

LEC2M laboratory, University Mouloud Mammeri, 15000 Tizi Ouzou, Algeria

\*University Mohand Oulhadj (UMOB) – 10000 Bouira, Algeria.

\*\* University of Pitesti, LSIM I134, 110040 Pitesti- Romania

\*\*\*Research group CNRS/SPMS-ECP/ SRMA-CEA, 91 Gif sur Yvette (France).

## Abstract

The crucial role of transport processes through oxide layers has long been acknowledged in the study of metal oxidation, but the experimental results are generally analyzed taking into account observations performed at room temperatures. In the present work, we present a formal treatment, derived by use of equations of irreversible thermodynamic as a general basis, to describe the kinetics of oxide layer growth. This has allowed us to show the influence of both the cation diffusion driving force and the cation kinetic demixing within the oxidation layer.

## I-Introduction

The purpose of this paper is to review the current state of understanding the growth of oxidation layers, by thermal oxidation, in terms of transport processes taking place within the growing oxide film. The term understanding may be sought at both phenomenological and atomistic level. At the phenomenological level, it means to relate the rate of growth to measurable transport properties, such as diffusion coefficients and electronic conductivity. At atomistic level, it means identify the way of which ions move in the lattice.

This survey concerns the rate of growth of p-type semiconducting oxide on coated-metal substrates, such as nickel which occupies a crucial position as a model material in studies of thermal oxidation of metals. The experimental results concern CeO<sub>2</sub> and CaO -coated nickel, at  $T \leq 1200^\circ\text{C}$ .

## II- General treatment of oxide film growth

To simplify the analysis, we consider p-type semiconducting oxides (AO-BO<sub>β</sub>) in equilibrium with a given oxygen partial pressure, within their range of stability. The prevailing defects in these oxides are electron holes ( $h^\circ$ ) and  $\alpha$  time ionized cationic vacancies ( $V^{\alpha'}$ ), whose concentrations depend on both temperature (T) and oxygen partial pressure ( $P_{O_2}$ ) [1-4]:

$$[h^\circ] = \alpha[V^{\alpha'}] = AK_V^{1/(\alpha+1)} (P_{O_2})^{1/2(\alpha+1)} \quad (1)$$

where  $K_V$  is the equilibrium constant of formation of defects ( $\frac{1}{2}O_2 \rightleftharpoons O_O + V^{\alpha'} + \alpha h^\circ$ ),  $O_O$  an oxygen ion on a normal lattice site,  $A = \alpha^{1/(\alpha+1)}$  and square brackets indicate molar fractions.

When one substitutes in a nickel site an impurity  $B^{\delta+}$ , with  $\delta > 2$ , the defect ( $B_{Ni}^{\beta\cdot}$ ) will have an effective positive charge ( $\beta = \delta - 2$ ). This impurity then increases the concentration of nickel vacancies, through the electroneutrality condition :

$$[h^\circ] + \beta[B_{Ni}^{\beta\cdot}] = \alpha[V^{\alpha'}], \quad (2a)$$

$$\text{with, in the extrinsic range: } \beta[B_{Ni}^{\beta\cdot}] = \alpha[V^{\alpha'}], \quad (2b)$$

$$\text{and the nickel diffusion coefficient } (D_{Ni}) : \quad x_v D_v = x_{Ni} D_{Ni} \quad (3)$$

In the considered oxides, the diffusivity of anions is much lower than that of cations, one may then take the anion sublattice as frame of reference for motions of cations and defects. When these oxides are exposed to an oxygen chemical potential gradient, fluxes of cations ( $J_i$ ) and cationic vacancies ( $J_V$ ) appear in the material, coupled through the condition:

$$J_V + \sum J_i = 0. \quad (4)$$

If the correlation effects are disregarded, these fluxes in the “z” direction can be written [3,6]:

$$J_i = -\frac{C_i}{RT} D_i \frac{d\eta_i}{dz} \quad (5)$$

where  $d\eta_i/dz$  is the electrochemical potential gradient of the charged species, related to the chemical potential gradient ( $d\mu_i/dz$ ) by the relation:

$$\frac{d\eta_i}{dz} = \frac{d\mu_i}{dz} + z_i F \frac{d\Phi}{dz}, \quad (6)$$

In addition,  $F$  is the Faraday constant,  $C_i = x_i C_M$  the concentration of cations “i” per unit volume ( $\text{mol}/\text{cm}^3$ ),  $z_i$  their valence,  $C_M$  the concentration of cationic sites in the lattice ( $\text{mol}/\text{cm}^3$ ) and  $d\Phi/dz$  the internal electric field, due to the difference of mobilities of cationic vacancies and electron holes..

Since the electronic conductivity ( $\sigma_h = e \mu_h p$ ) greatly exceeds the ionic conductivity in the considered oxides ( $\mu_h \approx 10^3 \mu_V$ ), the zero current condition in the oxide layer ( $I_t = F J_h = 0$ ) allows expressing the internal electric field, by the relation:

$$\frac{d\Phi}{dz} = -\frac{RT}{F} \frac{d \ln p}{dz} \quad (7)$$

where  $p$  is the electron hole concentration per  $\text{cm}^3$  ( $p = [h^\bullet] d N_A / M$ ),  $N_A$  the Avogadro number,  $d$  the density and  $M$  the molar mass of the oxide.

Therefore, substituting Eq.7 in Eq.6, and in view of the virtual chemical equilibrium between ions, electron holes and neutral atoms ( $A + 2h^\bullet \rightleftharpoons A^{2+}$ ,  $B + \delta h^\bullet \rightleftharpoons B^{\delta+}$ ), one obtains [11]:

$$d\eta_A^{2+}/dz = d\mu_A/dz = RT \ln a_A/dz \quad \text{and} \quad d\eta_B^{\delta+}/dz = d\mu_B/dz = RT \ln a_B/dz \quad (8)$$

where,  $\mu_A$  and  $\mu_B$  are the chemical potential gradient of electrically neutral species related to the thermodynamic activities ( $a_i$ ).

In order to be able to compare the fluxes of cations A and B in the solid solution  $AO, BO_\gamma$ , it is expedient to express them as a function of measurable variables, the oxygen potential gradient across the oxide scale for instance. In the following, we have assumed that the concentration of  $BO_\gamma$  in the layer ( $x_{BO_\gamma} = m \ll x_{AO}$ ) is low enough that the Raoult law may be applied ( $a_{AO} = x_{AO} = 1 - m$ ). Consequently, in view of the local chemical equilibrium between the different species in each element of volume ( $\gamma/2 O_2 + B \rightleftharpoons BO_\gamma$ ,  $1/2 O_2 + A \rightleftharpoons AO$ ), one can show that the flux of cations A and B (Eq.6), which appears in a material under non equilibrium conditions can be written, with respect to the oxygen sublattice [5]:

$$J_i = -\frac{C_i}{RT} D_i \frac{d\mu_i}{dz} = C_M D_i \left[ -\frac{dx_i}{dz} + x_i \gamma \ln a_O/dz \right] = C_M D_i \left[ -\frac{dx_i}{dz} + x_i \gamma \mathcal{F} \right] \quad (9)$$

where  $\mathcal{F} (= \mathcal{R}/T)$  is the reduced driving force of diffusion, related (Eq.1) to the gradient of oxygen activity ( $a_{O_2} = P_{O_2}^{1/2}$ ) or to the vacancy concentration gradient ( $x_V = [V^{\alpha}]$ ) [5,8]:

$$\mathcal{F} = d \ln a_{O_2} / dz = (1 + \alpha) d \ln (x_V / dz) \quad (10)$$

According to Eq.4 ( $J_V = -J_A^{2+} - J_B^{\delta+}$ ), new lattice sites are formed at the outer surface of the oxidation layer leading to a rate of growth of the scale given by [5,9]:

$$v_{\text{oxid}} = J_V / C_M = - (J_A^{2+} + J_B^{\delta+}) / C_M \quad (11)$$

Consequently, a cation kinetic demixing ( $dx_i/dz$ ) sets up progressively in multi-component oxides if the cations have different diffusivities.

Finally, substituting Eq.9 in Eq.11 allows to show that the rate of growth of a cation deficient p-type semiconducting oxide ( $AO, BO\gamma$ ) on a metal substrate (Eq.8) can be written, in the case of low concentrations of solute cations B ( $x_B \ll x_A \approx 1$ ) [5,9]:

$$v_{\text{oxid}} \approx (D_B - D_A) dm/dz - D_A \mathcal{F}_{(\text{NiO-dop})} \quad (12)$$

$$\text{while for a pure oxide: } v_{\text{oxid}} = -J_A^{2+} / C_M = -D_A \mathcal{F}_{(\text{NiO})} \quad (13)$$

where  $m = x_B$  is the mole fraction of the solute cations  $B^{\beta+}$  in the cationic sublattice,  $\mathcal{F}_{(\text{NiO-dop})}$  the reduced driving force in doped NiO and  $\mathcal{F}_{(\text{NiO})}$  in the pure oxide.

Consequently, the growth of oxidation layers, when the outward diffusion of cations prevails, depends of both the driving force of diffusion ( $\mathcal{F}$ ) and the cation kinetic demixing ( $dm/dz$ ), due to the cation different diffusivities.

### III- Oxidation of nickel.

We consider in the following the oxidation of coated-nickel substrates, which eliminates the effect of the reactive elements on the metal diffusion processes. The description of experiments is reported elsewhere [10],

#### 1 Thermal oxidation of a $\text{CeO}_2$ -coated nickel.

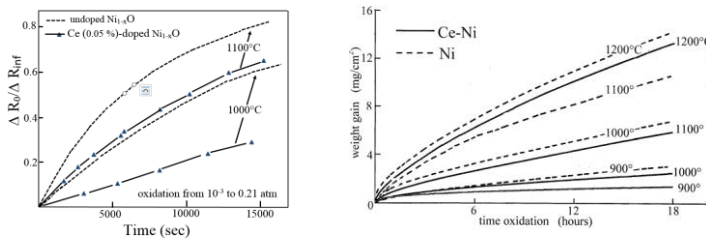


Figure 1 Weight gain versus time for uncoated and coated  $\text{CeO}_2$ -coated nickel, under  $P_{O_2} = 1$  atm.

In Fig.1 we have plotted the weight gain as a function of time, between 700° to 1200°C, and determined with a Setaram thermobalance. At  $T < 1200^\circ\text{C}$ , the  $\text{CeO}_2$  coating leads to a decrease of the oxidation rates. X-ray analyses show that the scales were  $\text{Ni}_{1-x}\text{O}$ . The cerium depth profiles through oxide layers were investigated by EPMA analysis (Fig.2). At 900°C, a high cerium concentration is observed in a localized zone, which coincides likely with the original metal surface (i.e. the inner/outer boundary). From either sides of this

maximum, the amount of cerium is higher near the metal interface, in agreement with the lower diffusivity of cerium [9]:

$$D_{\text{Ce}} < D_{\text{Ni}} \quad (14)$$

When the temperature increases, the cerium became progressively more diluted in the thicker films. At 1100°C for instance, cerium shows only a small increase near the metal/oxide interface.

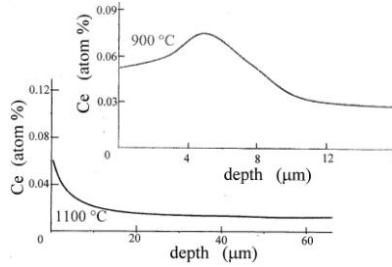


Figure 2 cerium concentration – depth profile through oxide layers formed on CeO<sub>2</sub>-coated nickel, after 18h of oxidation, at 900° and 1100°C. The metal/oxide interface was taken as the initial position.

According to both the foregoing results and Eqs 12 and 13, it follows that the beneficial effect of cerium, at  $T < 1200^\circ\text{C}$  can be explained:

*a-by the decrease of the driving force of diffusion*, due to the decrease of the concentration of  $\text{Ce}^{4+}$  (Eq.2) from the metal/oxide interface to the metal surface (Fig 2). Thus, one has a decrease of the concentration of cationic vacancies within the layer (Eq.2) leading to a decrease of the driving force of diffusion  $\mathcal{F}$  (Eq.10) and therefore of the oxidation kinetics (Eq.12).

*b-by the influence of the cation kinetic demixing across the oxide layer* (Fig.2), due to the lower diffusivity of cerium (Eq.14). Therefore, in view of the average cerium profile within the layer ( $dm/dz > 0$ ) and the relative values of the diffusion coefficients of the cations (Eq.14), the first term of Eq.12 is positif ( $(D_B - D_A)dm/dz > 0$ ). Consequently, in view of the positive value of  $\mathcal{F}_{(\text{NiO-Ce})}$ , the kinetic demixing of cerium in the growing oxide layer contributes also to the decrease of the oxidation rates of the coated samples.

*c- by the decrease of the diffusivity of  $\text{Ni}^{2+}$  with the amount of  $\text{Ce}^{4+}$  in  $\text{Ni}_{1-x}\text{O}$  [9] and the kinetic demixing of cerium* (Fig.2), it follows a decrease of the diffusivity of nickel in the outer layer, which yields a blocking effect on the diffusion of  $\text{Ni}^{2+}$  and the formation of new oxide units in the growing oxide scales, as observed by Atkinson in oxide layers grown on Ni,Cr alloys, for instance [12,13].

## 2 Thermal oxidation of a CaO-coated nickel.

First, it should be noted that calcium behaves as a reducing cation in  $\text{Ni}_{1-x}\text{O}$ , leading to the shift of the Ni/NiO phase boundary to higher  $P_{\text{O}_2}$  and the presence of singly ionized nickel cations ( $\text{Ni}^\circ$ ) in the stability range of  $\text{Ni}_{1-x}\text{O}$  [11],

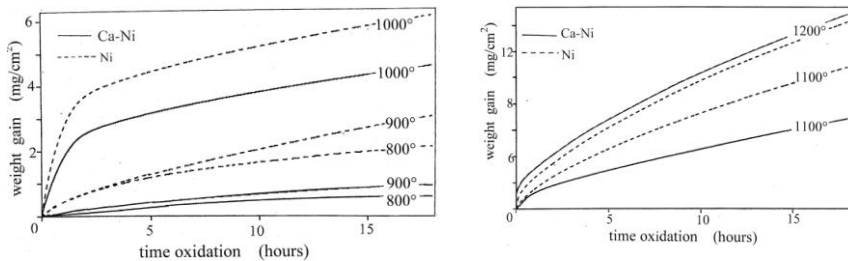


Fig 3 Figure 1 Weight gain versus time for uncoated and coated CaO-coated nickel, under  $P_{\text{O}_2} = 1 \text{ atm}$ .

In Fig.3, we have plotted the weight gain from 800° to 1200°C, as a function of time. It can be seen that  $\text{Ni}_{1-x}\text{O}$  layers grown by the outward diffusion of cations and that CaO coating leads to a decrease of oxidation

rates at  $T \leq 1200^\circ\text{C}$ , in agreement with literature results [14], The calcium depth profile through the oxide layers is reported Fig.4. At  $900^\circ\text{C}$ , it shows a high concentration of calcium, in a localized zone. From either sides of this maximum, the amount of calcium is higher in the outer layer, in agreement with the relative diffusion coefficients of calcium and nickel in Ca-doped  $\text{Ni}_{1-x}\text{O}$  ( $D_{\text{Ca}} > D_{\text{Ni}}$ ) [11].

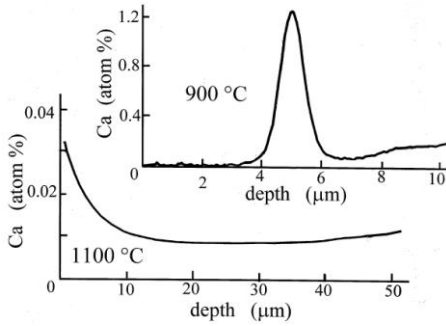


Figure 4 Calcium concentration–depth profile through oxide layers formed on CaO-coated nickel, after 18h of oxidation, at  $900^\circ$  and  $1100^\circ\text{C}$ .

Consequently, in view of Eqs 22, 23, it appears that the beneficial effect of CaO coatings on the oxidation kinetics can be explained:

*a-by the decrease of the driving force of diffusion ( $\mathcal{F}_{(\text{NiO-dop})}$ ), which depends of the oxygen potential gradient through the oxidation layer (Eq.10), and therefore of the shift of the Ni/NiO phase boundary to higher  $P_{\text{O}_2}$ , effect all the more important that the calcium amount is high [11].*

*b-by the influence of the cation kinetic demixing through the oxide layer, As previously, due to both the average calcium profile within the layer ( $dm/dz > 0$ ) and the relative values of the diffusion coefficients of the cations (Eq.14,  $D_{\text{Ca}} > D_{\text{Ni}}$ ), the first term of Eq. 12 is positif ( $(D_{\text{B}} - D_{\text{A}})dm/dz > 0$ ). Consequently, in view of the positive value of  $\mathcal{F}_{(\text{NiO-Ca})}$ , the kinetic demixing of calcium in the layer also contributes to the decrease of the oxidation rates of coated samples.*

**Remark-** One can recall that blocking effects, ascribed to CaO precipitates have been invoked in the literature [14] to explain the beneficial effect of CaO coatings. Unfortunately, it is not possible to make good estimate from observations of precipitates at room temperature. This is confirmed in the case of CaO-coated nickel, whose thickening of oxidation layers is controlled by the outward diffusion of cations. Indeed, in view of the increase concentration of calcium, from the metal/oxide interface to the external oxide surface (Fig.4), it follows an increase of diffusion processes across the oxidation layers (Eqs.2), which excludes blocking effects for the diffusion of cations and the formation of precipitates in the oxidation layers.

#### IV-Conclusion

The foregoing analysis, on the basis of transport equations of irreversible thermodynamic, has made possible to analyze the results of oxidation of coated nickel samples. It has allowed to show the influence of both the diffusion driving force of cations and their diffusion coefficients, related to the composition of layers. Furthermore, it has allowed us to show that analysis of oxidation kinetics, based only on observations done at room temperature, cannot be retained.

#### Aknowledgements

The authors are grateful to Dr G Baldinozzi and Prof C.Petot, from research group CNRS/SPMS-ECP/SRMA-CEA, for fruitful discussions.

#### Bibliography

1- P.Kofstad, High temperature corrosion, Elsevier Applied Science (1988)

- 2- A. Atkinson, Reviews of Modern physics, 57, 2, 437-470 (1985)
- 3- P. Kofstad, Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides, Wiley Interscience, New York (1972)
- 4- J. Philibert, Atom movements, Diffusion and Mass transport in solids, les Editions de Physique, les Ullis, France (1991)
- 5- G. Petot-Ervas, C. Petot, J. Phys. and Chem. of Sol., 51, 8, 901-906 (1990)
- 6- C. Wagner, Progress, in Solids State Chemistry, 7, 1-36 (1972)
- 7- C. Wagner, Corrosion Science, 9, 91-100 (1969)
- 8- D. Monceau, C. Petot, G. Petot Ervas, *Sol. St. Ionics*, 45, 231-235 (1991).
- 9- N. Mahiouz, Z. halem, N. Halem, G. Petot Ervas, *Sol. St. Ionics*, in press.
- 10- Z. Halem, N. Halem, M. Abrudeanu, S. Chekroude, C. Petot, G. Petot-Ervas, *Sol. St. Ionics*, 297, 13-19 (2016)
- 11- H. Aïdrous, L. Cieniek, N. Halem, J. Kusinski, C. Petot, G. Petot Ervas, *Sol. St. Ionics*, 261, 117-124 (2014)
- 12- A. Atkinson, D. W. Smart, *J. Electrochem. Soc. Solid State Science and Technology*, 2886-2889 (1988)
- 13- A. Atkinson, R. I. Taylor, P. D. Goode, *Oxid. Meztals*, 13, 6, 519-543 (1979)
- 14- J. Gonzales, thesis N°1050, Institut National Polytechnique, Toulouse, France (1995)