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Influence of Calcium on the Thermal Oxidation of Ca-Doped CoO and of CaO-Coated Cobalt

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Abstract: The present study concerns the influence of calcium on the thermal oxidation of Ca-doped $Co_{1-x}O$ and of CaO-coated cobalt. We have found that calcium enhanced the thermal oxidation of $Co_{1-x}O$ single crystals while a CaO coating leads to a decrease of the oxidation kinetic of cobalt polycrystals, at T<1200°C. From a formal treatment, based on the thermodynamic of irreversible processes, we have shown that the increase of the thermal oxidation of Ca-doped $Co_{1-x}O$ is due to the increase of the diffusion coefficient of cobalt in Ca-doped samples, while the beneficial effect of a CaO coating on the cobalt oxidation is due to the shift of the $Co/Co_{1-x}O$ phase boundary to higher P_{O_2}, leading to a decrease of the driving force of diffusion in the oxide scale.

Key words: Oxygen chemical potential gradient, Diffusion driving force, Diffusion, Kinetic demixing

Introduction

Although it is recognized that at high temperature transport of reactants plays a crucial role in metal oxidation processes (Kofstad, 1988; Wagner, 1951; Wagner, 1975), metal corrosion studies are generally performed from observations performed at room temperature (Kofstad, 1988). These analyses are influenced by reactions occurring during cooling, such as the formation of precipitates, for instance. It is then understandable that important mechanisms still remain unexplained.

The purpose of this work was to investigate the influence of sputter-coatings CaO on to Co polycrystalline surfaces, prior to oxidation. This allows to eliminate calcium effects on metal diffusion processes and to understand the difference observed with the oxidation of Ca-doped $Co_{1-x}O$ single crystals, in their stability range. The results have been analyzed taking into account the thermodynamic and transport properties of pure and Ca-doped $Co_{1-x}O$ single crystals, at equilibrium and under non equilibrium conditions, and a formal treatment based on the thermodynamic of irreversible processes (Petot-Ervas, 1990).

Theoretical Background

General Equations

Oxidation of $Co_{1-x}O$ is governed by cation exchanges with cationic vacancies α times negatively ionized (V^{α}'), whose concentrations depend on both, temperature (T) and oxygen partial pressure (P_{O2}) in thermodynamic equilibrium with the sample [5,6]. By application of the mass action law to the equation of formation of the prevailing defects in undoped $Co_{1-x}O$ ($½O_2 <=> O_O + V^{\alpha}' + \alpha h^{\circ}$) and according to the charge neutrality condition, one can show that (Kofstad ,1972; Philibert , 1991; Atkinson ,1985):

$$[h^{\circ}] = \alpha[V_{Co}^{\alpha'}] = AK_V^{1/(\alpha+1)} (P_{O2})^{1/2(\alpha+1)} \quad (1)$$

where K_V is the equilibrium constant of formation of defects, P_{O2} the oxygen partial pressure in the surrounding atmosphere, O_O an oxygen ion on its normal site, h° an electron hole, $A = \alpha^{1/(\alpha+1)}$ and square brackets denote concentrations in mole fraction.

The thermodynamic and transport properties of undoped and Ca-doped $Co_{1-x}O$ single crystals were determined from electrical conductivity measurements (Halem, 2022):

$$\sigma = e\,\mu\,p = \sigma_o (P_{O2})^{1/2(\alpha+1)} \exp(-\Delta H_{\sigma})/RT) \quad (2)$$

where e is the electrical charge of electrons, p the hole concentration per cm^3, μ the hole mobility, regarded generally as a thermally activated hopping process ($\mu = \mu_o \exp -\Delta H_{\mu}/RT$), ΔH_{σ} the enthalpy of conductivity, with $\Delta H_{\sigma} = (\Delta H_{\mu} + \Delta H_V)/(1+\alpha)$, ΔH_V the enthalpy of formation of the defects, ΔH_{μ} the hole enthalpy of mobility and α the mean electrical charge of the cobalt cationic vacancies, which can be determined from the slopes (Eqs.1,2) , (Atkinson ,1985; Halem , 2022).

$$(d\ln\sigma / d\ln P_{O2})_T = 1/2(\alpha+1) \quad (3)$$

One can recall that the thermodynamic properties of undoped and Ca-doped $Co_{1-x}O$ single crystals show that calcium has a reducing behaviour in $Co_{1-x}O$, leading to both, the formation of singly ionized cobalt cations (Co^{+}) and the shift of the Co/CoO and CoO/Co_3O_4 phase boundaries to higher and lower $P_{O2,}$ respectively (Halem, 2022). This reduction behavior, of elastic nature, is due to local strains when larger homovalent solute cations are present in oxides (Atkinson, 2012). The thermodynamic properties of Ca-doped samples are then governed by the formation of extrinsic defects ($Ca_{Co}^{x} <=> Ca_{Co}^{\bullet} + e'$), which influence the concentration of intrinsic defects (Eq.1) through the electroneutrality condition:

$$\alpha[V_{Co}^{\alpha'}] + [e'] = [h^{\circ}] + [Ca_{Co}^{\bullet}] \quad (4)$$

Transport Processes Under Non-Equilibrium Conditions

Statement of the Problem

Under non equilibrium conditions, fluxes of cations (J_i) and cationic vacancies (J_V) appear in p-type semi conducting oxides, coupled through the condition (Petot-Ervas, 1990; Kofstad ,1972; Schmalzried, 1986)

$$J_V + \Sigma J_i = 0 \quad (5)$$

Taking into account that no electrical current flows through the film ($I_t = FJ_h = 0$) and assuming a virtual local equilibrium between electrically charged species and neutral atoms ($A + \alpha h^{\circ} <=> A^{\alpha+}$) (Wagner, 1951; Wagner, 1975) has shown that in a p-type semi-semiconducting oxide the cationic fluxes in the "z" direction, with respect to the oxygen sublattice (or laboratory reference frame) can be written:

$$J_i = -\frac{C_i}{RT} D_i \frac{d\eta_i^{\alpha+}}{dz} = -\frac{C_i}{RT} D_i \left(\frac{d\mu_i^{\alpha+}}{dz} + z_i F \frac{d\Phi}{dz}\right) = -\frac{C_i}{RT} D_i \frac{d\mu_i}{dz} \quad (6)$$

where $d\mu_i/dz = RT d\ln a_i$ is the chemical potential gradient of the neutral species, $d\eta_i\alpha+/dz$ the electrochemical potential gradient of the charged species, F the Faraday constant, Φ the Nernst potential, $C_i = x_i C_M$ the cation concentration per unit volume (mol/cm^3), D_i the diffusion coefficient of cations i, z_i their valence and C_M the concentration of cationic sites in the lattice.

To express Eq.6 in a form including measurable parameters, it was assumed (Petot-Ervas, 1990) that in the solid solution (AO-BOγ) the concentration of BOγ ($x_{BO\gamma} = m$) is low enough ($x_{AO} << m$) that the Raoult law may be applied ($a_{AO} \approx x_{AO} = 1-m$). Therefore, taking into account the local equilibrium between the different species in each element of volume ($1/2O_2 + A <=> AO$, $\gamma/2O_2 + B <=> BO_\gamma$), it follows (Petot-Ervas, 1990):

$$J_A = -\frac{C_A}{RT} D_A \frac{d\mu_A}{dz} = C_M D_A \left[\frac{dm}{dz} + (1-m)\, d\ln a_O/dz\right] = C_M D_A \left[\frac{dm}{dz} + (1-m)\, \mathcal{F}\right] \quad (7)$$

$$J_B = -\frac{C_B}{RT} D_B \frac{d\mu_B}{dz} = -C_M D_B \left[\frac{dm}{dz} - m\,\gamma\, d\ln a_O/dz\right] = -C_M D_B \left[\frac{dm}{dz} - m\,\gamma\, \mathcal{F}\right] \quad (8)$$

where $\mathcal{F}$ is the external driving force of diffusion depending of the oxygen potential gradient ($d\ln a_O/dz$) across the oxide ($a_O = P_{O_2}^{1/2}$), which can be related to the cationic vacancy concentration gradient ($V^{\alpha\prime}$) (Eq.1) :

$$\mathcal{F} = d\ln a_O/dz = \tfrac{1}{2}\, d\ln P_{O_2}^{1/2} = (1+\alpha)\, d\ln[V^{\alpha\prime}]/dz \quad (9)$$

The previous equations (Eqs 7,8) show that the cationic fluxes are influenced by the kinetic demixing of cations (dm/dz) which occur in multi component oxides However, when the concentration of solute cations is very low (xCo>>xCa), the flux of solute cations can be neglected and the shift velocity of the oxidation front (Eqs.11,12) can be written:

$$v_{oxid} = J_V / C_M = -(J_A^{2+} + J_B^{\delta+})/C_M \approx -J_A^{2+}/C_M \quad (10)$$

Substituting Eq.7 in Eq.10, assuming that kinetic demixing processes (dm/dz) can be neglected, one obtains for the oxidation rate of a p-type semiconducting oxide (AO,BOγ) in presence of a driving force ($\mathcal{F}$):

$$v_{oxid} = -D_A \left[\frac{dm}{dz} + (1-m)\, \mathcal{F}_{(\text{Ca-doped CoO})}\right] \approx -D_A\, \mathcal{F}_{(\text{Ca-doped CoO})} \quad (11)$$

while for a pure oxide: $v_{oxid} = -J_A^{2+}/C_M = -D_A\, \mathcal{F}_{(CoO)}$ (12)

where $m = x_{Ca}$ and $(1-m) = x_{Co}$ are the mole fractions of calcium and cobalt cations in the cationic sublattice, respectively.

Kinetic Demixing in Ca-doped $Co_{1-x}O$ Single Crystals

From a practical point of view, experiments were performed in presence of an applied electric field. The experimental arrangement is described previously ((Monceau ,1994**)**. The driving force is then due to the cationic vacancy concentration gradient (Eq.9), which depends of the electric field, E (Monceau ,1994**)**:

$$\mathcal{F} = q_i E/kT. \quad (14)$$

where $q_i=z_ie$ is the charge of the diffusing species and k the Boltzman constant.

This driving force (Eq.14) leads to a flux of cations "i" toward the direction of the cathode, coupled to a flux of cationic vacancies in the opposite direction (Fig.1). During the transport processes the conservation of sites implies that (Eq.5):

$$J_V= -\Sigma J_i \quad (15)$$

New lattice sites are then formed at the surface where cations arrive and the shift velocity of displacement of this surface (v_i), with respect to the laboratory reference state (Schmalzried, 1986), (Monceau ,1994**),** (Mahiouz ,2018), is given by:

$$v_i=\Sigma J_i/C_i \quad (16)$$

Consequently, a concentration gradient (dx_i/dz) sets up progressively in an oxide (A,B,O) if the diffusion coefficients of cations A^{2+} and $B^{\alpha+}$ are different (Eqs.7,8).

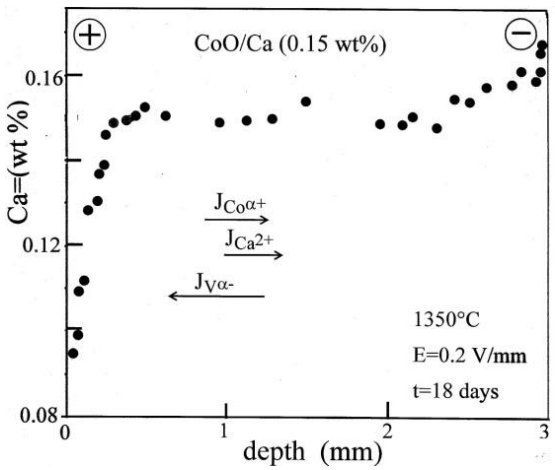

Figure 1. Kinetic demixing profile of a Ca^{2+} - doped $Co_{1-x}O$ single crystal, maintained in air under 0.2V, for 18 days at 1350°C.

In Fig.1, we have reported the kinetic demixing results in a Ca (0.15 wt%)-doped $Co_{1-x}O$ single crystal maintained under an applied electrical field (E) of 0.2 V/mm in flowing air, at 1350°C for 18 days. Starting from a homogeneous parallelepipedic single-crystal of 3mm long, EPMA analysis show an enrichment of calcium near the cathode. Therefore, it follows (Eqs.7,8) that:

$$D_{Ca}>D_{Co} \quad (17)$$

It should be noted that this result is in discrepancy with the results reported in literature for undoped $Co_{1-x}O$ single crystals (Fig.2), in equilibrium with the surrounding atmosphere (Dieckman ,1984), (Chen , 1980).

$$D^*_{Ca} < D^*_{Co} \quad (18)$$

This difference was explained by correlation effects (Eq.19), whose primary cause is due to the Ca^{2+}: size (Ca^{2+}: r=0.1nm, Co^{2+}: r=0.074nm, Co^{3+}/0.063nm]. Calcium influences the binding enthalpy (Δh_A) and the jump frequency (w) of a vacancy and a neighbouring cation close to a Ca^{2+} (Chen ,1980) :

$$(D^*_{Ca} / D^*_{Co}) = (w_{Ca}/w_{Co})\,(f_{Ca}/f_{Co})\exp(-\Delta h_A/kT) \quad (19)$$

where f_{Co} is the cobalt correlation factor in undoped $Co_{1-x}O$ (f_{Co}=0.78) and f_{Ca} a complicated function of all the jump frequencies in the vicinity of calcium cations in a Ca- doped $Co_{1-x}O$ samples (Philibert , 1991)

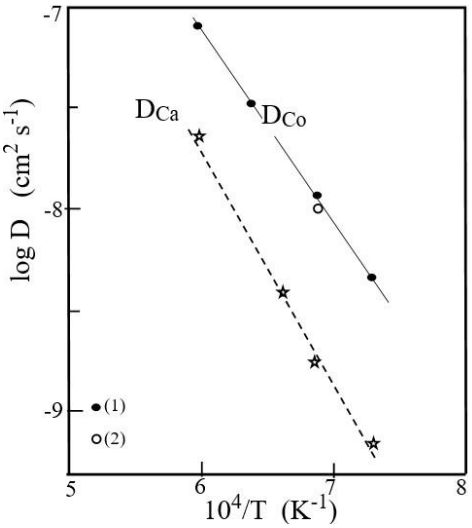

Figure 2. Arrhenius plot of the self-diffusion coefficient of cobalt (Dieckman ,1984), (Chen , 1980). and of the diffusion coefficient of Ca^{2+} [16] in undoped $Co_{1-x}O$ single crystal, at P_{O2}=0.21 atm.

Experimental Results

Oxidation in the Stability Range Of Undoped and Ca-doped $Co_{1-x}O$ Single Crystals

Oxidation Results

The experiments have been performed by measuring the electrical conductivity of a single crystal as a function of time, following a sudden change in external P_{O2} (Farhi ,1978), at constant temperature. Just after the change of P_{O2}, the point defect concentrations near the gas/oxide interface (Eqs1,4) correspond to the new imposed equilibrium conditions. Therefore, a defect concentration gradient sets up near the surface, leading to defect fluxes in the oxide. They develop in the bulk and decrease then, to disappear after a time ″t″, when the new equilibrium conditions are reached. The effective diffusion coefficient of the defects, being due to a vacancy concentration gradient (dx_V/dz), is called chemical diffusion coefficient ($\widetilde{D}$). According to the Fick law, the coupled fluxes of cations (J_i) and cationic vacancies (J_V) can be written (Kofstad ,1972; Philibert , 1991; Halem , 2022),

$$J_V=-\Sigma J_i =-\widetilde{D}\ (dx_V/dz) \qquad (20)$$

The chemical diffusion coefficient ($\widetilde{D}$) allows to determine the mean penetration depth (Δz) of the oxidation (or reduction) front in the oxide, after a time t, and to evaluate the time to reach the new thermodynamical equilibrium conditions of the sample (Kofstad ,1972; Farhi ,1978)

$$\Delta z=\sqrt{\widetilde{D}t} \qquad (21)$$

As an example, we have reported in Fig.3 the electrical conductivity results after 5000 s, at 1000°C. They were obtained with a brick–shape sample (5x2x2mm) of undoped and Ca-doped $Co_{1-x}O$ single crystals after an abrupt change of P_{O2}, between 10^{-3}atm (argon) and 0.21atm (air). These results show that calcium increases the oxidation kinetics from the beginning of the oxidation. One can recall that the first terms of the general equation of these representations are rapidly negligible when the time increases and the simplified relation is given by the following expression (Farhi ,1978) :

$$\left(\frac{\sigma(t)-\sigma_\infty}{\sigma_0-\sigma_\infty}=\left(\frac{8}{\pi^2}\right)^3 \exp\left[-\pi^2\left(\frac{1}{H^2}+\frac{1}{L^2}+\frac{1}{l^2}\right)\widetilde{D}t\right]\right). \qquad (22)$$

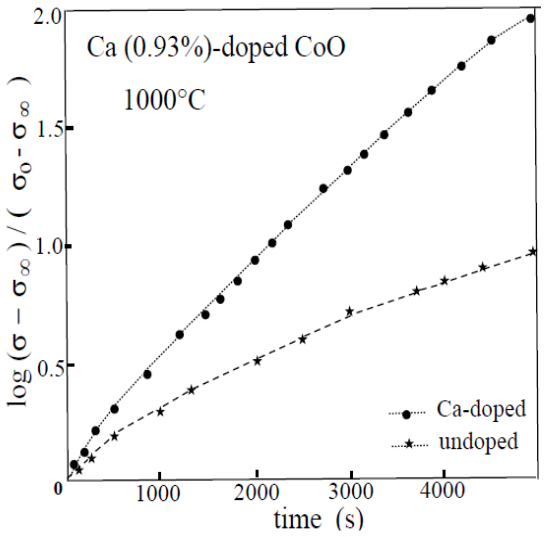

Figure 3. Re-equilibration kinetics of pure and Ca-doped $Co_{1-x}O$ single crystal after an abrupt change of P_{O2} (argon ⇨ air), followed by electrical conductivity measurements as a function of time, at 1000°C.

The chemical diffusion was then determined from the linear plots of log $(\sigma(t)-\sigma_\infty)/\sigma_0-\sigma_\infty)$ as a function of time. The Arrhenius plots of the values of $\tilde{D}$ obtained with undoped and Ca-doped $Co_{1-x}O$ single crystals are reported in Fig.4. In agreement with the results reported in Fig.3, they show that calcium leads to an increase of the chemical diffusion, i.e. of the oxidation kinetic of $Co_{1-x}O$ in it stability range (Halem, 2022). The kinetic demixing processes being negligible ($x_{AO}<<x_{BO\gamma}$), the chemical diffusion coefficient of undoped and of diluted solid solution (AO-BOγ) can be expressed by the relation (Kofstad ,1972; Philibert , 1991; Halem , 2022):

$$\tilde{D} = (1+\alpha)\, D_V \qquad (23)$$

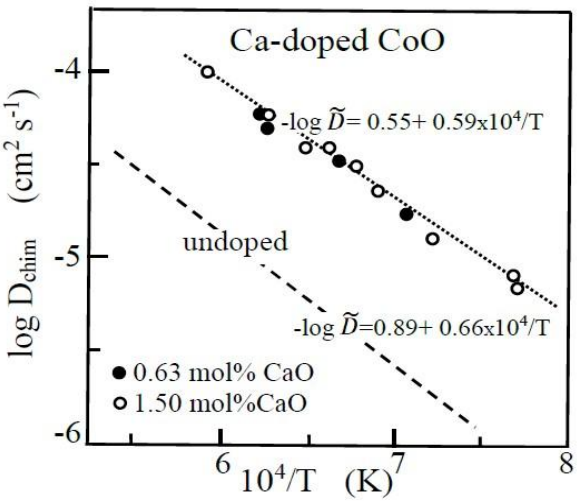

Figure 4. Arrhenius plots of the chemical diffusion coefficient of undoped and Ca-doped $Co_{1-x}O$ single crystals.

According to the close values of the mean charge (α) of the cationic vacancies in doped and undoped single crystals, for $P_{O2}>10^{-3}$atm [8], the greater chemical diffusion coefficient values determined for the doped samples (Fig.4) is due to an increase of the diffusion coefficient of the cationic vacancies:

$$D_V\text{ (Ca-doped CoO)} > D_V\text{ (undoped CoO)} \qquad (24)$$

Therefore, taking into account that the diffusion coefficient of the cationic vacancies depends of the diffusion coefficient of cations

$$x_V D_V = x_{Co}\, D_{Co} + x_{Ca}\, D_{Ca} \approx D_{Co} \quad (25)$$

and that the concentration of electron holes and cationic vacancies are not significantly influenced by calcium in the doped samples, for $P_{O2}>10^{-3}$atm (Halem , 2022), it follows that:

$$D_{Co}(\text{Ca-doped CoO}) > D_{Co}\,(\text{undoped CoO}) \quad . \quad (26)$$

Consequently, for $P_{O2}>10^{-3}$ atm, the higher oxidation rate of Ca-doped $Co_{1-x}O$ single crystals (Figs 3,4) is mainly due to an increase of the cobalt diffusion coefficient (D_{Co}) in these samples.

Thermal Oxidation of Uncoated and CaO-coated Cobalt Polycristals

Oxidation Results

Metal specimens were square cobalt coupons (0.4cm^2 by 01cm thick), sintered from high purity Johnson Mattey cobalt powders. As described previously (Mahiouz ,2018), (Aïdrous ,2014), the coupons were first oxidized at 1250°C. The oxide scale was removed on one main surface (0.4cm^2), which was then polished to a 1μm diamond finish. The coating deposition on this face was achieved by sputtering a CaO target in an ambient of $7x10^{-2}$ mbar argon, during one hour and under the deposition energy of a few eV, causing no sample heating during deposition. Deposited films were uniform in thickness (≤50nm), without crack and spall.

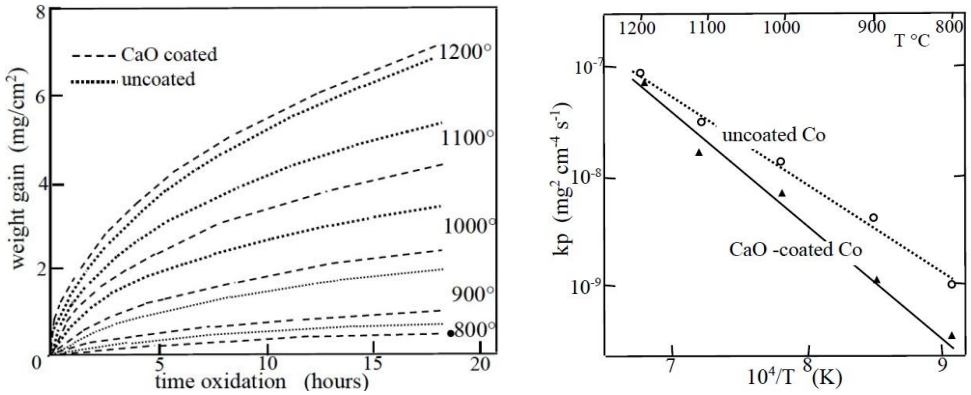

Figure 6.a. Weight gain versus time of uncoated and CaO coated cobalt polycrystals, under P_{O2}=0.21 atm.

Oxidation experiments were performed in a Setaram thermobalance (Mahiouz ,2018), (Aïdrous ,2014), (Halem, 2016) by following the weight-gain as a function of time, from 800° to 1200°C (Fig.6a). At temperatures lower than 1200°C, these results show that CaO coatings reduce the oxidation rates. Furthermore, in agreement with the Wagner theory (Kofstad, 1988), these results follow parabolic law (Fig.6b), and the weight gain per unit area (Δ m/s) can be expressed by the following relation:

$$(\Delta \text{ m/s}) = k_p \sqrt{t} + k_o \quad (27)$$

where kp is a parabolic rate constant.

3.3.2 Composition of scales

T

The calcium profile through the oxidation layers developed on CaO-coated cobalt was determined on fracture sections, by EPMA analyses. At 900°C, the profile presents a maximum in a localized zone, which coincides approximately with the position of the initial cobalt surface. From either side of this maximum, the amount of calcium is low and increases in the outer layer, in agreement with the kinetic demixing of calcium in Ca-doped $Co_{1-x}O$ single crystals (Fig.1). When the temperature increases, the calcium becomes progressively more diluted in the thicker layers. At 1100°C, its shows only a small increase close to the metal/oxide interface, due to equilibrium segregation.

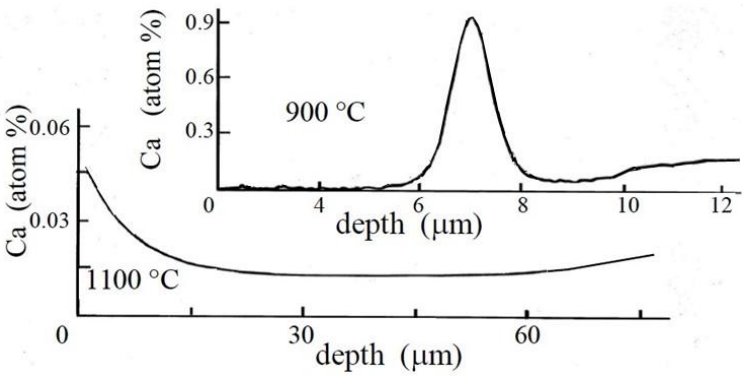

Figure 7. Calcium concentration–depth profiles in oxide films, after 18h of oxidation at 900°C and 1100°C. Metal/oxide interface taken as initial position of analysis.

Discussion

The results reported previously show that CaO coatings reduce the oxidation kinetics of cobalt at T<1200°C (Fig 6). They have been analyzed taking into account the thermodynamic and transport properties of undoped and Ca-doped $Co_{1-x}O$ single crystals [8].

Taking into account that the calcium concentration is low in oxidation layers developed on CaO-coated cobalt (Fig.7), their rate of growth can be described by Eqs.11,12:

CaO-coated cobalt polycrystals: $v_{oxid} \approx - D_{Co}\, \mathcal{F}_{(Ca\text{-}doped\ CoO)}$ (28)

uncoated cobalt polycrystals: $v_{oxid} = - D_{Co}\, \mathcal{F}_{(CoO)}$ (29)

with $\mathcal{F} = d\ln a_O/dz = d\log (P_{O2})^{1/2}/dz$ (30)

These relations predict that the rate of oxidation of coated and uncoated cobalt polycrystals depends of the diffusion coefficient of cobalt (D_{Co}) and of the driving force of diffusion ($\mathcal{F}$).

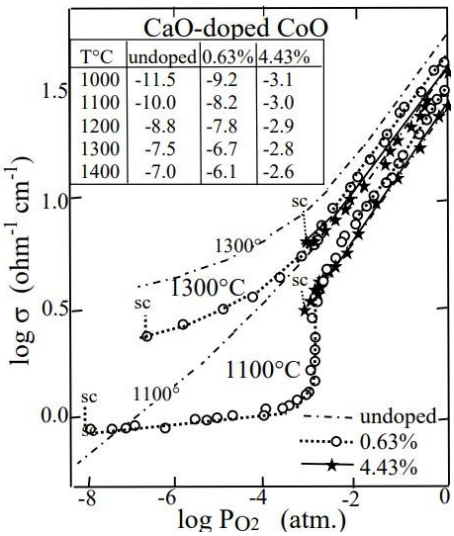

Figure 8. Influence of the calcium concentration on the electrical conductivity of undoped and Ca-doped $Co_{1-x}O$, at 1100° and 1300°C (Halem,2022) The dissociation pressure of undoped and Ca-doped $Co_{1-x}O$ single crystals is reported in the Table between 1000° and 1400°C. It is also indicated (sc) on the □ plots

Concerning the driving force of diffusion (Eq.30), it depends of the oxygen potential gradient across the oxidation scale. The shift of the $Co/Co_{1-x}O$ phase boundary to higher P_{O2} [8] in Ca-doped $Co_{1-x}O$ single crystals (Fig.8), all the more important that the calcium amount in the oxide is high, leads to a decrease of the oxygen potential

gradient ($dlna_O/dz$) across the oxidation layer. It follows a decrease of F and of the oxidation kinetics of the CaO-coated $Co_{1-x}O$ polycrystals, as it was observed experimentally, at T<1200°C(Fig.6).

When the temperature increases, the calcium concentration in the oxidation layer (Fig.7) decreases. The transport processes are then controlled progressively by the same parameters of the uncoated samples and, at T=1200 °C, the experimental results (Fig.6) show that the oxidation rates of uncoated and CaO-coated cobalt polycrystals are practically the same.

Conclusion

This set of results was analyzed taking into account the thermodynamic and transport properties of undoped and Ca-doped $Co_{1-x}O$ single crystals and a formal treatment, based on the thermodynamic of irreversible process. From the general expressions obtained, it was shown that the rate of oxidation is mainly controlled by a competitive effect of D_{Co} and F.

Concerning the oxidation of undoped and Ca-doped CoO single crystals, the results being obtained in the same oxygen partial pressure range (same driving force of diffusion), they are only influenced by the diffusion of cations. In agreement with the increase of D_{Co} in Ca-doped $Co_{1-x}O$ single crystals (Eq.26), they show that calcium leads to an increase of the oxidation kinetic in the stability range of the oxide.

Concerning the CaO-coated cobalt polycrystals, the shift of the $Co/Co_{1-x}O$ phase boundary to higher P_{O2} (Fig.8) in Ca-doped $Co_{1-x}O$ single crystals to higher P_{O2}, all the more important that the calcium amount in the oxide is high, leads an decrease of the driving force of diffusion (F) and of the oxidation kinetics of the CaO-coated polycrystal (Fig.6). When the temperature increases, the calcium concentration in the oxidation layer decreases with the thickening of the layer. The oxidation kinetics are then progressively controlled by the same parameters than uncoated samples and, at T=1200°C, the experimental results show that the oxidation rates of uncoated and CaO-coated Co samples are practically the same.

Scientific Ethics Declaration

* The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Conflict of Interest

* The authors declare that they have no conflicts of interest

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