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Thermodynamic and transport properties of Ca-doped nickel oxide and relevance to the oxidation of CaO-coated- nickel

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ABSTRACT

The electrical conductivity and thermoelectric power of CaO (2 and 2.6 mol%)-doped $Ni_{1-x}O$ single crystals have been measured in the temperature range 1000–1400 °C, as a function of oxygen partial pressure. These results show that Ca^{2+} leads to the shift of the $Ni/Ni_{1-x}O$ phase boundary to higher P_{O2}, to a doping effect and to a mixed conductivity (e' and h), at $P_{O2} < 10^{-4}$ atm. From electrical conductivity measurements in transient state, it was found that the chemical diffusion coefficient and the cationic vacancy diffusion coefficients are higher in the doped samples than in undoped $Ni_{1-x}O$. Furthermore, kinetic demixing experiments in an applied electric field show that $D_{Ca} > D_{Ni}$, due to the decisive role of correlation effects in the Ca-doped samples. These results have allowed us to explain the beneficial influence of CaO coatings on the oxidation of Ni polycrystals, at $T < 1200$ °C. It was found that the key features are the decrease of the driving force of diffusion due to the shift of the Ni/NiO phase boundary to higher P_{O2}, which increases with the amount of calcium, and blocking effects due to CaO precipitates near the position of the original metal surface, all the more important that the temperature is low and the oxidation time short.

1. Introduction

When Ni-based alloys are used in oxidizing environments, at high temperature, many instances have shown [1–8] that small additions of reactive cations, such as Ca^{2+}, Ce^{4+}, Al^{3+} or Zr^{4+}, for instance, usually lead to a reduction in the growth rate of the oxidation scale and to an improvement of the oxide adhesion to the substrate. During the high temperature oxidation, these cations are incorporated into the growing oxide scale influencing the diffusion processes. However, in spite of the importance of these effects in materials in which high temperature corrosion resistance is required, such as super-alloys, many important mechanisms still remain unexplained. This is mainly because of the complexity of the metal/oxide reactivity with respect to oxygen, which results from the interplay between several factors. Consequently, introduction of reactive elements as surface coatings has the advantage to eliminate their effect on the metal diffusion processes. If transport properties in the oxide are known, then the chances to get a better insight regarding the mechanism of scale growth are improved.

In the present study, coatings were produced by sputtering a target of CaO directly on polycrystalline nickel coupons. Thermogravimetric analysis and structural characterizations were performed to study their effect on both nickel oxidation kinetics and oxide layer morphologies. These results have been analyzed taking into account the thermodynamic and transport properties of undoped and Ca-doped $Ni_{1-x}O$ single crystals, at equilibrium and under non-equilibrium conditions.

2. Materials and methods

2.1. Electrical conductivity and Seebeck coefficient measurements

The brick-shaped samples (typically 5 × 2 × 2 mm) were cut from single crystals prepared from Johnson Mattey high purity powders (impurity content <10 ppm) in an arc image furnace [9–11,20]. They were annealed in air at 1300 °C, for 2 or 3 weeks, to remove any remaining strains and in-homogeneities from the growth. Their main impurities are Si (5–8 ppm), Cr (0.5–2.0 ppm) and Al (0.5–2.0 ppm). Details of the experimental arrangement were given elsewhere [9–13,20]. The electrical conductivity and Seebeck coefficient (or thermoelectric power) measurements were performed with the same specimens. The thermoelectric power ($Q = \Delta V/\Delta T$) of the sample, put in a temperature gradient included between 20 and 50 °C, was obtained from the voltage (ΔV) measured at the cell platinum terminals (A and B): (A) Pt^{To}–Pt^{T1}/$Ni_{1-x}O$/Pt^{T2}–Pt^{To} (B), corrected by the voltage generated by the platinum junctions [13–15,20]. The oxygen partial pressure was measured near the sample using a zirconia electrochemical gauge [9–13,20].

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2.2. Corrosion experiments

The metal specimens were square coupons (1 cm^2 by 0.1 cm thick). They were cut from polycrystals ($d \approx 97\%$), prepared from high purity Johnson Matthey nickel powders (99.995 wt.%), isostatically pressed at 1000 bar, and sintered at 1100 °C, during 3 h, under a secondary dynamic vacuum. To ensure the reproducibility of the experiments a standard preparation of the oxidation surface was followed. The coupons were first oxidized at 1250 °C, for 30 h. The oxide scale was removed on one main surface (1 cm^2), which was then slightly polished to a 1 μm diamond finish. The coating deposition on this face was achieved by sputtering a CaO target in an ambient of 7×10^{-2} mbar argon, during 1 h. The advantage of the cathodic deposition method used in this work is its simplicity, its high degree of control and the energy of deposition of only a few electronvolts, causing no sample heating during deposition. Deposited films were uniform in thickness (usually ≤50 nm) and without crack and spall.

Oxidation experiments were carried out at temperatures between 800° and 1200 °C, in a Setaram thermobalance [8]. The samples, suspended to a platinum wire, were rapidly brought into the hot zone of the apparatus in high purity flowing argon. Isothermal weight changes were followed in flowing air, during 18 h. At the end of the thermal treatments, the specimens were rapidly cooled down under argon. The microstructure of the oxide scales was examined by optical (OM) and scanning electron microscopy (SEM) and their composition was evaluated by EPMA analysis.

3. Transport properties of pure and Ca-doped $Ni_{1-x}O$ single crystals

3.1. General equations

One can briefly recall that $Ni_{1-x}O$ is a member of an important series of transition metal oxides having a rock-salt crystal structure and which are cation deficient p-type semiconductors [8–12,14–19]. The prevailing defects are electron holes (h°) and α time ionized cationic vacancies ($V_M^{\alpha'}$), whose concentrations depend of both temperature (T) and oxygen partial pressure (P_{O2}) in equilibrium with the sample [8]:

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

where O_O is an oxygen ion in a normal site, $A = \alpha^{1/(\alpha+1)}$, K_V the equilibrium constant of formation of the defects ($\frac{1}{2}O_2 <=> O_O + V^{\alpha'} + \alpha h^\circ$) and the square brackets denote concentrations in mole fractions.

It is worth noting that PEELS analysis performed in undoped and Ca-doped $Co_{1-x}O$ single crystals [20,21] has allowed us to show that Ca^{2+} behaves as a reducing cation in $Co_{1-x}O$, leading to the formation of singly ionized cobalt cations (Co^+). This is likely due to size effects ($\Phi_{Ca}2+ = 0.99$ Å, $\Phi_{Co}2+ = 0.74$ Å). A similar effect is expected in $Ni_{1-x}O$ ($\Phi_{Ni}2+ = 0.72$ Å), whose properties are close to those of $Co_{1-x}O$. It is then suggested that calcium leads to the formation of singly ionized nickel cations (Ni^+). Consequently, when one substitutes on a Ni^+ site a divalent Ca^{2+} impurity, the defect (Ca_{Ni}) will have an effective single positive charge. The oxide properties are then also governed by the equilibrium:

$$Ca_{Ni}^{x} <=> Ca_{Ni}^{\cdot} + e' \quad (2)$$

A Ca^{2+} in substitution on a Ni^+ site then influences the concentration of defects (Eqs. (1) (2)) through the electroneutrality condition:

$$\alpha\left[V_{Ni}^{\alpha'}\right] + [e'] = [h^\circ] + \left[Ca_{Ni}^{\cdot}\right] \quad (3)$$

where [e'] and [h°] are the molar fractions of electrons and electron holes, respectively.

3.2. Calcium diffusion in $Ni_{1-x}O$

To our knowledge, the diffusion coefficient of calcium (D_{Ca}) in $Ni_{1-x}O$ was until now the only available data concerning this cation [22]. The Arrhenius plot is reported in Fig. 1, together with the nickel self-diffusion coefficient D_{Ni}^* [24] whose defect concentration dependence obeys the following equation [19,23–25]:

$$D_{Ni}^* \approx f_{Ni}\left[V_{Ni}^{\alpha'}\right]D_V = f_{Ni}\left[V_{Ni}^{\alpha'}\right]a^2 w_o \quad (4)$$

In this expression f_{Ni} is the correlation factor in undoped $Ni_{1-x}O$ ($f_{Ni} = 0.78$), D_V is the diffusion coefficient of cationic vacancies, a is the lattice parameter and w ($= \nu \exp(\Delta S_m/R)\exp(-\Delta H_m/RT)$) is the rate of exchange between a vacancy and a neighbouring cation, related to the vibration frequency (ν) of an atom about its equilibrium position and to the entropy (ΔS_m) and enthalpy (ΔH_m) of migration of the defects.

If the calcium impurity diffuses by the same point defect mechanism as the host, it diffusion coefficient D_{Ca}^* is related to (D_{Ni}^*) by the relation [24,25]:

$$(D_{Ca}^*/D_{Ni}^*) = (w_{Ca}/w_{Ni})\,(f_{Ca}/f_{Ni})\exp(-\Delta h_A/kT) \quad (5)$$

The observed difference between D_{Ca}^* and D_{Ni}^* (Fig. 1) can be explained by size effects. Indeed, if the correlation factor for impurity diffusion (f_{Ca}) is a complicated function of all the jump frequencies in the vicinity of the impurity, the higher ionic radius of Ca^{2+} (0.99Å) compared to that of Ni^{2+} (0.72Å) influences the impurity-vacancy binding enthalpy (Δh_A) [25] and the exchange frequency (w) between a vacancy and a neighboring ion

3.3. Electrical conductivity in thermodynamical equilibrium condition

For a p-type semiconducting oxide (Eq. (1)), the electrical conductivity (σ) is mainly controlled by electron holes [8,9,16]:

$$\sigma = e\mu p = \sigma_o(P_{O2})^{1/2(\alpha+1)}\exp(1/RT)\left[-\Delta H_\mu - \Delta H_v/(1+\alpha)\right] \quad (6)$$

where e is the charge of the electron, 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_μ the hole enthalpy of mobility and

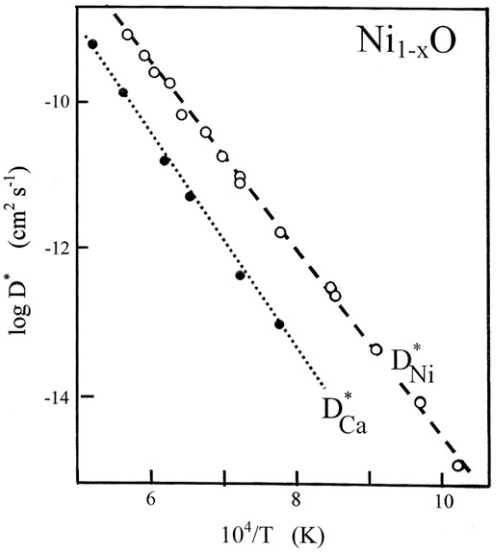

Fig. 1. Arrhenius plot of the self-diffusion coefficient of nickel [24] and of the diffusion coefficient of Ca^{2+} in nickel oxide [22], at $P_{O2} = 0.21$ atm.