Grain boundary segregation of impurities and point defects in ionocovalent materials
The case of NiO bicrystals

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Abstract

Point defects and impurities may interact with an extended defect: surface, dislocation, grain boundary, etc.... Such an interaction leads, at thermodynamic equilibrium, to a species concentration in extended defects different from the bulk's, together with electrical charge phenomena; such concentrations, in the proximity of these interfaces, vary in turn, to screen the core charge; a redistribution of these entities can then be observed showing concentration profiles, thereby indicating a segregation phenomena.

The aim of our work falls in with that framework and consists firstly in studying the segregation and potential of three impurities, namely, Aluminium, Cobalt and Cerium in NiO bicrystal grain boundaries, for two given orientations, $F(1\bar{2}2)/[011]$ and $F(310)/[001]$.

The problem is tackled in the case of diluted solutions as well as real ones; for the latter, the use of Debye–Hückel theory enables us to calculate the activity coefficients of the given species whose values have a significant effect upon the variations of the impurities intergranular concentration curves.
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1. Introduction

It is nowadays taken for granted that interfacial segregation influences a good many crystalline material properties, such as growth, corrosion, creep or diffusion [1,2].

However, our knowledge of the link between this phenomenon and the grain boundary structure (and even more, its structure defects) is not comprehensive enough, and requires numerous efforts from the theoretical standpoint as well as experimental one, especially in oxides.

Among the latter, nickel oxide is a very interesting illustrative case because it is an ionocovalent compound, nonstoichiometric, having p-type semi-conductor properties in which the prevailing defects are Nickel vacancies charged once or twice negatively, V'_{Ni} and V''_{Ni} [3].

The characteristics of grain boundaries have been the object of numerous studies on the experimental [4,5] as well as theoretical approaches [6–8]. It has been proved, for instance, through static calculations, that the introduction of a Schottky pair (a cationic plus anionic vacancies grain boundary) per unity of the coincidence network has a stabilizing effect on the structure of the NiO twist grain boundary $\Sigma 5(310)/[001]$.

Moreover, such studies have highlighted not only the role played by point defects on the stability of ionic material grain boundaries, but also the fact that the latter may be formed by the coupling together of imperfect surface.

The intergranular segregation phenomena that spring up at thermodynamic equilibrium conditions produce an accumulation of defects and impurities charged at the grain boundary plane, thus locally breaking up the crystal electroneutrality. This charge excess is compensated by the formation of a space charge zone, of opposite sign, due to the redistribution of all the charged species in which the segregating element concentration is modified [9].

Falling in with that framework, our contribution has a twofold objective; the first consists in studying the influence of the impurity type on segregation in NiO by calculating its

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concentration variation, as well as that of the electrical potential in terms of the grain boundary distance. The second objective concerns the study of the orientation effect of the grain boundary on segregation.

To do so, calculations on NiO doped Al, Co and Ce with two grain boundary types $F(1\bar{2}2)/[011]$ and $F(310)/[001]$ are carried out. The respective equilibrium of the prevailing defects within their sub-networks as well as the impurities likely to segregate are described according to the formalism of Kröger and Vink [10] and this, in the case of diluted and real solutions, on the basis, for the latter, of the Debye–Hückel [11].

2. Bases of the model

Let us consider the segregation of two charged species, $Y_M^{\bullet}$ and V_M', in a bicrystalline compound MX, on the sites (M, S) of a grain boundary favorable to the M type. The signs " $'$ " and " $\bullet$ " recall the fact that the defects introduce negative or positive charges with regard to the species normally occupying the M sub-network site. The Kröger and Vink formalism enables us to write the formation equations of these entities in the following way:

$$Y_M^{\bullet} + M_{M,S}^{\times} \leftrightarrow Y_{M,S}^{\bullet} + M_M^{\times} \tag{1}$$

$$V_M' + M_{M,S}^{\times} \leftrightarrow V_{M,S}' + M_M^{\times}. \tag{2}$$

$Y_M^{\bullet}(V_M')$ and $Y_{M,S}^{\bullet}(V_{M,S}')$ represent, respectively, Y impurities (M vacancies) charged once positively (once negatively) and occupying a site of the M sub-network, in bulk and at the grain boundary, in segregated position.

$M_M^{\times}$ and $M_{M,S}^{\times}$ are neutral M atoms occupying, respectively, one site of the volume and another one of the grain boundary.

Each of these equilibriums is characterized by a difference in free standard energy and such disymmetry leads to an excess of one of the two species from the grain boundary core and therefore, to a clear-cut charge responsible for the presence of a potential difference $\Phi(x=0)=\Phi_0$ in relation to the bulk.

The mass action law of reactions (1) and (2) gives us:

$$K_Y^{Seg} = \frac{a_{Y_{M,S}^{\bullet}} a_{M_M^{\times}}}{a_{Y_M^{\bullet}} a_{M_{M,S}^{\times}}} = \exp-\frac{\Delta G_{Y^{\bullet}}^{Seg}}{k_B T} \tag{3}$$

$$K_{VM}^{Seg} = \frac{a_{V_{M,S}'} a_{M_M^{\times}}}{a_{V_M'} a_{M_{M,S}^{\times}}} = \exp-\frac{\Delta G_{V_M'}^{Seg}}{k_B T} \tag{4}$$

where K_i^{Seg}, ΔG_i^{Seg} and a_i stand for, respectively, the segregation constant, the free enthalpy of segregation and the activity of species i.

Generally speaking, the thermodynamic activity a_i is connected with the concentration of a given entities C_i by:

$$a_i = \gamma_i C_i \tag{5}$$

with γ_i, the activity coefficient.

In case the segregating species i are charged, the electrochemical potential η_i can be considered as constant in the whole material; it is written:

$$\eta_i = \mu_i + q_i \phi = \mu_i + Z_i e\phi \tag{6}$$

where μ_i stands for the chemical potential of species i, of $q_i=Z_i e$ charge, e representing the electron charge and Z_i a number that depends on the considered elements; it can be expressed as:

$$\mu_i = \mu_i^0 + k_B T \log a_i \tag{7}$$

μ_i^0 corresponds to the reference state (far from the grain boundary, for example), k_B, the Boltzmann constant and T, the absolute temperature.

The equality of electrochemical potentials at any given point x and to infinity, gives:

$$\eta_i(x) = \eta_i(\infty). \tag{8}$$

That is to say:

$$C_i(x) = \frac{\gamma_i(\infty)}{\gamma_i(x)} C_i(\infty) \exp\left(-\frac{Z_i e\phi(x)}{k_B T}\right) \tag{9}$$

where $\Phi(\infty)$ is assumed equal to zero.

It is to be noticed that if the defect and the impurity concentrations are weak, the ratio of activity coefficients is close to the unity, $\forall x$.

Besides, if the considered grain boundary is flat, the effective charge density ñ and the electrical potential must yield to the one-dimension Poisson equation:

$$\frac{\partial^2 \phi(x)}{\partial x^2} + \frac{4\pi}{\varepsilon} \rho(x) = 0 \tag{10}$$

where ε stands for the material dielectric constant.

$\rho(x)$ is also determined by the charged species concentrations:

$$\rho = Ne \sum_i Z_i C_i. \tag{11}$$

N representing the crystal molecule number per volume unity.