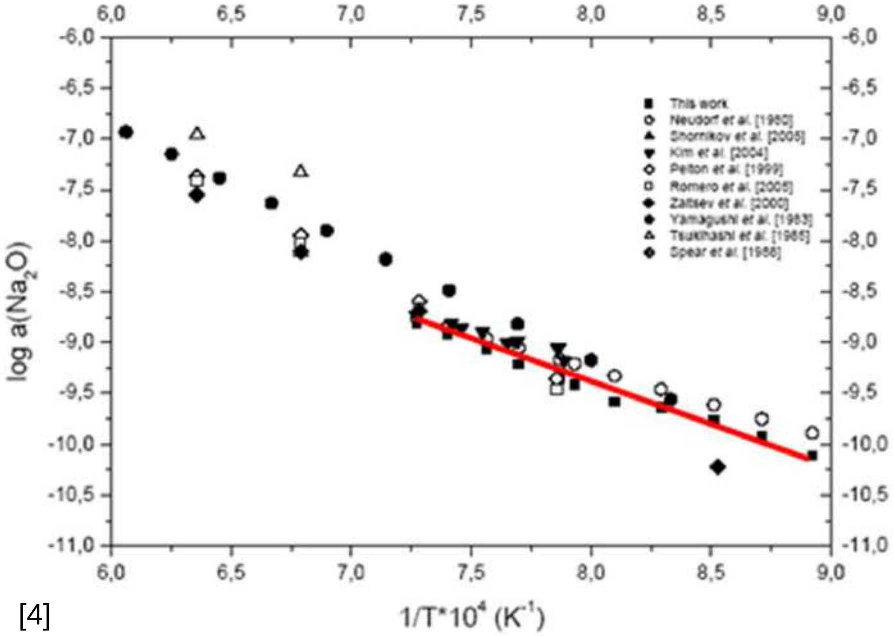
➢ Experimental device for EMF measurement of a(Na_2O)

At low T< 1000°C
(Neudorf *et al.*)

Refrence ½ Cell

Measurement ½ Cell

Platine	$O_{2(g)}$, Na_2O Na_2O-$yWO_{3(liq)}$ Or Na_2O-$yMoO_{3(liq)}$	Na^+ Alumine β	Na_2O, $O_{2(g)}$ xNa_2O-$ySiO_{2(liq)}$	Platine



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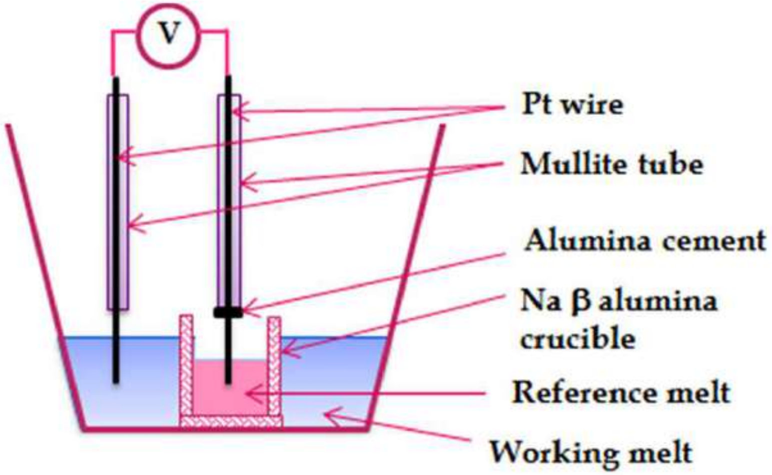
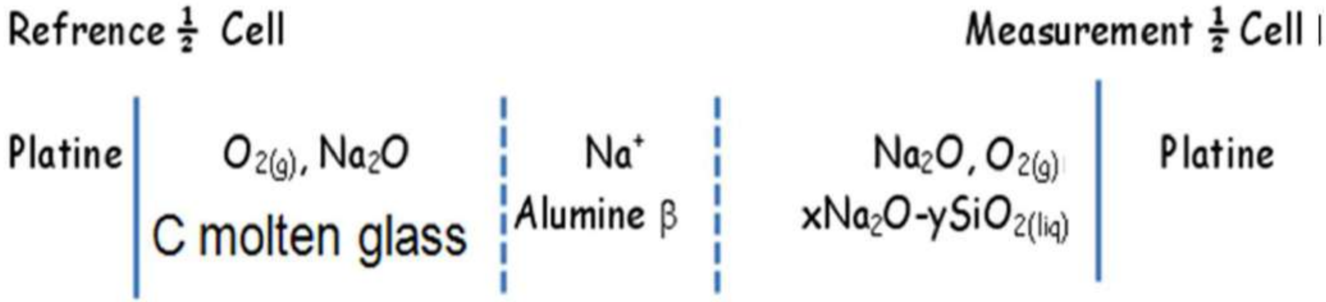


Experimental device for EMF measurement of a(Na_2O)

For high T> 1200°C
(Abdelouab *et al.*)



Refrence ½ Cell

Measurement ½ Cell

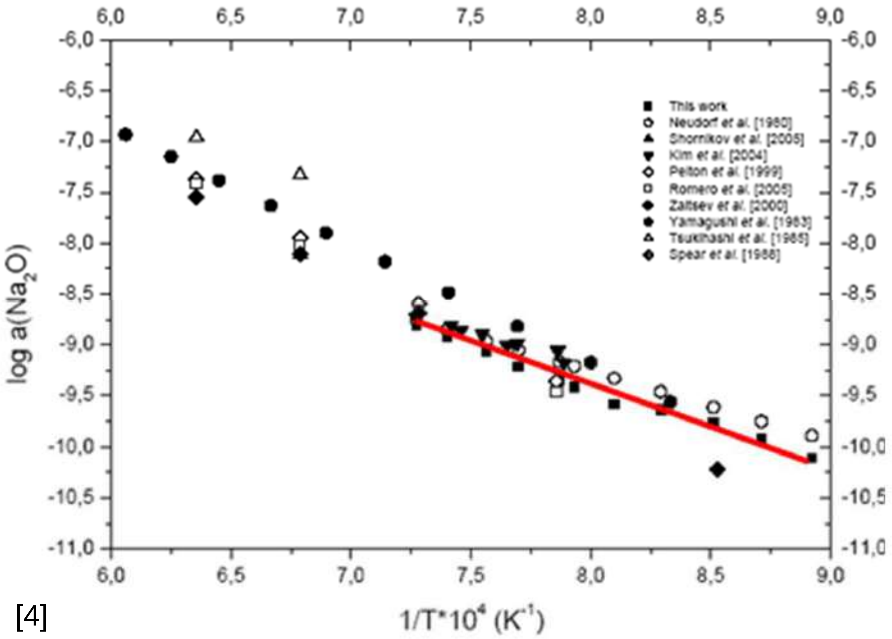
Platine

$O_{2(g)}$, Na_2O
C molten glass

Na^+
Alumine β

Na_2O, $O_{2(g)}$
$xNa_2O\text{-}ySiO_{2(liq)}$

Platine



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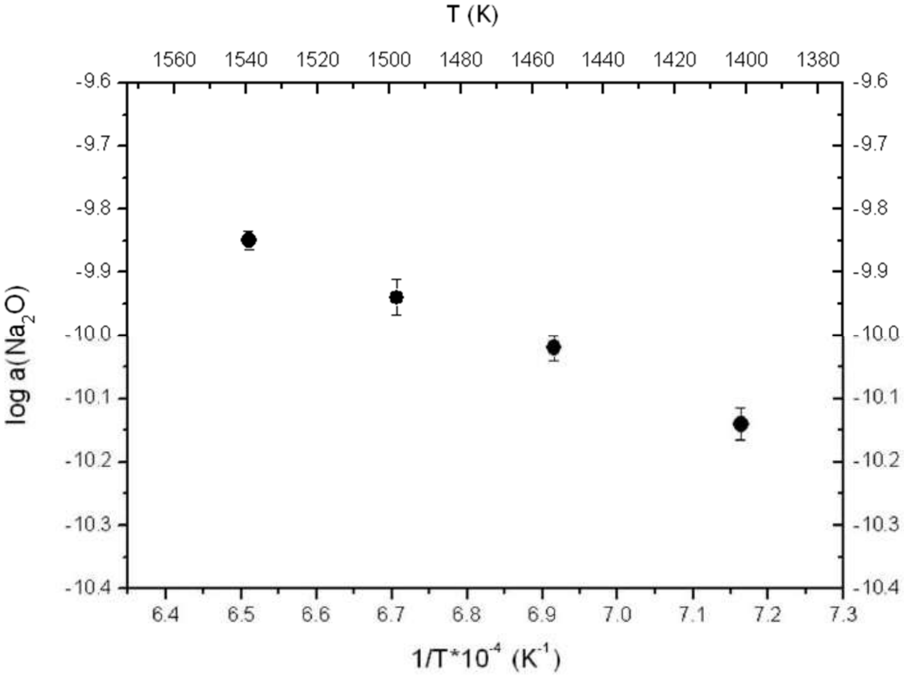


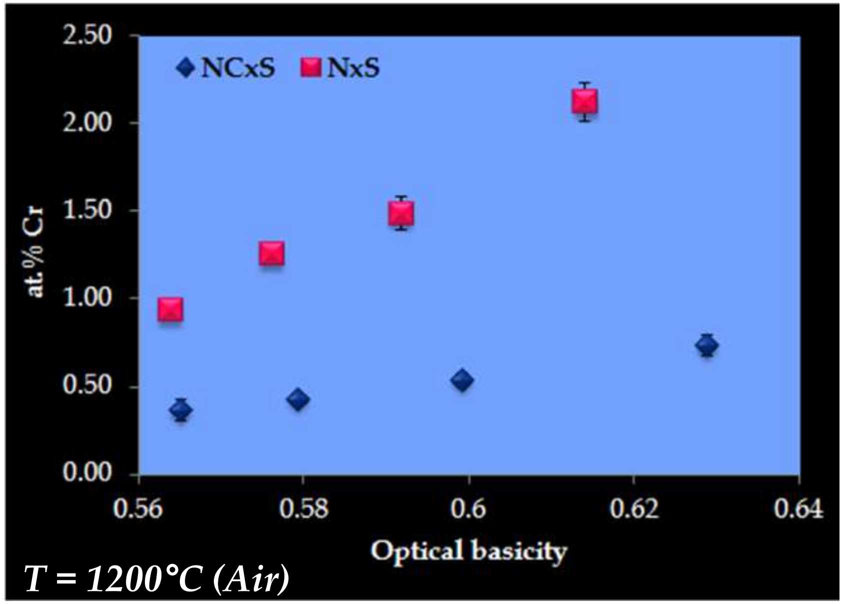
Verre C : 65,2 SiO_2 3,3Al_2O_3 4,1B_2O_3 7,3CaO 3MgO 15,7Na_2O 1,25K_2O 0,15Fe_2O_3

Comparison of Cr solubility in binary (NxS) and ternary (NCxS) melts

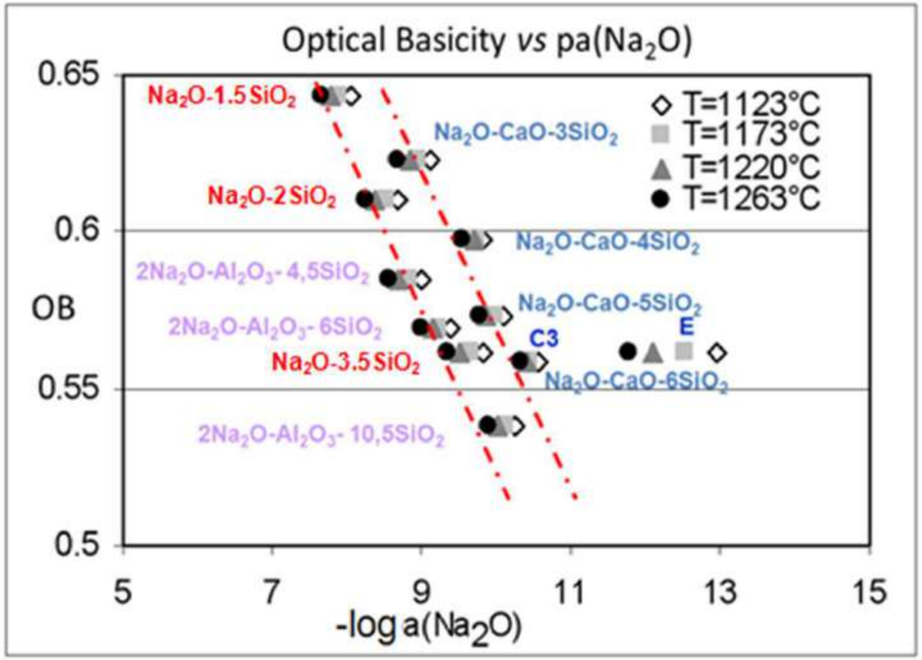
Na_2O-xSiO_2 (x = 2, 2.5, 3 and 3.5) *(Khedim et al. 2008)*

and

Na_2O-CaO-xSiO_2 (x = 3, 4, 5 and 6) *(Katrina et al. 2013)*



[18]



For the same optical basicity (Λ) Cr solubility is greater in (NxS)

⇒ a(Na_2O) determines the Cr solubility

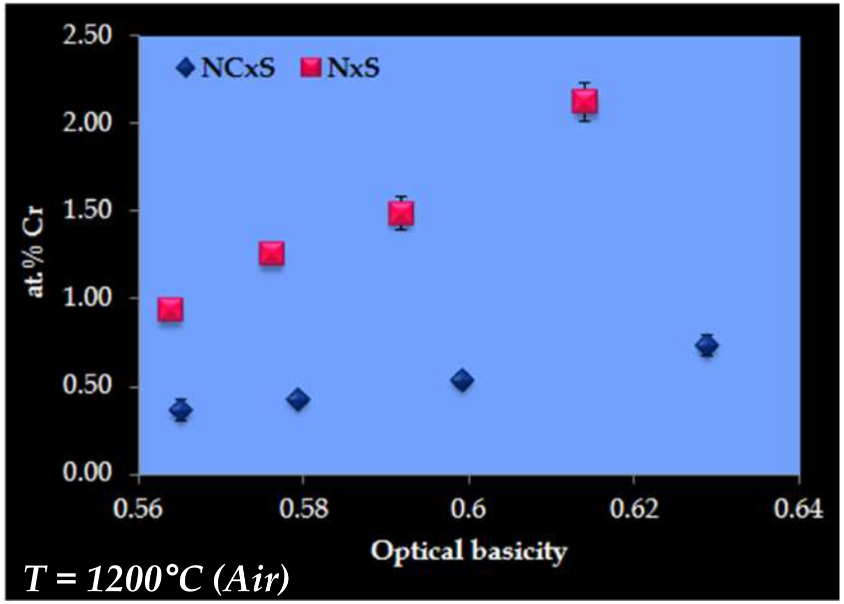
⇒ a(Na_2O) determines the « fluxing » capability of melt regarding Cr_2O_3 layer

Comparison of Cr solubility in binary (NxS) and ternary (NCxS) melts

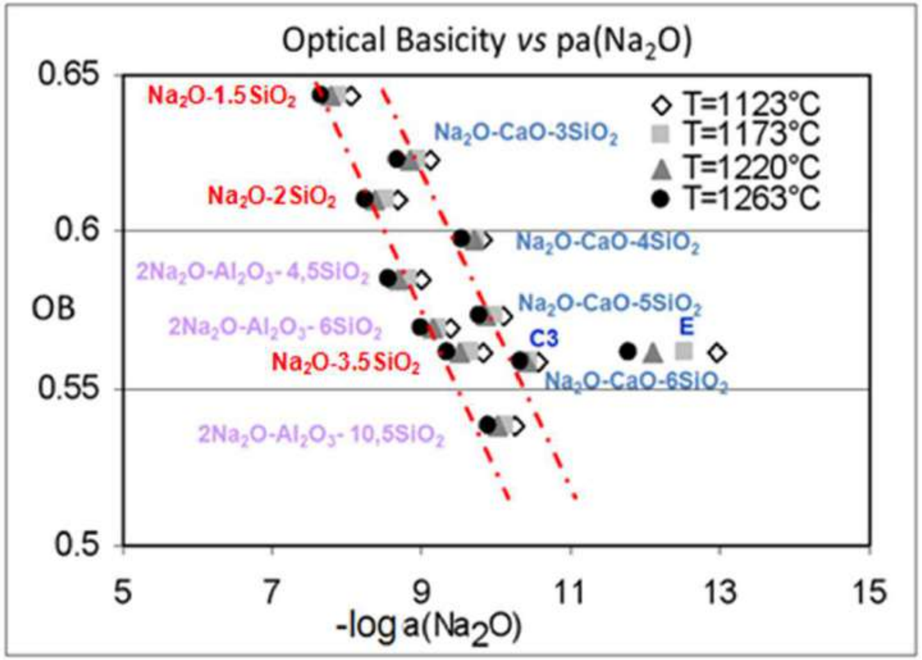
Na_2O-xSiO_2 (x = 2, 2.5, 3 and 3.5) *(Khedim et al. 2008)*

and

Na_2O-CaO-xSiO_2 (x = 3, 4, 5 and 6) *(Katrina et al. 2013)*



T = 1200°C (Air)



[18]

- ➢ **The optical basicity (Λ) is not the relevant criterion for Corrosion Prediction => "O^{2-}" sensor useful**

- Comportement des alliages métalliques dans les silicates fondus

Oxydation électrochimique

A. Tools for predicting the chemical reactivity

➢ Physico-chimical characteristics of molten glasses

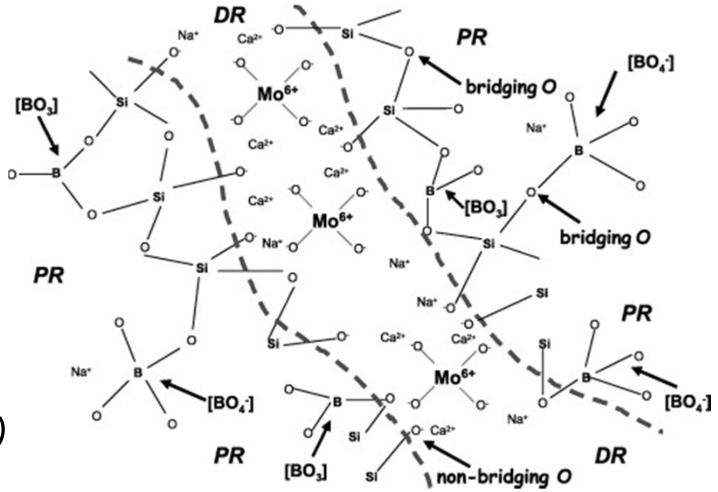
Acido-basic properties allowing the exchange of O^{2-} :

$Na_4SiO_4 \Leftrightarrow 4\ Na^+ + 2O^{2-} + SiO_2$ $K_T^{ionisation}$?

$K_{298}^{H_2O} = 10^{-14}$

Oxo-complexing properties: formation of octa-, tétrahedra

Hydrine$Al(H_2O)_6^{3+}$



D. Caurant et al (2010)

Like water, molten glasses are electrolytic liquids having solvating properties

Oxydo-reducing properties:

$SiO_4^{4-} \Leftrightarrow SiO_2 + O_2(g) + 4e-$ ${}_1E°$?

$SiO_4^{4-} + 4e- \Leftrightarrow Si + 4\ O^{2-}$ ${}_2E°$?

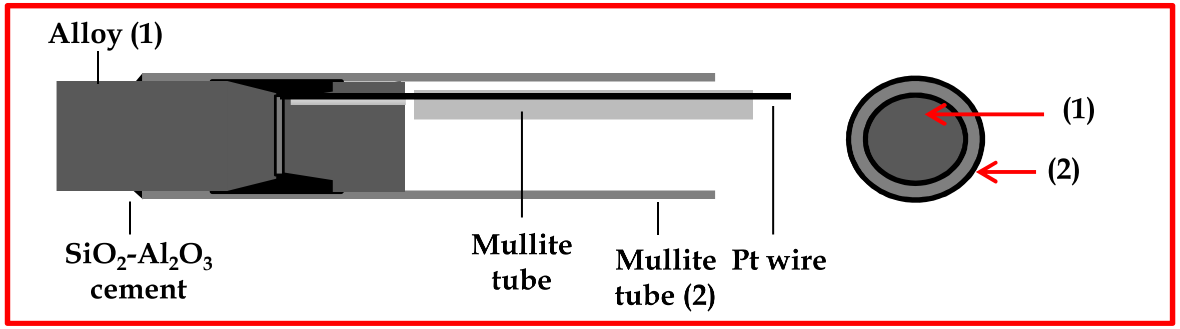
${}_1E°_{O2/H2O}$ =1.23V/ENH

${}_2E°_{H2O/H2}$ =0V/ENH

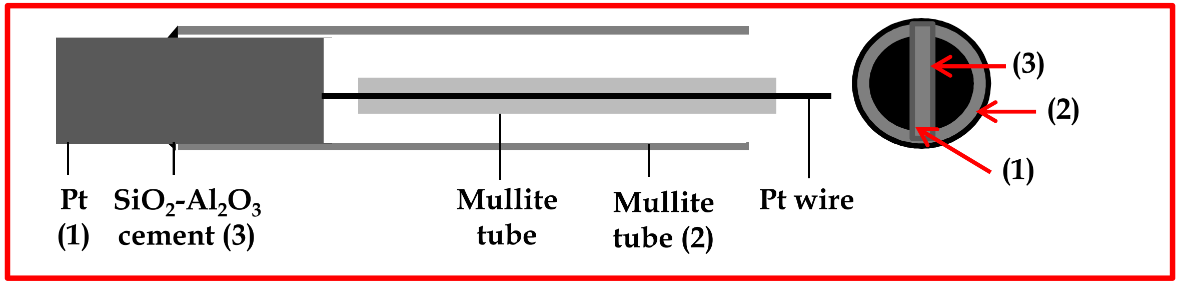
Corrosion of alloys by molten glass

Electrochemical measurements

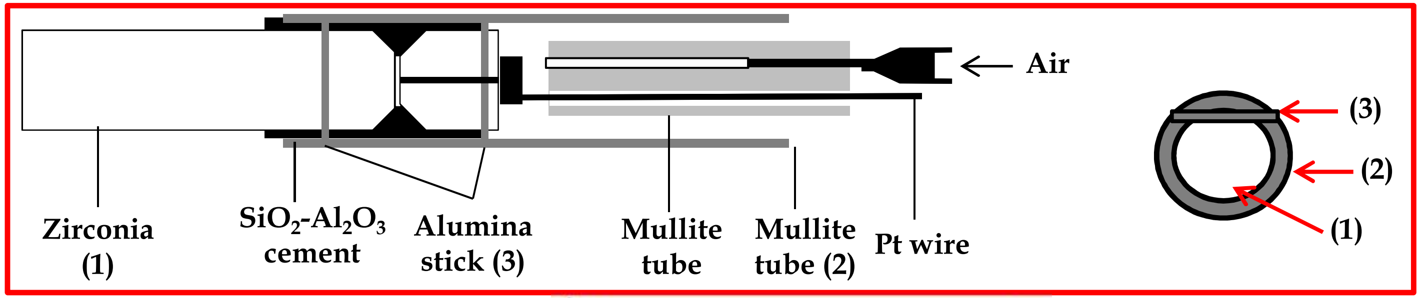
Electrodes:



Working electrode



Counter electrode



Yttria stabilized zirconia reference electrode (YSZ)

$$1/_2 O_2 + 2e^- \leftrightarrow O^{2-}$$

Corrosion of alloys by molten glass

Electrochemical measurements

- Polarization resistance and free potential measurements at high temperature.

Furnace

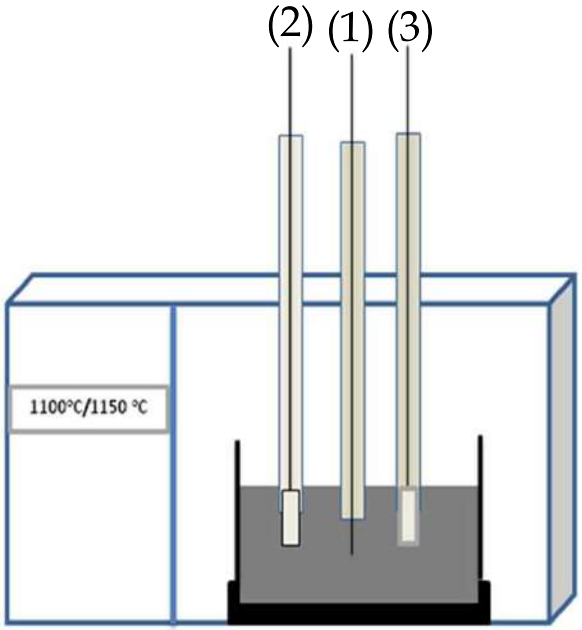
Acquisition system

3 specific electrodes:

1) Working electrode
   (Pt wire and alloy rods)

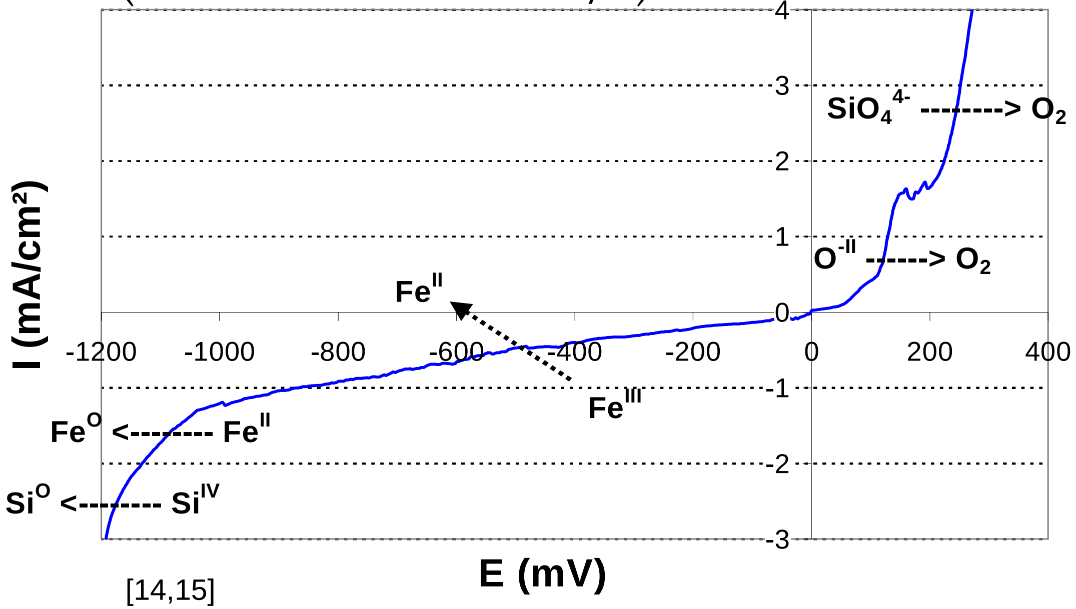
2) Counter electrode (Pt plate)

3) Reference electrode
   (Yttria stabilized zirconia)



➢ Eletroactivity domain of the molten glass

(scan rate v = 1.66 mV/s)



[14,15]

✓ Pertinent information

- **Extention** of the domain:
  from -1.2 V to 0.2 V at 1050°C
- **Cathodic** limit:

$$SiO_4^{4-} + 4\,e^- \rightarrow Si + 4\,O^{2-}$$

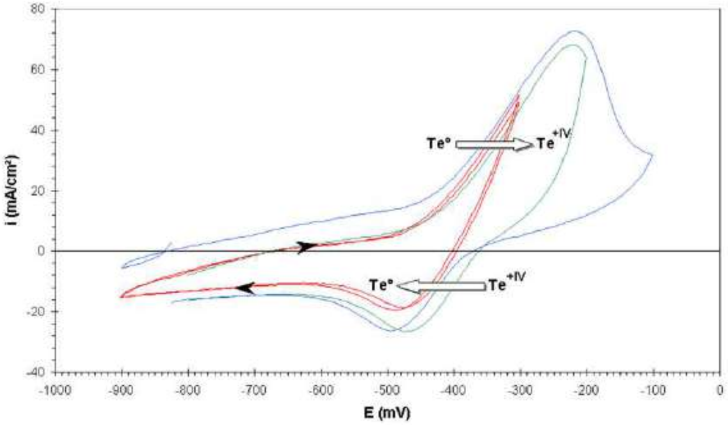
- **Anodic** limit:

$$SiO_4^{4-} \rightarrow SiO_3^{2-} + \tfrac{1}{2}\,O_{2\,(g)} + 2\,e^-$$

✓ NB : Fe was often present as impurity into industrial glass melt

➢Study of Te^{+IV}/Te by cyclic voltammetry in CE57 molten glass

[14]

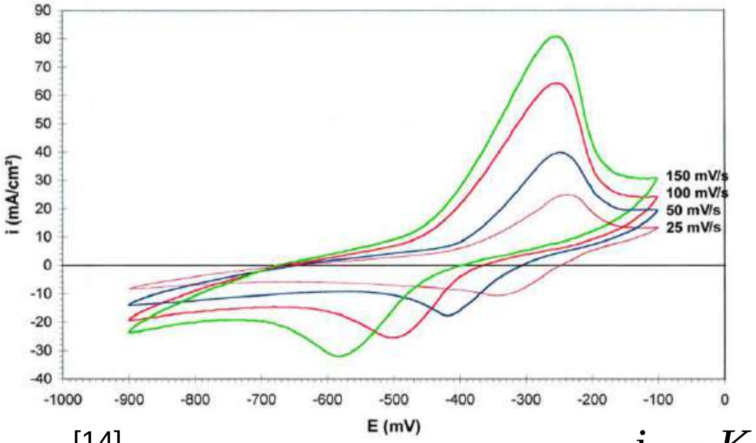


✓ **Thermodynamic features**

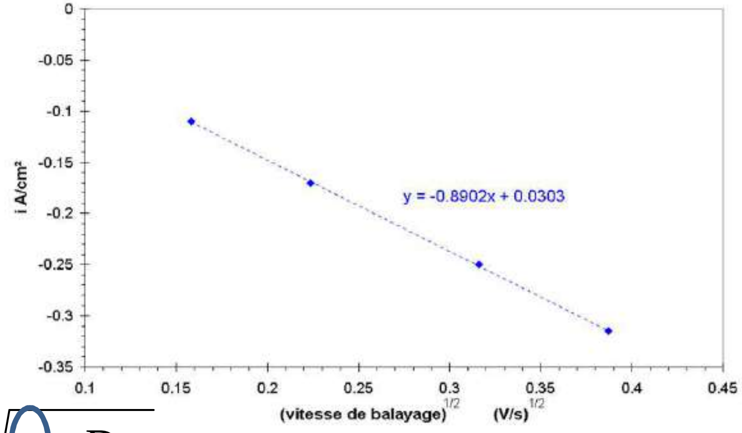
- **Single oxidation state** Te°=> Te $^{+IV}$
- $E_{1/2}^{ox} - E_{1/2}^{red} > 0.34V$ => **irreversible process**
- $E_{(Te^{+IV}/Te°)} = -0.33V / E_{ZrO2}$

The oxidizing capability of Te^{+IV} is close to that of Fe^{+III}

✓ **Kinetic features:** the **diffusion coefficient** of Te^{+IV} can be deduced from the Randles-Sevcic equation : $D = 2.5x10^{-7}\ cm^2.s^{-1}$.

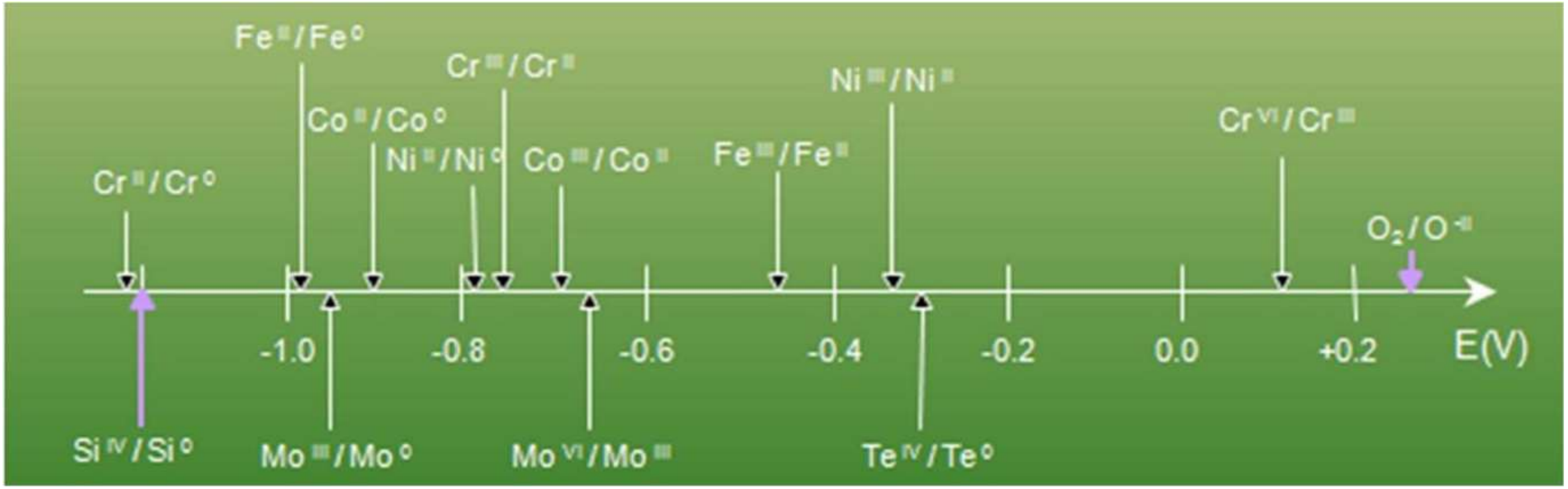


[14]



$$i_p = K.n.\Im.C_o^{Ox}.\sqrt{\frac{n.\Im}{R.T}}.\sqrt{v.\pi.D_{Ox}}$$

➢ Determination of a scale of “formal” potentials



[14,15]

1000°C < T < 1400°C

Corroborate data obtained by other researchers: Claes, Pinet, Schreiber, Rüssel,….

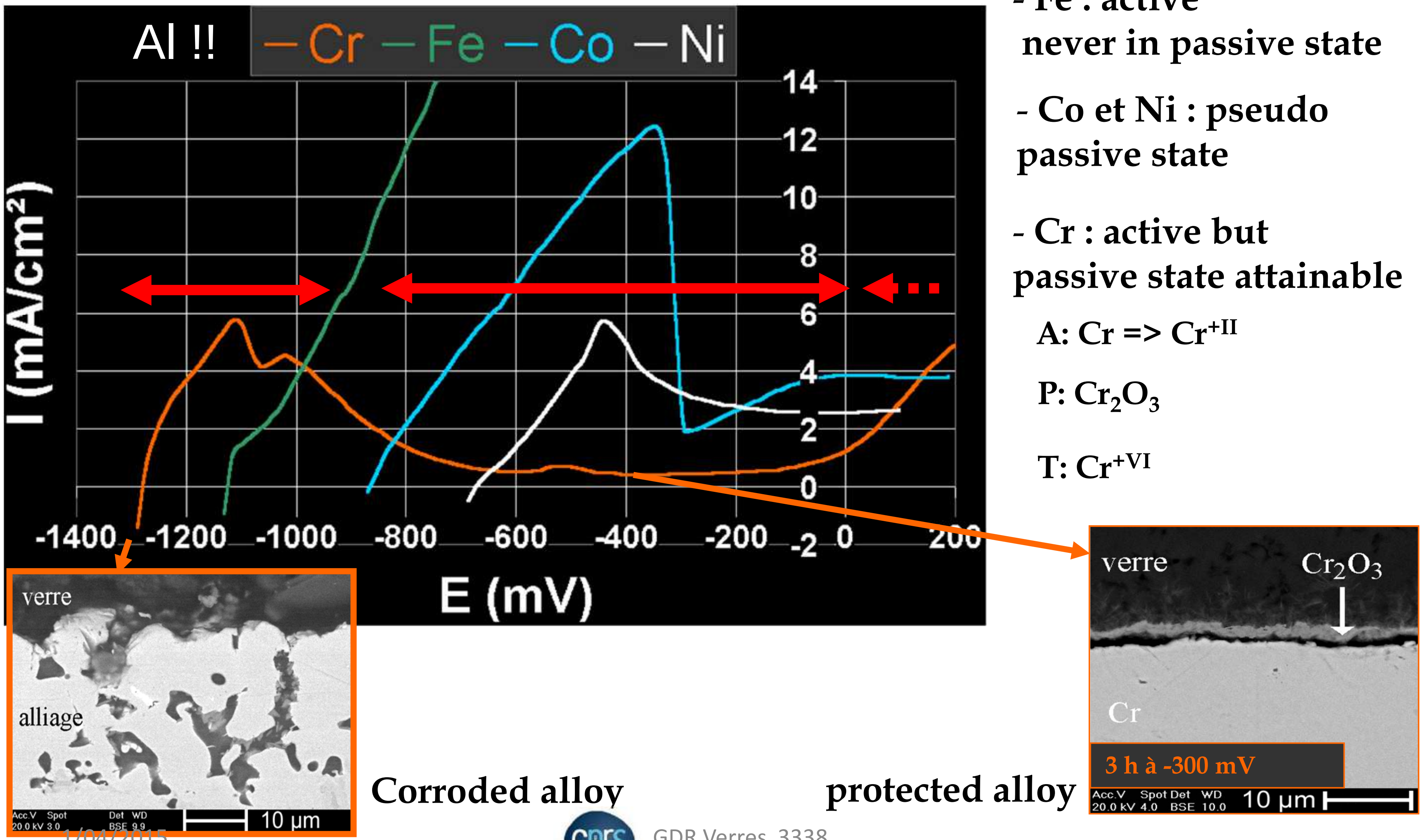
- ✓ Allows predicting the chemical reactions ($\Delta G° = -nF\ E°$)

  => Giving access to corrosion mechanism

B. Kinetic parameters of the corrosion

➢ Behavior of pure metals : dynamic polarisation at 1050°C

[15]



Corroded alloy

protected alloy

- Fe : active never in passive state

- Co et Ni : pseudo passive state

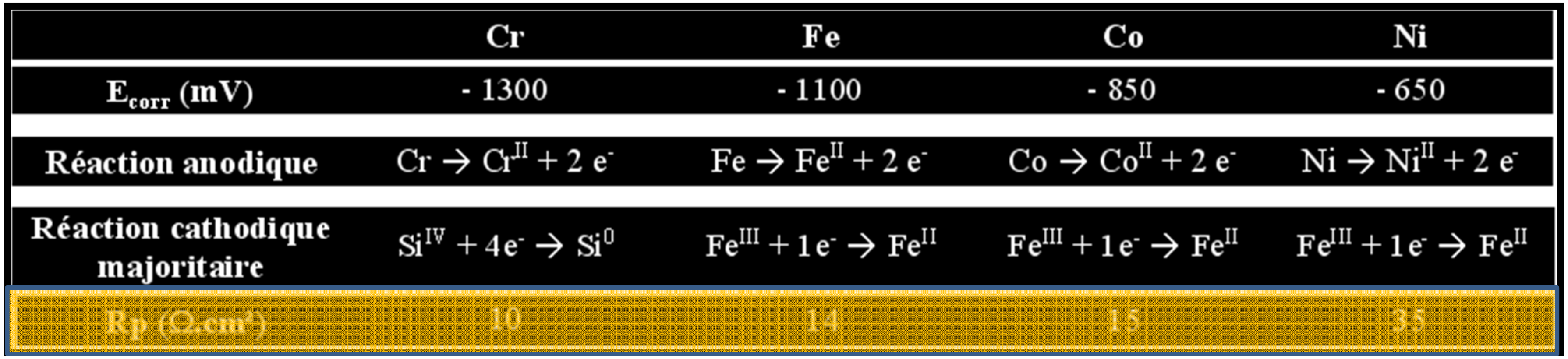
- Cr : active but passive state attainable

A: Cr => Cr^{+II}

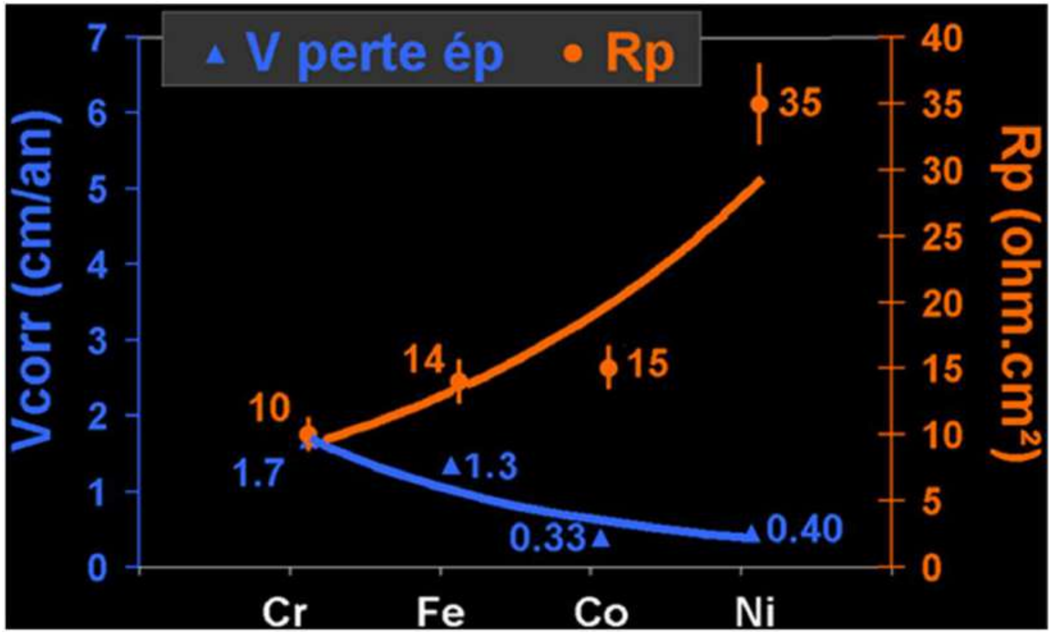
P: Cr_2O_3

T: Cr^{+VI}

[15]

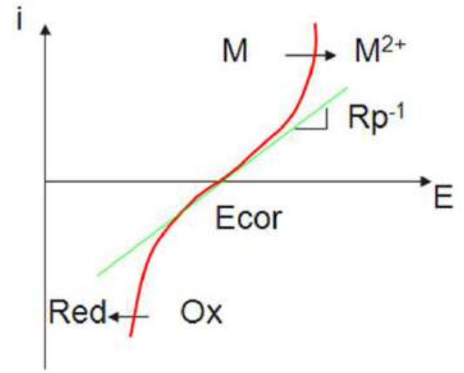


	Cr	Fe	Co	Ni
E_{corr} (mV)	- 1300	- 1100	- 850	- 650
Réaction anodique	$Cr \rightarrow Cr^{II} + 2\,e^{-}$	$Fe \rightarrow Fe^{II} + 2\,e^{-}$	$Co \rightarrow Co^{II} + 2\,e^{-}$	$Ni \rightarrow Ni^{II} + 2\,e^{-}$
Réaction cathodique majoritaire	$Si^{IV} + 4e^{-} \rightarrow Si^{0}$	$Fe^{III} + 1e^{-} \rightarrow Fe^{II}$	$Fe^{III} + 1e^{-} \rightarrow Fe^{II}$	$Fe^{III} + 1e^{-} \rightarrow Fe^{II}$
Rp (Ω.cm²)	10	14	15	35



[15]

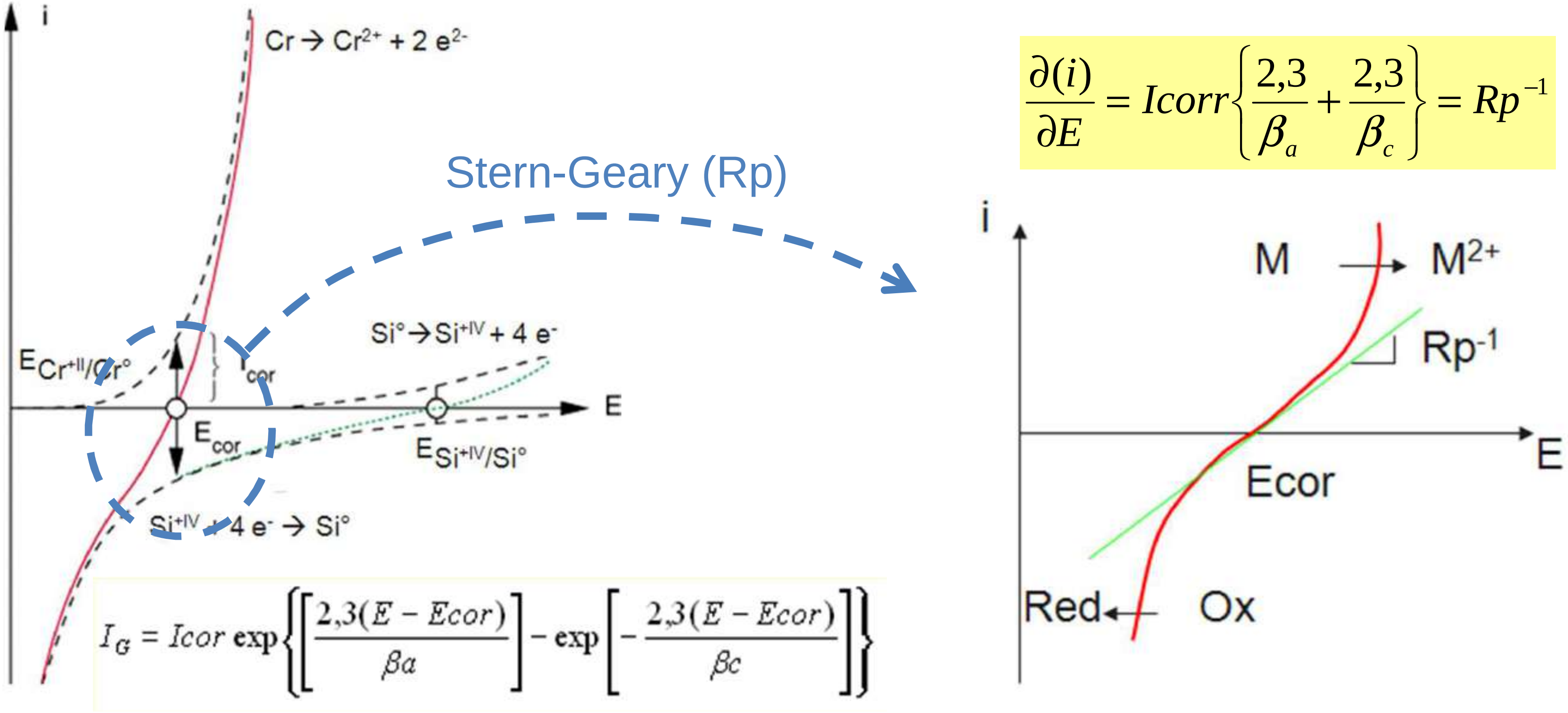
- ✓ Polarisation resistance



- ✓ Metallographic measurement of the corrosion rate

Rp is an indicator of the corrosion rate

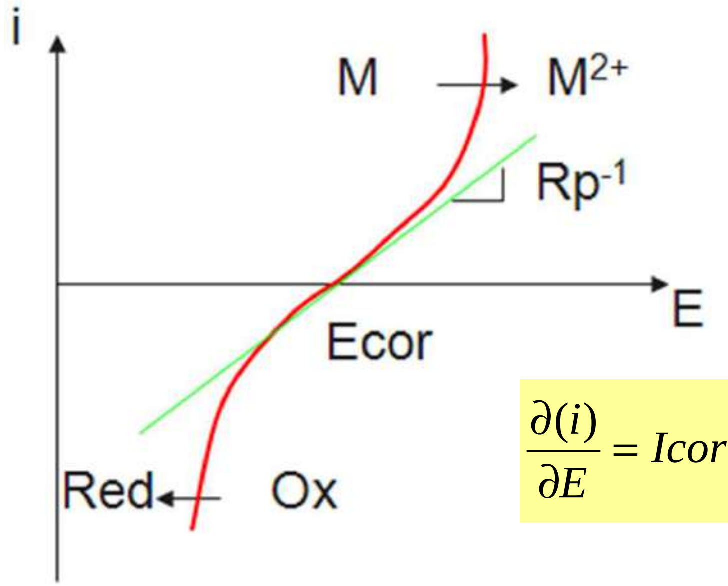
➢ Evaluation of the metal recession ⬄Corrosion rate



$$I_G = Icor\ \exp\left\{\left[\frac{2{,}3(E - Ecor)}{\beta a}\right] - \exp\left[-\frac{2{,}3(E - Ecor)}{\beta c}\right]\right\}$$

$$\frac{\partial(i)}{\partial E} = Icorr\left\{\frac{2{,}3}{\beta_a} + \frac{2{,}3}{\beta_c}\right\} = Rp^{-1}$$

➢ Corrosion rate deduced from the electrochemical tests: Rp



(2.3RT/αnF) 0<α<1	n=1e	n=2e	n=4e
β_i	0.525	0.262	0.131

- valeurs pour α = 0,5

$$\frac{\partial(i)}{\partial E} = Icorr\left\{\frac{2,3}{\beta_a} + \frac{2,3}{\beta_c}\right\} = Rp^{-1}$$

$$B = \frac{\beta a.\beta c}{2,3(\beta a + \beta c)}$$

$$Icorr = \frac{B}{Rp}$$

$$Icorr \times t = nF\frac{m_{metal}}{M_{metal}}$$

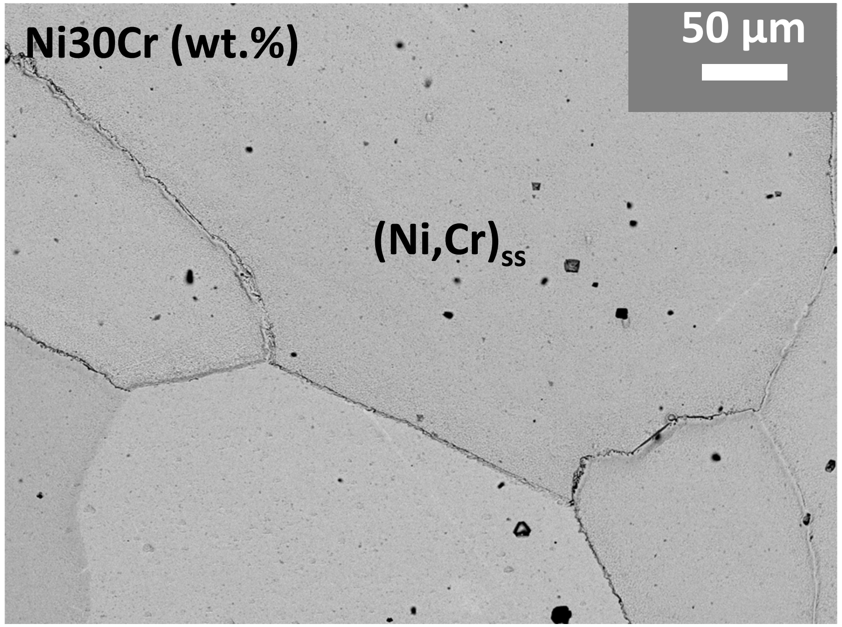
Approximation sur la valeur de βi car les variations du courant en fonction du potentiel ne suivent pas une loi de « Tafel » dans les conditions d'étude

=> Les vitesses de corrosion ne représentent qu'un ordre de grandeur

➢ Corrosion of alloys by molten glass

Alloys preparation

- Induction heating in high frequency furnace



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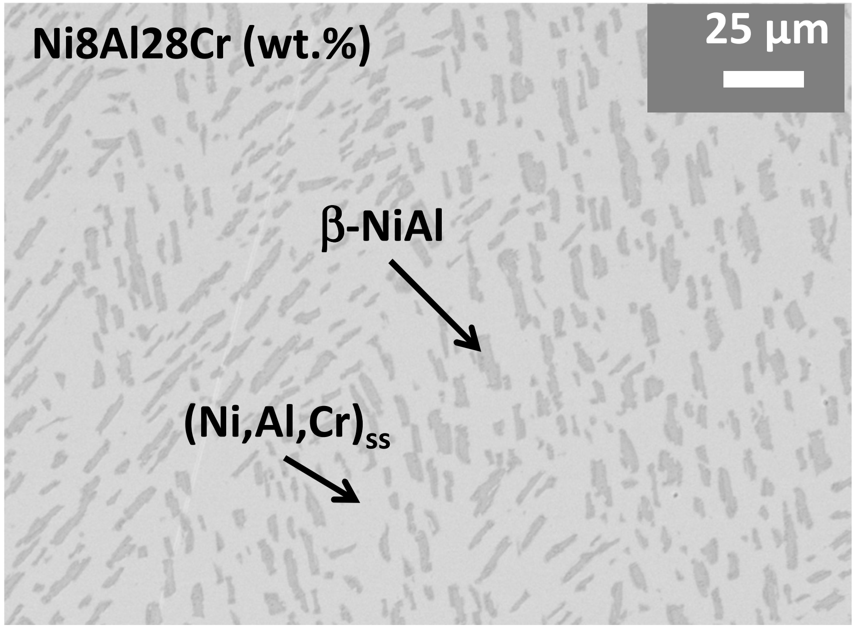
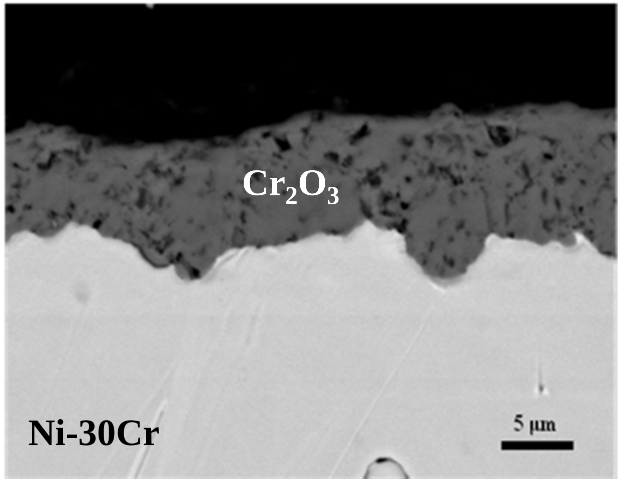


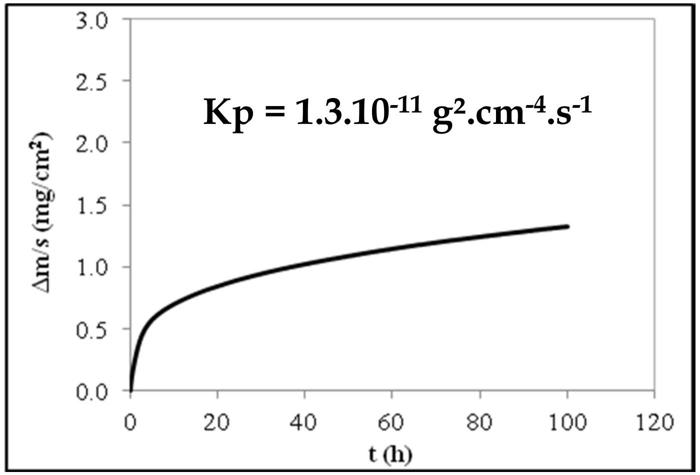
[7]

➢ Corrosion of alloys by molten glass [7]

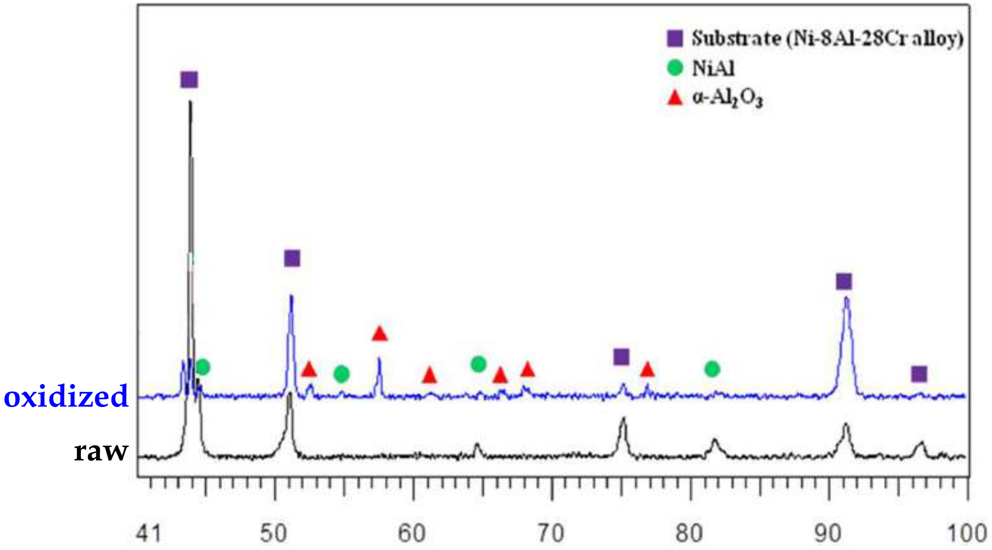
Hot air oxidation of the alloys at 1100°C (100 h)

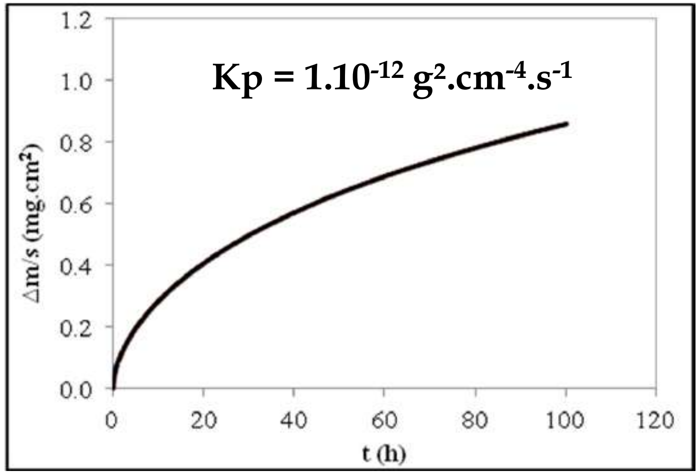
Ni30Cr





Ni8Al28Cr

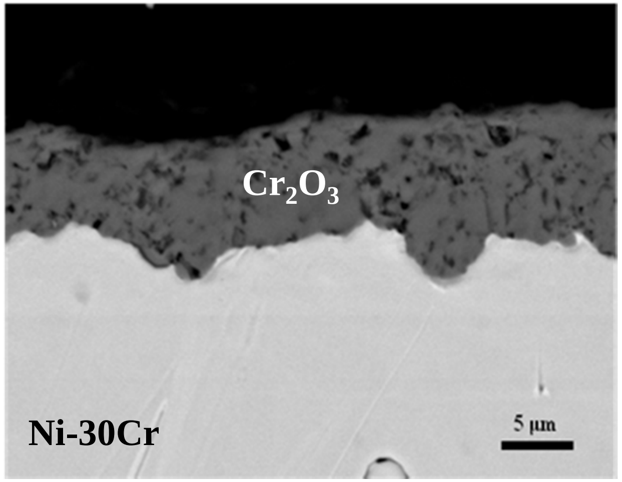




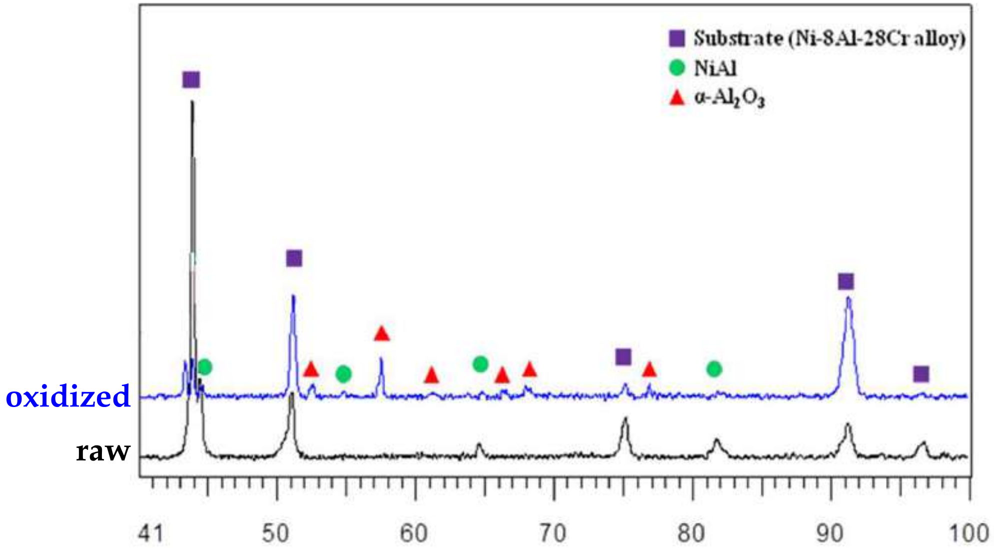
➢ Corrosion of alloys by molten glass [7]

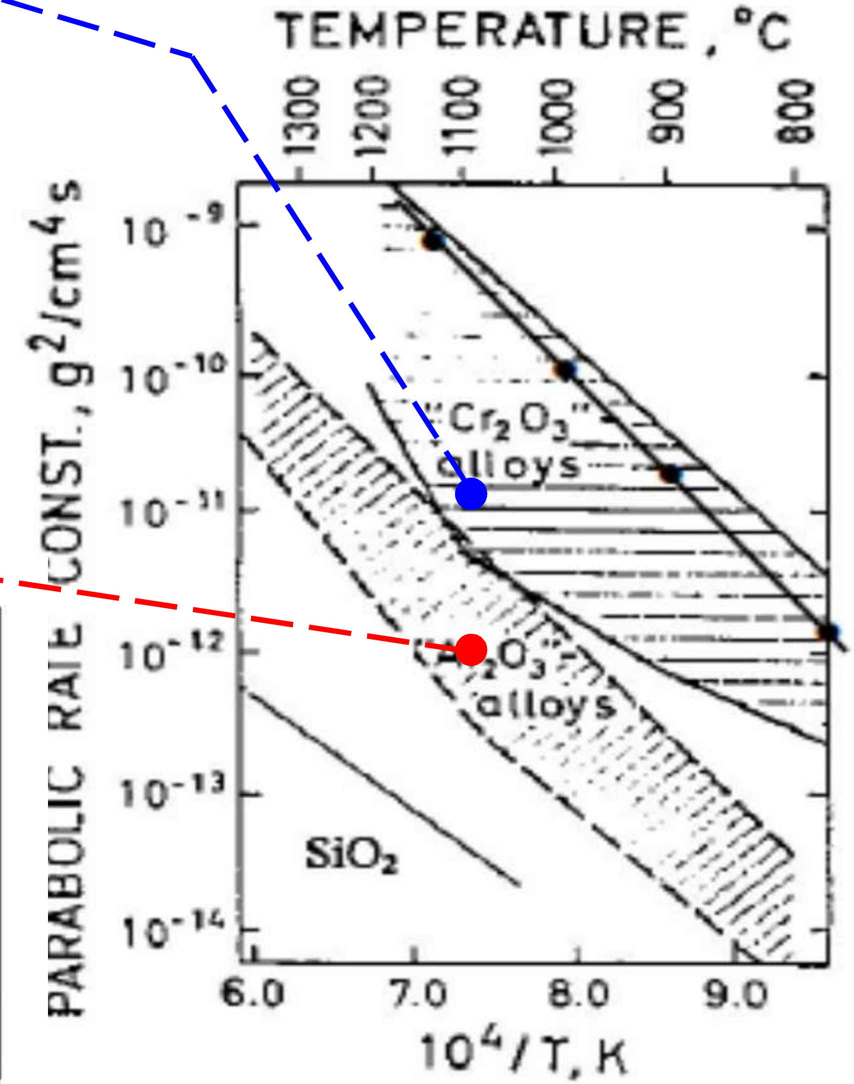
Hot air oxidation of the alloys at 1100°C (100 h)

Ni30Cr



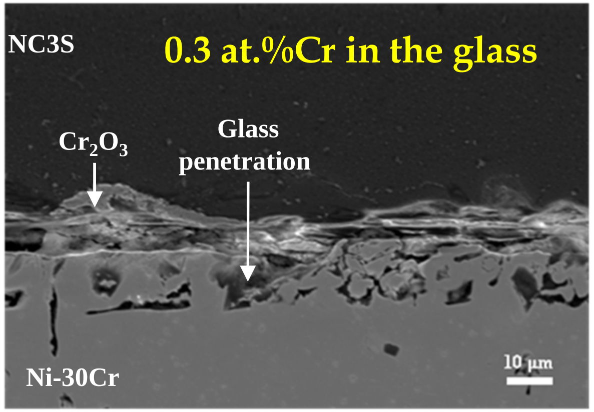
Ni8Al28Cr



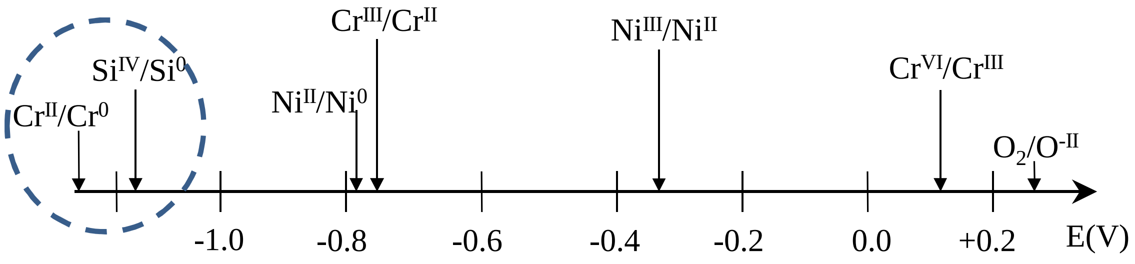


Corrosion of Ni30Cr by molten glass [7]

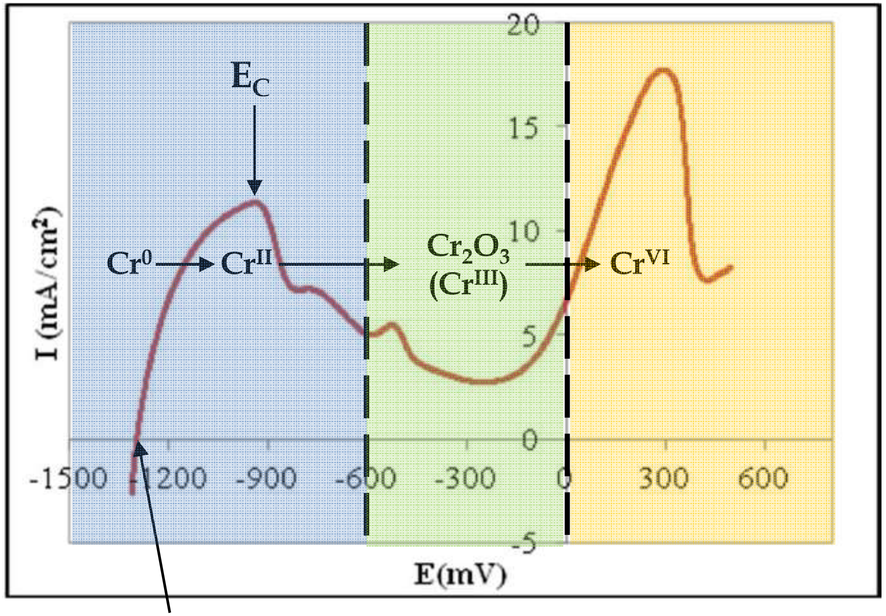
Raw immersion in molten NC3S (1100°C/ 24 h)



CORROSION !



Electrochemical measurements (1100°C)



E_{corr} ~ -1300 mV

R_p ~ 9 Ω.cm²

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

active state

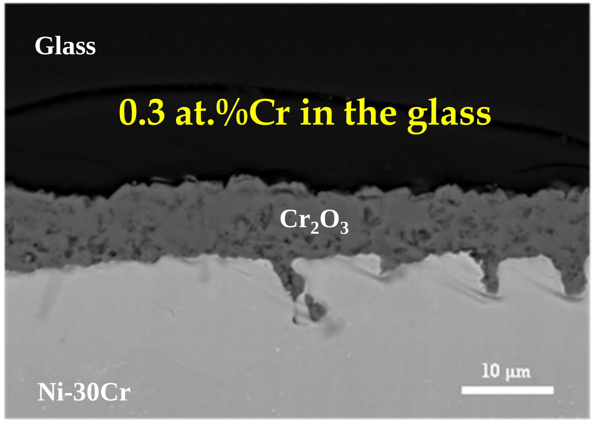
$I_C > 10$ mA.cm^{-2}

Passivation by preoxidation heat treatment ?

Corrosion of Ni30Cr by molten glass [7]

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

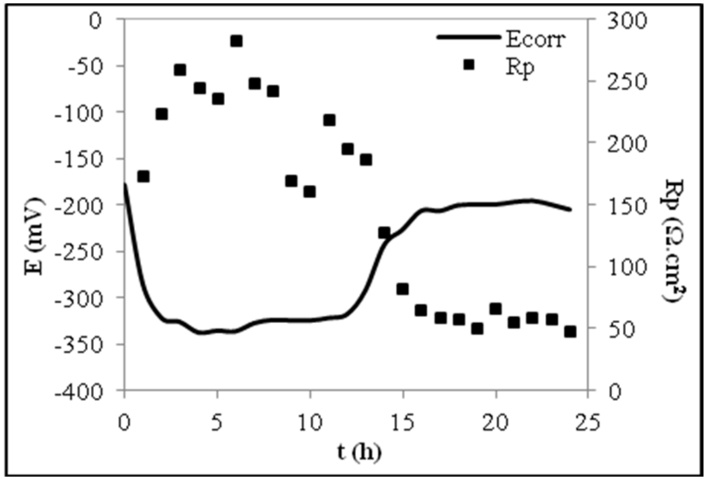
Raw immersion in molten NC3S (1100°C/24 h)



e ~ 6-10 µm

PROTECTION

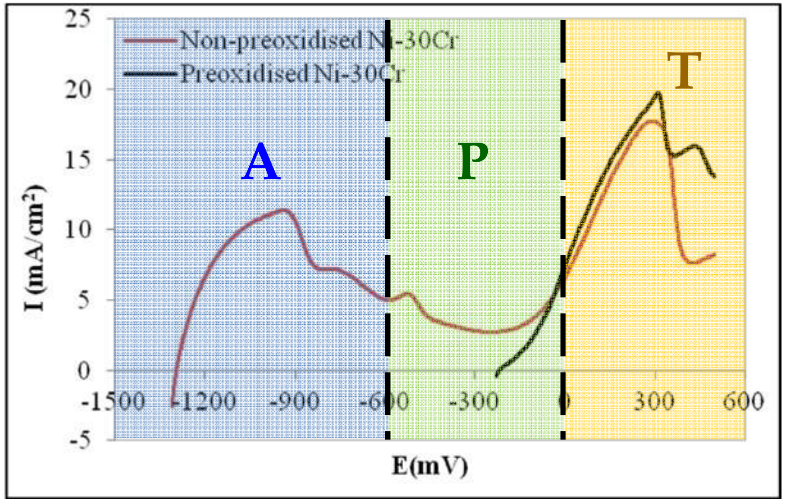
E_{corr} and R_P measurements (24 h)

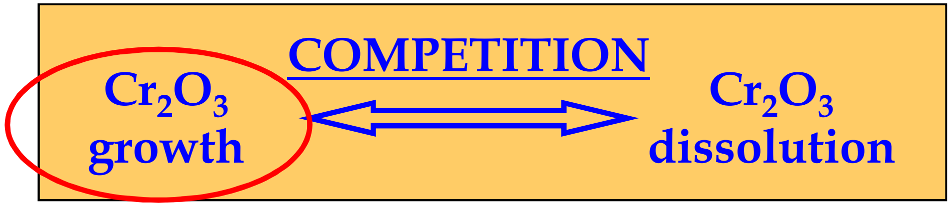


60 Ω.cm² < R_p < 250 Ω.cm² -320 mV < E_{corr} < -200 mV

PASSIVE STATE

Linear polarization after 24 h in NC3S





COMPETITION

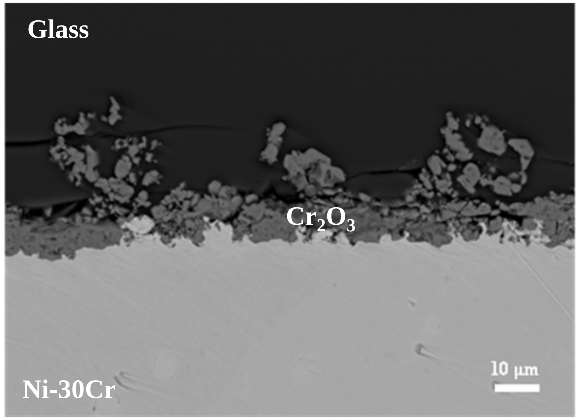
Cr_2O_3 growth

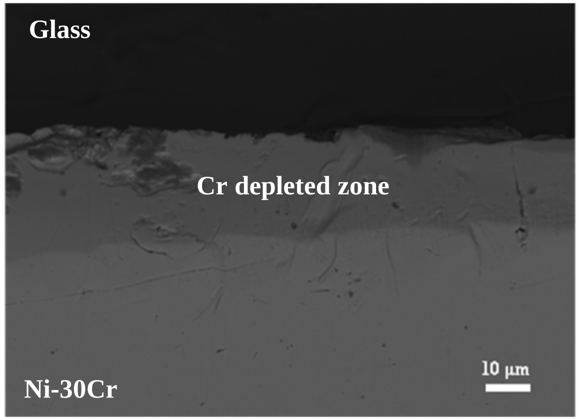
Cr_2O_3 dissolution

Corrosion of Ni30Cr by molten glass [7]

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

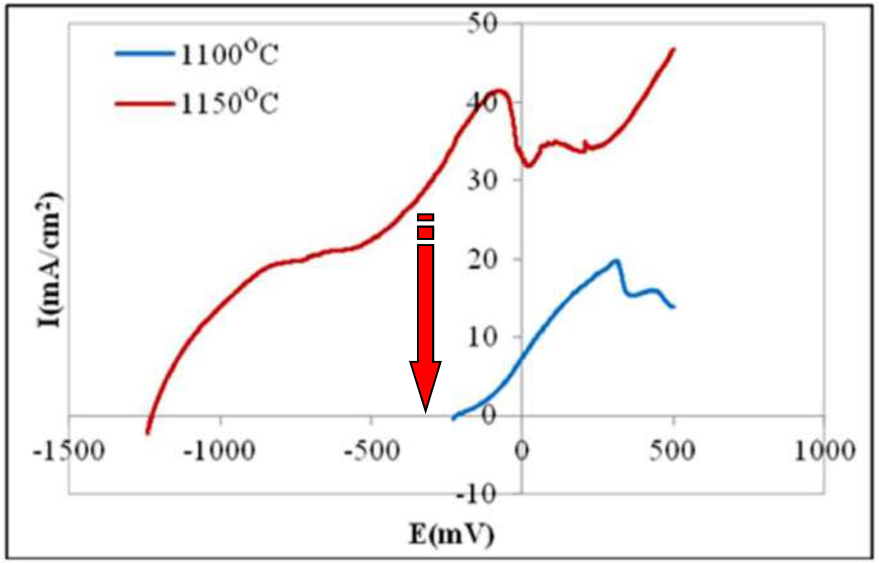
Raw immersion in molten NC3S (1150°C/24 h)





CORROSION !

Linear polarization after 24 h in NC3S



Impossible to obtain passivation at 1150°C

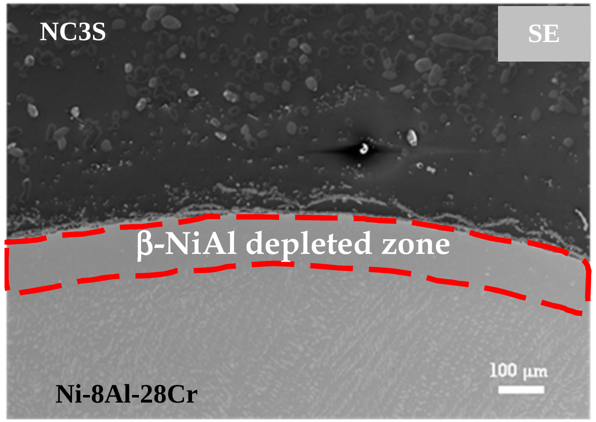
COMPETITION

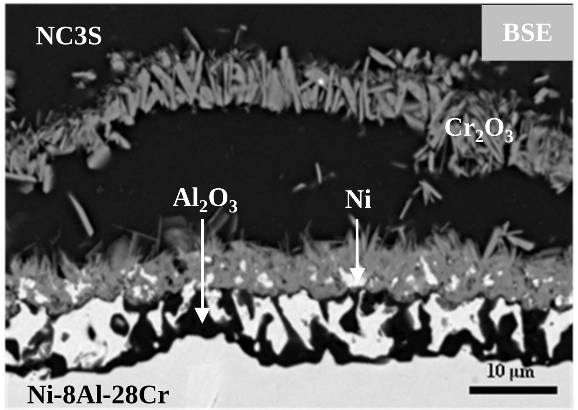
Cr_2O_3 growth ⇔ Cr_2O_3 dissolution

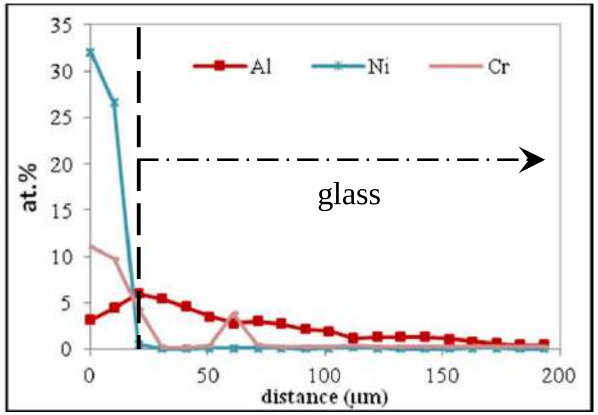
In NC3S, 1100°C < $T_{depassivation}$ < 1150°C

Corrosion of Ni8Al28Cr by molten glass [7]

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



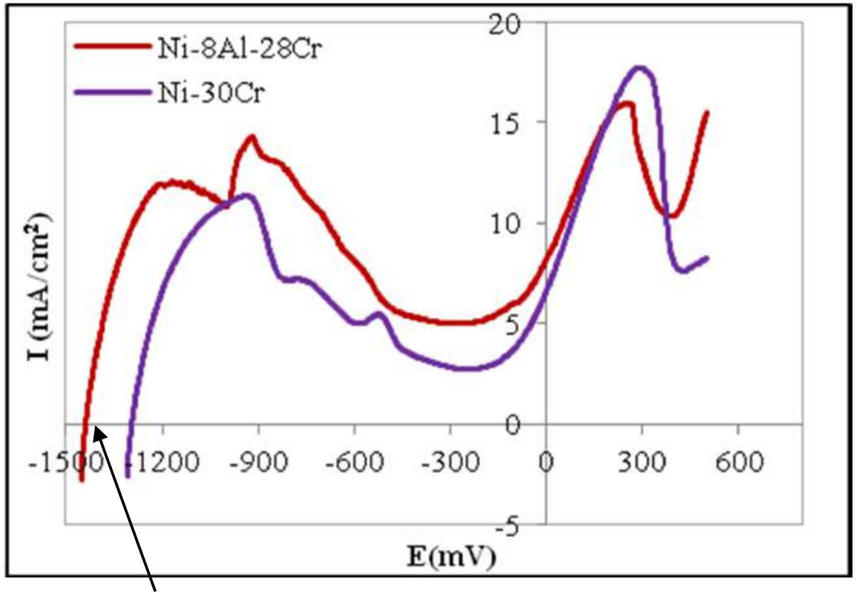




Linear polarization after 24 h in NC3S

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)



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:

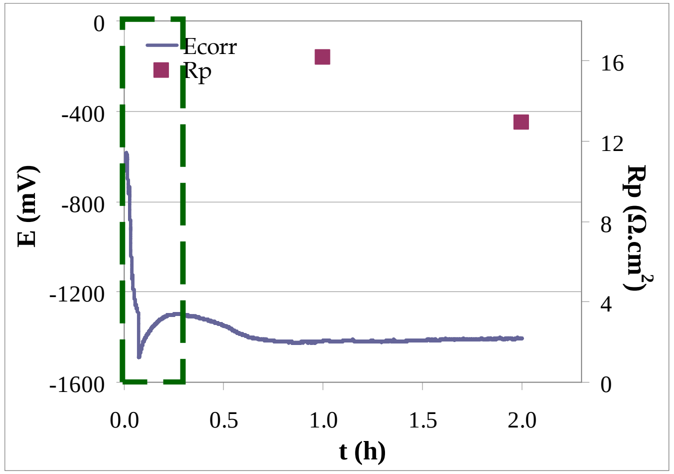
- higher critical current density
- higher current density on the passivation plateau

⇒ **Protection by Al_2O_3 scale ?**

Corrosion of Ni8Al28Cr by molten glass [7]

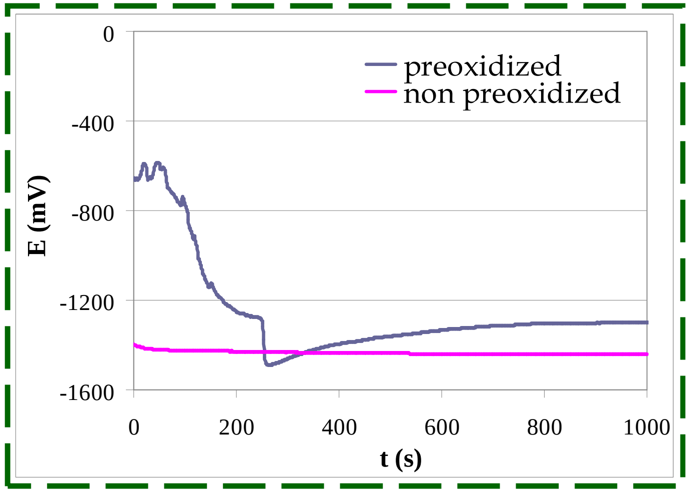
TGA analysis → preoxidation at 1100°C/24h ~ 2 µm thick Al_2O_3 layer

E_{corr} and R_P measurements (2 h)

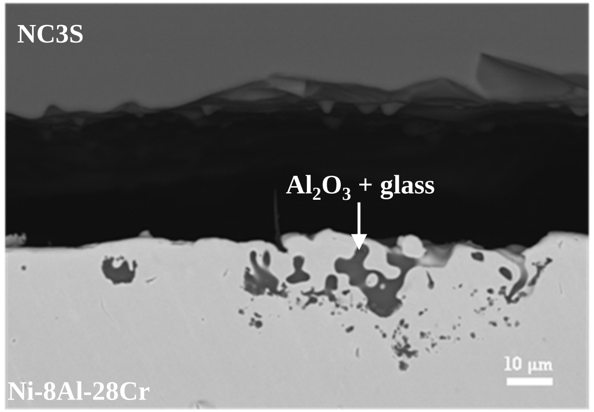


- t = 0 ; E_{corr} ~ -550 mV
  → **passive state**
- t = 5 min ; E_{corr} ~ -1.3 V
  → **active state**

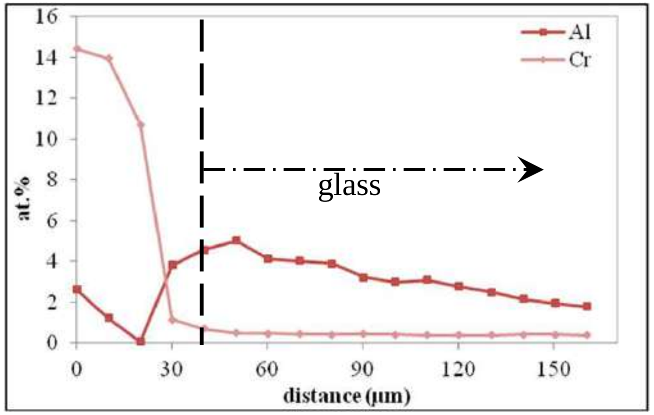
Dissolution of the Al_2O_3 layer in NC3S in 5 min !



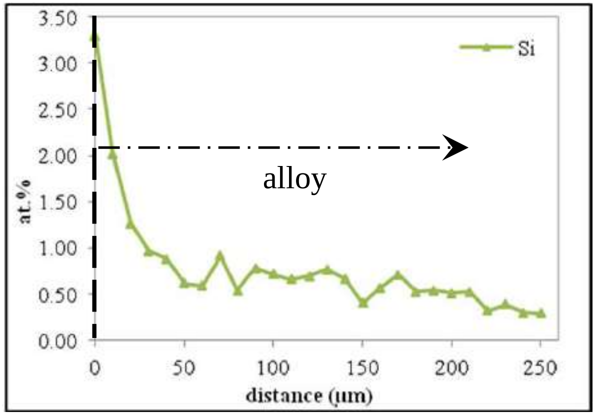
Raw immersion in molten NC3S (1100°C/24 h)



No protective scale

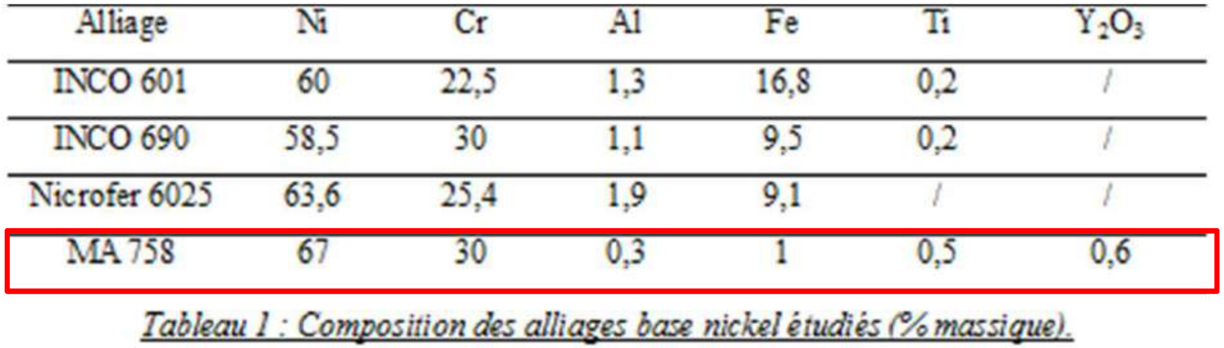


High dissolution of Al in NC3S



Presence of Si in the alloy

➢ Compositions des alliages et microstructures adaptées [14]

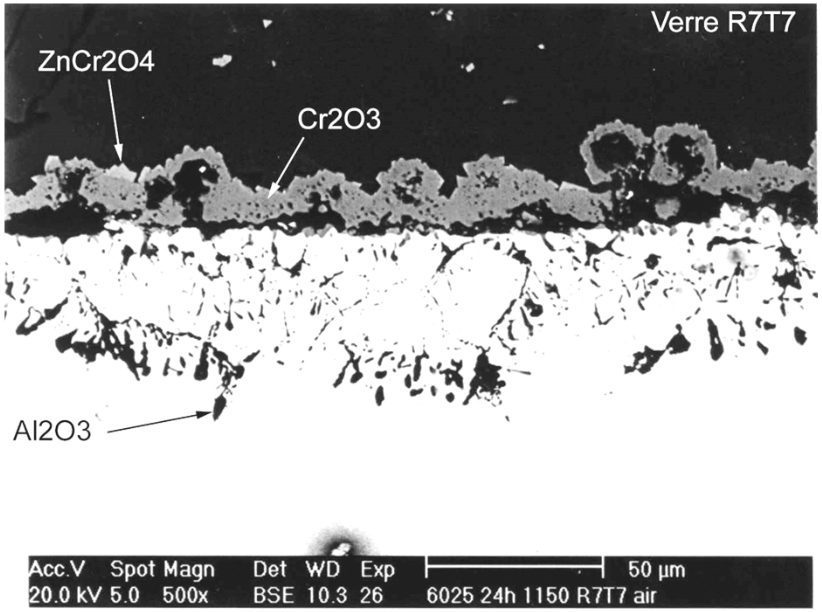


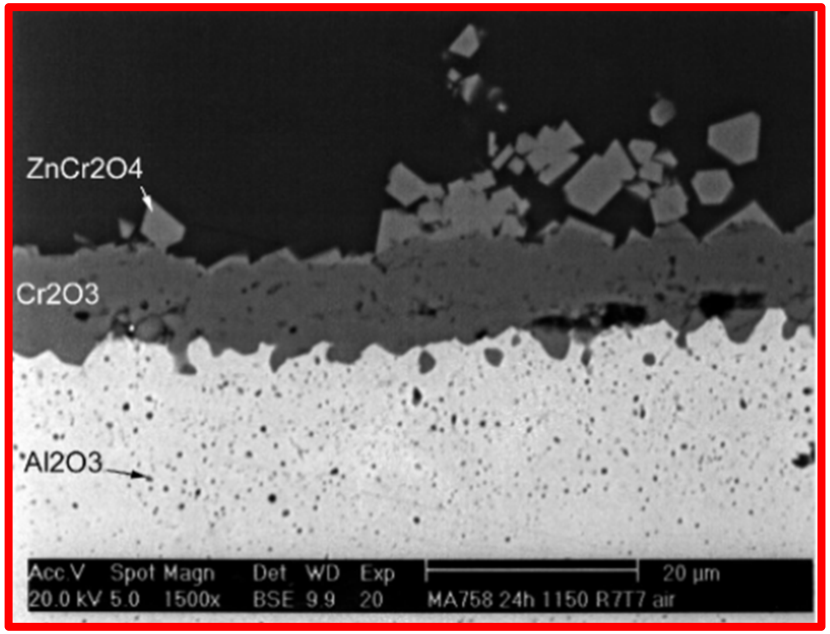
Alliage	Ni	Cr	Al	Fe	Ti	Y_2O_3
INCO 601	60	22,5	1,3	16,8	0,2	/
INCO 690	58,5	30	1,1	9,5	0,2	/
Nicrofer 6025	63,6	25,4	1,9	9,1	/	/
MA 758	67	30	0,3	1	0,5	0,6

Tableau 1 : Composition des alliages base nickel étudiés (% massique).

Alliage ODS MA758:
Composition optimisée : + **de Cr et retrait de Al**
Microstructure optimisée : gros grains au lieu de petits grains => **moins de joints de grains**

Dispersoïdes Y_2O_3 : **durcissement et puits de lacunes**





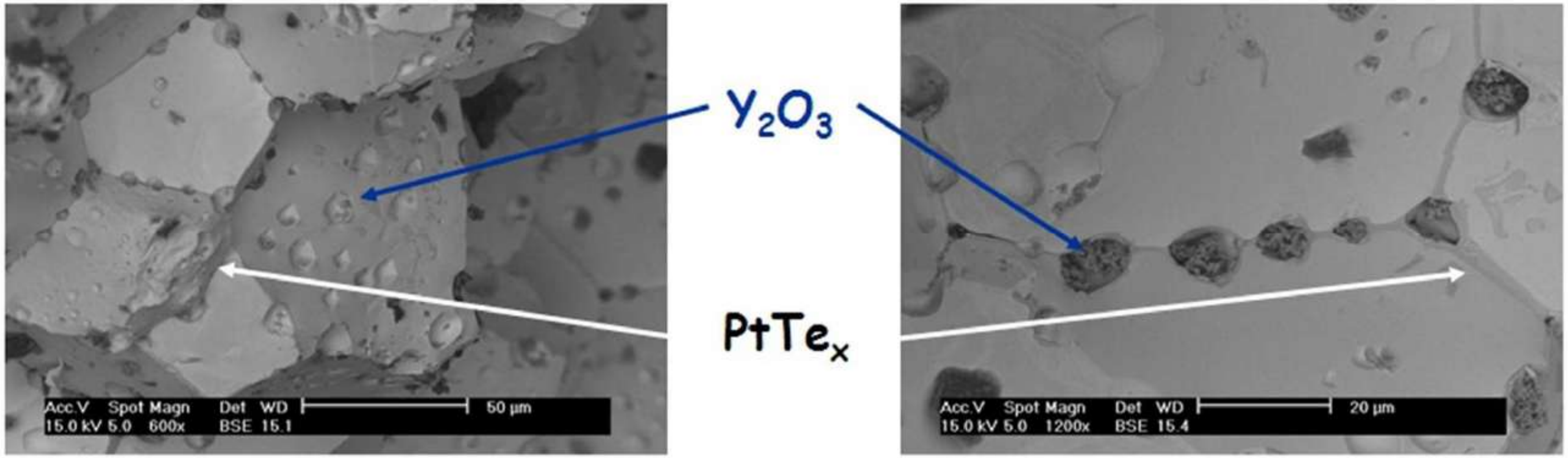
3 cases of corrosion showing the effect of:

- oxygen fugacity
- basicity of melt
- temperature

➢ Effect of $f(O_2)$

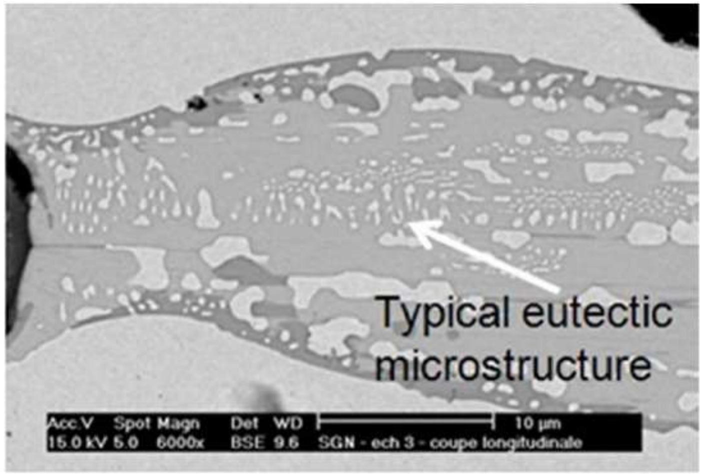
1rst example: Use of Pt in a Te-bearing glass under argon atmosphere

- Eutectic formation $PtTe_x$ (T_f = 830°C)



- Destruction of Pt-based material

W. C. Heraeus GmbH & Co. KG

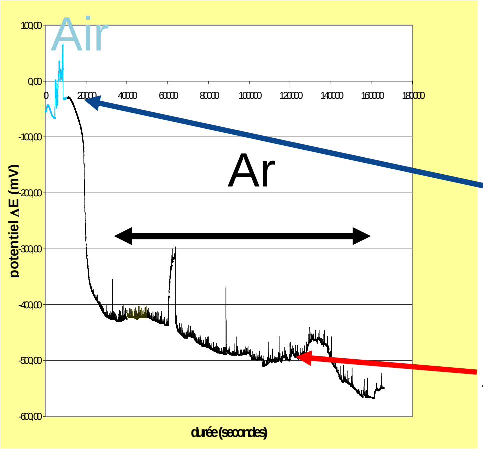


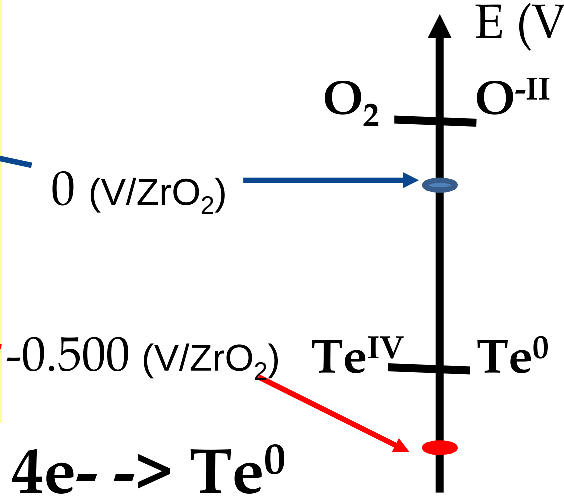
[14]

➢ Effect of f(O_2)

1rst example: Use of Pt in a Te-bearing glass under argon atmosphere

✓ Evolution of the glass potential





0 (V/ZrO_2)

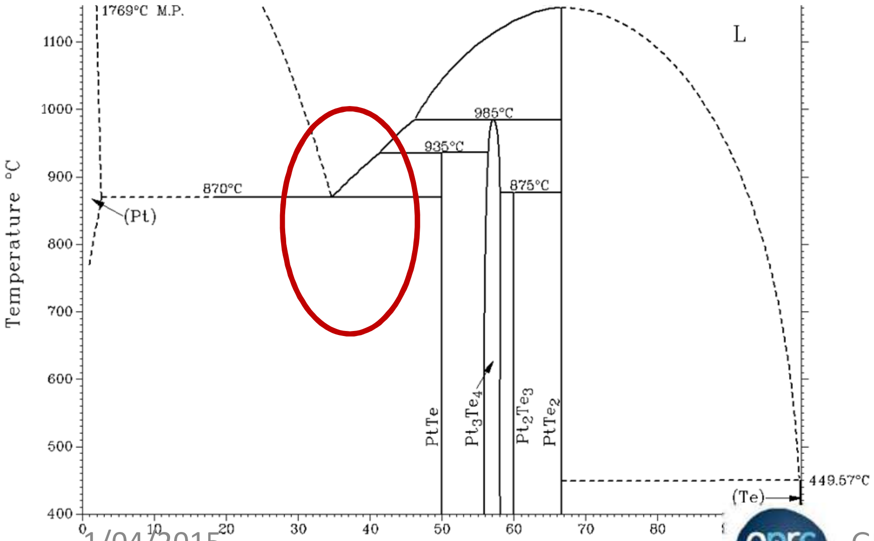
-0.500 (V/ZrO_2)

- 0.33 = E_{formal}

Potential of the glass equilibrated under an air atmosphere

Potential of the glass equilibrated under an argon atmosphere

✓Te^{IV} + 4e- -> Te^0

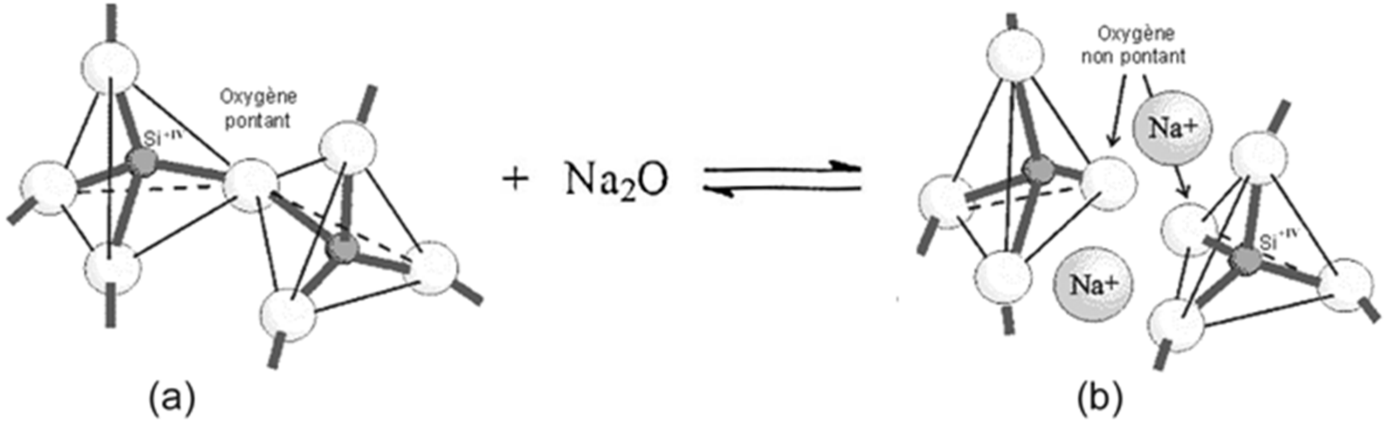


Reaction of Pt with Te nodules

Formation of eutectic with low melting temperature (Pt-PtTe at 870°C)

➢ Effect of Basicity

Definition of the glass basicity ?



- ✓ Considering corrosion mechanism, the acido-basic dissolution of oxide is due to an exchange of "O^{2-}"ion.

=> The basicity concept of Lux-Flood is pertinent to describe this process (fluxing).

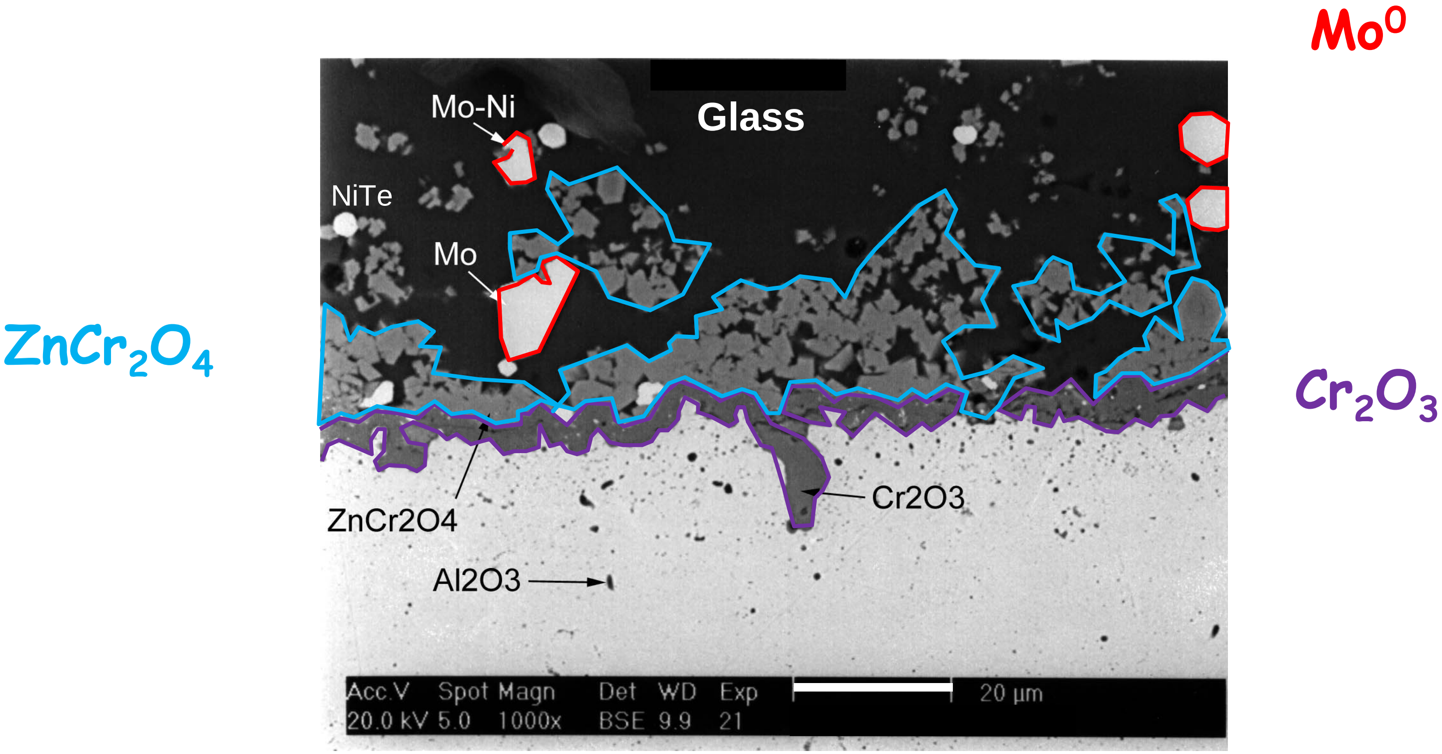
- ✓ The nature and the concentration of network modifier oxides (CaO, Li_2O, Na_2O, K_2O, …) is the main parameter to control

➢ Effect of Basicity

2^{nd} example: Ni alloy tested in a Mo +Zn bearing glass

Test under argon atmosphere [14]

✓ Potential stabilized at -900mV/E_{ZrO2}
✓ Reduction of Mo^{VI} to Mo^{III} and Mo^0
✓ Formation of a discontinuous Cr_2O_3 layer and of numerous $ZnCr_2O_4$ crystals



➢ Effect of Basicity

2nd example: Ni alloy tested in a Mo +Zn bearing glass

➜Local increase of O^{2-} activity during Mo^{VI} reduction:

$$3/2\ O_2 + 2Cr = Cr_2O_3$$

$$MoO_4^{2-} + 2Cr(alloy) = Cr_2O_3 + Mo + O^{2-}$$

➜ The O^{2-} ion liberation promotes the dissolution of chromia by basic fluxing

$$Cr_2O_3 + O^{2-} = Cr_2O_4^{2-}$$

➜ The interaction with zinc produces spinel

$$Zn^{2+} + Cr_2O_4^{2-} = ZnCr_2O_4$$

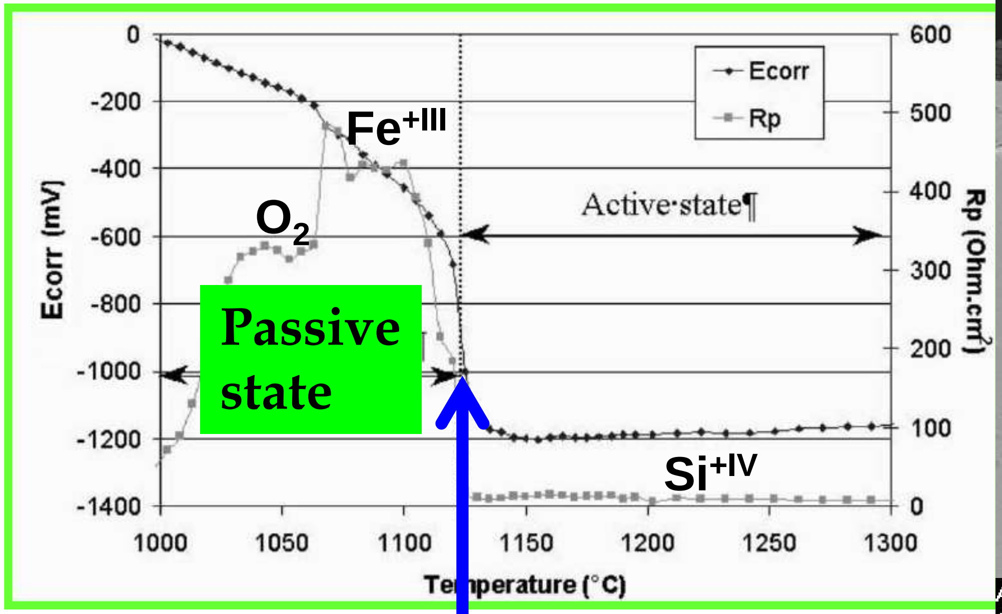
➢ Effect of Temperature

3^{rd} example: Co-Cr alloy tested in C glass

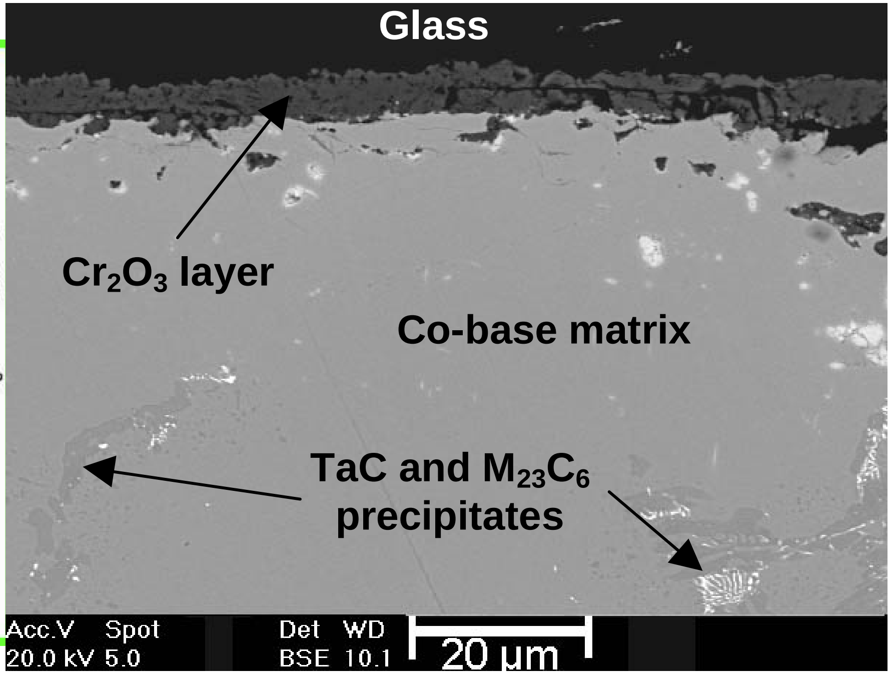
Pre-oxydation in air : new protective method

Use of Co-based alloys is possible at T=1000°C

✓Chromia is highly electrically resistant (100H at 500-800Ω.cm^2)
✓Chromia has a quite high Ecorr (-350mV/E_{ZrO2})



[15]



[15]

Control of electrochemical potential => Depassivation temperature

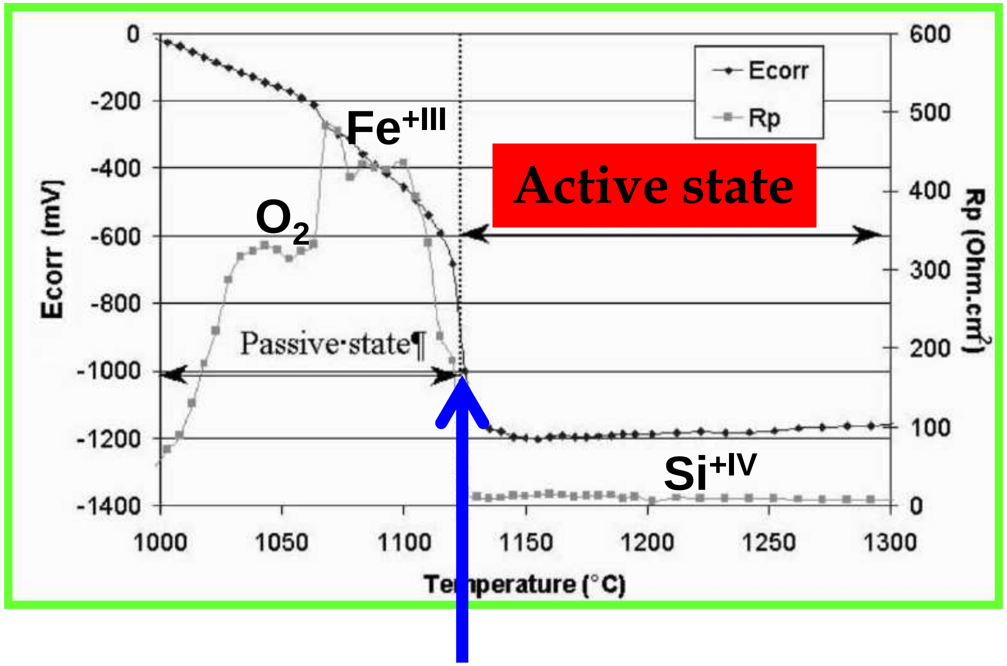
➢ Effect of Temperature

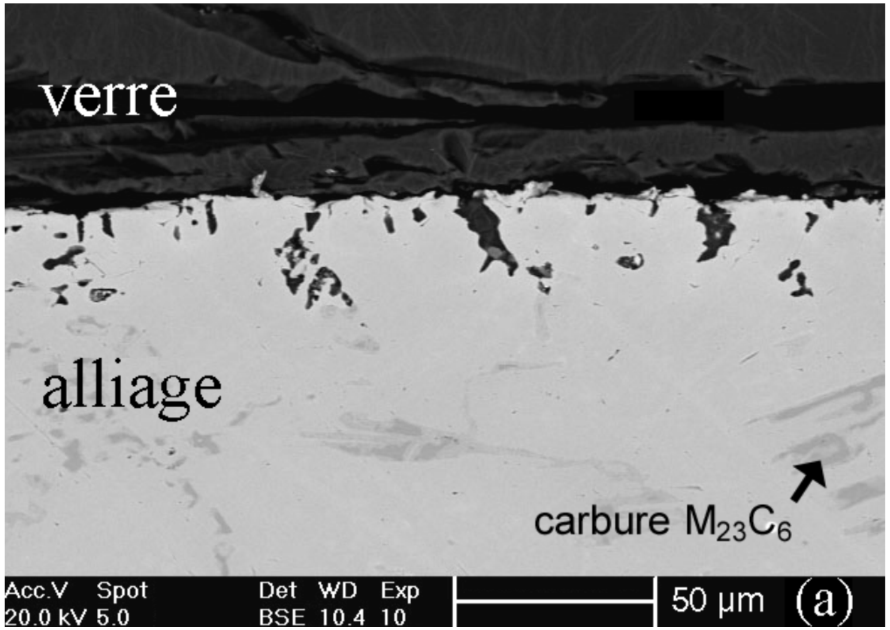
3rd example: Co-Cr alloy tested in C glass

Pre-oxydation in air : new protective method

Use of Co-based alloys is possible at T=1000°C

✓Chromia is highly electrically resistant (100H at 500-800Ω.cm^2)
✓Chromia has a quite high Ecorr (-350mV/E$_{ZrO2}$)





[15]

Control of electrochemical potential => Depassivation temperature

Conclusion

✓ The reported corrosion cases illustrate the ability of molten glass to corrode metallic materials devoted to high temperature glass contact in specific conditions.

✓ The choice of materials must be done taking into account :

- the glass composition
- the temperature of use
- the atmosphere in contact with the glass.

✓ The determination of the corrosion mechanisms is often difficult. Its prediction needs the good knowledge of the physico-chemistry of the silicate melt.

=> The use of electrochemical techniques is particularly relevant for characterizing:

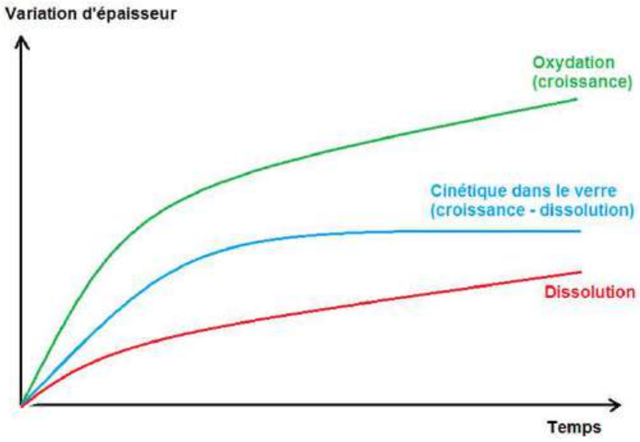
(i) the oxidative attack of metallic alloys
(ii) the protectiveness of passive layers
(iii) the parameters of protection treatments (***depassivation temperature, pre-oxidation in air***)

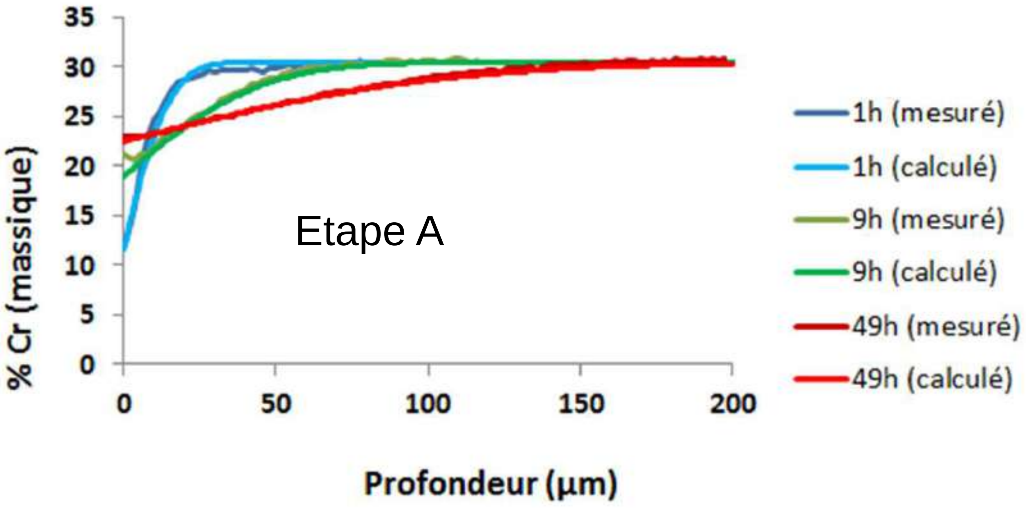
✓ The formation and the stability of Cr_2O_3 is the key factor of the good resistance of metallic alloy used in molten glass. The knowledge of chromia physico-chemistry in molten glasses is needed and must be improved concerning ***ionic conductivity of Cr_2O_3 as passive layer,….***

Outlooks

✓ Thèse CIFRE : Eric Schmucker – AREVA-CEA (Saclay et Marcoule)

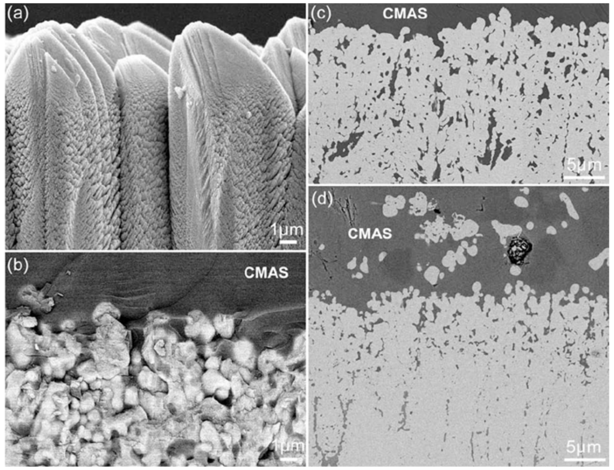
Modélisation de la cinétique de formation et dissolution de la chromine en milieu « Vitrification R7T7 » => Prédiction de la durée de Vie





Etape A : Oxydation dans l'atmosphère gazeuse modélisée => préoxydation

✓ In progress (ANR CINATRA), the corrosion study of the aircraft Thermal Barrier Coatings (TBC) by molten CMAS glass (CaO-MgO-Al_2O_3-SiO_2) at 1200°C will be performed



Catlos Levi et al.

Materials Department, University of California, Santa Barbara (USA)

The impact of CMAS basicity on the oxides constituting TBC (ZrO_2, Y_2O_3, Gd_2O_3, Nd_2O_3,…) will be the determining parameter.

Merci
pour votre attention

68

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✓ Colloque International de référence

High temperature corrosion and protection of materials ; se tiendra du 23-29 Mai 2016 Embiez (Var).

✓ Société savante : CEFRACOR

Optical basicity

Duffy and Ingram have constructed a scale (Table I-3) for the optical basicity of the oxides based on the position of absorption spectrum of the s → p electronic transition of the reference cation (Pb2+, Bi3+) introduced in small amount in the probes.

The frequency of the absorption band is dramatically lowered by an increase of the ability of oxygen to donate negative charge. This latter is at maximum when it exists as the "free" O^{2-} " => allow chharacterizing the basicity of the glass

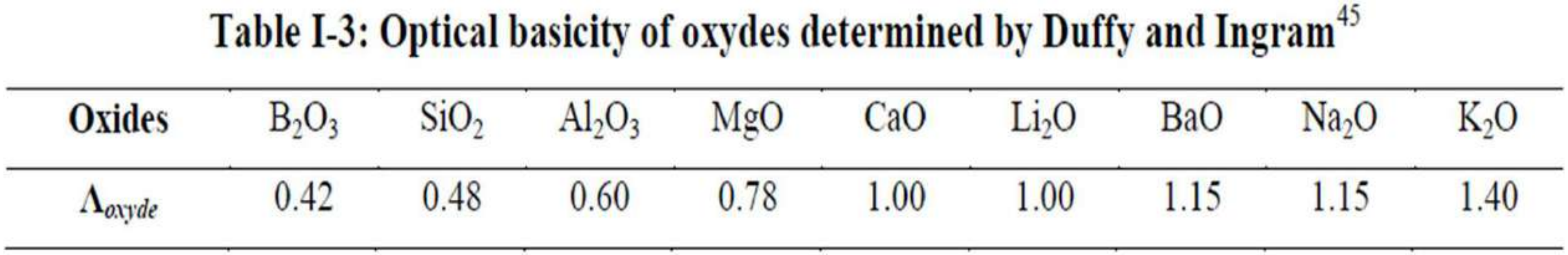

Table I-3: Optical basicity of oxydes determined by Duffy and Ingram[45]

Oxides	B_2O_3	SiO_2	Al_2O_3	MgO	CaO	Li_2O	BaO	Na_2O	K_2O
Λ_{oxyde}	0.42	0.48	0.60	0.78	1.00	1.00	1.15	1.15	1.40

$$\Lambda = X_A \times \Lambda_A + X_B \times \Lambda_B + \ldots$$

Effect is due to orbital expansion of the probe ions while receiving the electron donation by the oxygen with high electron donor power.