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Contributed Paper

Theory of Doping in Indirect Determination of Concentration and Mobility of Native Point Defects in Metal Oxides

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ABSTRACT

In the present paper the application of doping effect to the calculations of concentration and mobility of point defects in transition metal oxides has been discussed. The proposed method consists in determination of the deviation from stoichiometry and thereby the concentration of prevailing point defects in a given oxide from the influence of aliovalent additions on the formation kinetics of this oxide, i.e., from doping effect. The possibilities offered by this method have been illustrated using diluted binary Ni-Cr and Ni-Li alloys, from the oxidation rates of which the defect concentration and defect mobility in Ni_{1-y}O have been calculated. It has been shown that the results of such calculations are in satisfactory agreement with experimentally determined data, using direct gravimetric method.

Keywords: doping effect, nonstoichiometric nickel oxide, oxidation kinetics, defect concentration, defect mobility

1. INTRODUCTION

It is well known that small amounts of impurities in pure metals may in some cases dramatically influence on the oxidation rate of these metals at high temperatures [1-5]. Such a situation is a result of the fact that the oxidation rate at enough high temperatures (at which the formation of the oxidation product of the metal called scale, is controlled by lattice diffusion), strongly depends on the native point defect concentration in the growing oxide and impurities can radically change the concentration of these defects. This effect, known as the doping effect,

may play an important role, if the grain-boundary diffusion can be neglected and the concentration of native point defects in the growing oxide on pure metal is very low. At present, it is generally assumed in the literature that the doping effect depends virtually only on the valency of impurity atoms. It has been found, for instance, that three-valent chromium cations increase the oxidation rate of nickel, while univalent lithium cations provide opposite effect⁶. It should be noted, however, that in addition to the native point defect concentration and

the valency of impurity, the mode of impurity dissolution (incorporation) into the crystal lattice of the growing scale may decisively influence the rate of corrosion and the mechanism of scale growth [1-3,7]. The influence of impurity on the oxidation rate at high temperatures is generally explained in terms of Hauffe-Wagner theory [5]. If, on the other hand, grain boundary diffusion predominates and the impurities accumulate along grain boundaries, like in the case of chromium oxidation, their influence may not be considered in terms of doping in classical sense of this term.

Doping effect in sense of Hauffe-Wagner theory [5] allows for the control of the type and concentration of predominant point defects in transition metal oxides. It plays an essential role in the case of defect dependent properties or processes (mass transport in solids, solid state reactions, high temperature creep, electronic conductivity, thermoelectric power, electro-optical properties, etc.). Consequently, defect concentration in transition metal oxides are being extensively studied since more than 50 years in many scientific centers in the world [1-9].

It should be noted, that doping effect can also be used for determination of concentration and mobility of native point defects in metal oxides. The description of such possibility is the purpose of this work. The idea of proposed method is based on the assumption that the deviation from stoichiometry and thereby the concentration of prevailing point defects in a given oxide can be calculated from the influence of aliovalent metallic additions on the oxidation kinetics of a given metal, in the reaction product of which the nonstoichiometry is calculated, i.e. from doping effect. The validity of this method has been proved using diluted binary Ni-Cr and Ni-Li alloys, from the oxidation rates of which the concentration

and mobility of defects in nonstoichiometric nickel oxide, $Ni_{1-y}O$, have been calculated.

Basis of The Method

The proposed method is based on the chemistry of point defects in ionic crystals [1-3, 10, 11], Wagner's theory of metal oxidation [12] and Wagner-Hauffe theory of doping [5]. First of all, it is assumed that the oxidation process of both, pure metals and diluted binary alloys proceeds in agreement with parabolic rate law, being thus diffusion controlled.

The discussed method consists in the calculating of enthalpy and entropy of defect formation and their migration in a given oxide from the comparison of the kinetics of the oxidation of appropriate two binary alloys carried out as a function of temperature and oxidant activity, with theoretical relationships, describing these processes. Determination of these thermodynamic parameters allows for the calculation of the concentration and the mobility of predominant defects in the studied oxides as a function of temperature and oxidant activity. The difference between two applied alloys consists in the formation of solid solution oxide scales, in which the oxidation state of alloying addition is higher or lower than the oxidation state of a given metal in the oxide of which the concentration and the mobility of defects is to be determined. This difference is reflected in different dependence of oxidation rate on temperature and oxidant partial pressure.

It should be pointed out that in order to derive theoretical relationships necessary for interpretation of the results of kinetic rate measurements, one has to know the type of predominant defects in the studied oxide. In particular, it is necessary to know if cation or anion sub-lattice is predominantly defecting and if the defects are cation or anion vacancies

or else interstitials. The degree of defect ionization should also be known. In fact, these information are already available in the majority of cases. In those ones, when these information are not available, the application of discussed method must be preceded by appropriate investigations, using well known experimental methods, like marker [13-18] or two-stage oxidation techniques [19-21], using radioactive or stably isotopes.

Experimental Verification

The proposed method was verified on the example of nonstoichiometric nickel oxide, Ni_{1-y}O , in which defect concentration and defect mobility have been calculated from the results of oxidation rates of diluted binary Ni-1at.%Cr and Ni-1at.%Li alloys [6]. It should be noted that nonstoichiometric nickel oxide is very good example for verification of proposed method, because deviation from stoichiometry, y , in Ni_{1-y}O as well as the defect mobility in this material have been lately determined as a function of temperature and oxygen activity, using direct thermogravimetric technique [22,23]. Consequently, the results obtained in direct experimental procedures with those calculated from proposed method can be easily compared.

Before the description of succeeding steps leading to the calculated values of y in Ni_{1-y}O , the thermodynamics of point defects in this oxide must shortly be mentioned. It is known that doubly ionized cation vacancies and electron holes are the predominant point defects in nonstoichiometric nickel oxide [22,23]. These defects are created according to the following reversible quasi-chemical reaction:



where V_{Ni}'' and h^\bullet denote double ionized cation vacancies and electron hole, respectively; O_{O}^x is the oxygen ion in normal lattice site (Kröger-Vink notation [24] of defects is used throughout of this paper).

Applying to this defect equilibrium the mass action law and the appropriate electroneutrality condition one obtains the following dependence of the concentration of cation vacancies and electron holes on oxygen pressure at a given constant temperature:

$$[V_{\text{Ni}}''] = \frac{1}{2}[h^\bullet] = \left(\frac{1}{4}K\right)^{1/3} \cdot p_{\text{O}_2}^{1/6} \quad (2)$$

where rectangular brackets denote the concentration of defects, expressed in mole fraction, K is equilibrium constant of reaction presented by eq.1 and p_{O_2} is oxygen pressure. Eliminating from this equation equilibrium constant, K , by the following relation:

$$-RT \ln K = \Delta G_f = \Delta H_f - T \Delta S_f \quad (3)$$

one obtains finally theoretical relationship, describing the dependence of nonstoichiometry and thereby the concentrations of predominant ionic and electronic defects in Ni_{1-y}O on temperature and oxygen pressure:

$$y = [V_{\text{Ni}}''] = \frac{1}{2}[h^\bullet] = \left(\frac{1}{4}K\right)^{1/3} \cdot p_{\text{O}_2}^{1/6} = 0.63 \cdot p_{\text{O}_2}^{1/6} \cdot \exp\left(\frac{1}{3} \frac{\Delta S_f}{R}\right) \cdot \exp\left(-\frac{1}{3} \frac{\Delta H_f}{RT}\right) \quad (4)$$

where ΔH_f and ΔS_f denote enthalpy and entropy of defect formation, respectively. It has been found previously, that the determined experimentally deviation from stoichiometry, y , in Ni_{1-y}O , is the following function of oxygen pressure and temperature [22]:

$$y = 0.153 \cdot p_{\text{O}_2}^{1/6} \cdot \exp\left(-\frac{80 \text{ kJ/mol}}{RT}\right) \quad (5)$$

From the comparison of empirical relationship, described by equation 5 with theoretical equation 4, the enthalpy and entropy of defect formation in Ni_{1-y}O can be easily calculated: $\Delta H_f = 240$ kJ/mol and $\Delta S_f = -35.3$ J/mol K [22,23].

On the other hand, the defect diffusion coefficient (in this case the vacancy diffusion coefficient, D_v) in nickel oxide was found to be dependent only on temperature [23]:

$$D_v = 0.062 \cdot \exp\left(-\frac{152 \text{ kJ/mol}}{RT}\right) \quad (6)$$

The theoretical relationship describing the vacancy diffusion coefficient as a function of temperature, in turn, can be written as follows [1,3]:

$$D_v = \alpha a_0^2 \chi \nu \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(-\frac{\Delta H_m}{RT}\right) \quad (7)$$

where α denotes geometrical factor, a_0 is the distance traveling by cations during their jumps from the lattice sites to neighboring vacancies, χ transmission coefficient (equal 1 in the discussed case), ν is the vibration frequency of ions, being in the first approximation equal to the Debye frequency, ΔH_m and ΔS_m denote the activation enthalpy and the activation entropy of defect migration. The exact value of vibration frequency of ions can be calculated using the following relationship [25]:

$$\nu = \frac{2 \cdot \sqrt{\frac{\Delta H_m}{M_{\text{Ni}}}}}{\pi a_0} = 2.44 \cdot 10^{12} \text{ s}^{-1} \quad (8)$$

where M_{Ni} denotes atomic mass of nickel.

From the comparison of empirical relationship, described by equation 6 with theoretical equations 7 and 8, the enthalpy and entropy of defect formation in Ni_{1-y}O have been calculated: $\Delta H_m = 152$ kJ/mol and $\Delta S_m = 22.2$ J/mol K [22,23].

The analogous forms of experimentally

obtained relationships 5 and 6 with theoretical equations 4 and 7 denote that point defects in nickel oxide are randomly distributed and do not interact, what means that point defect chemistry can be used for description of defect situation in the discussed oxide. This conclusion is supported by the results obtained during oxidation of pure nickel at high temperatures. It has been found, namely, that the parabolic rate constant of nickel oxidation, k'_p , determined in direct microthermogravimetric measurements as a function of temperature and oxygen pressure [22]:

$$k'_p = 0.033 \cdot p_{\text{O}_2}^{1/6} \cdot \exp\left(-\frac{239 \text{ kJ/mol}}{RT}\right) \quad (9)$$

remains in good agreement with the calculated value of the parabolic rate constant from the Wagner's theory of metal oxidation, using the experimentally obtained data of the deviation from stoichiometry and the vacancy diffusion coefficient (i.e. eqs. 5 and 6) [22]:

$$k'_p = 0.028 \cdot p_{\text{O}_2}^{1/6} \cdot \exp\left(-\frac{232 \text{ kJ/mol}}{RT}\right) \quad (10)$$

It means, that the point defect situation in nickel oxide fulfills all assumption described above, enabling the application of proposed method for indirect calculation of concentration and mobility of point defects in nickel oxide.

To determine the concentration and mobility of point defects in nickel oxide using proposed method, it is necessary to study in the first step the oxidation behavior of two low percentage binary alloys of nickel with such a metal, which can be at lower or higher oxidation state in oxide with comparison to the oxidation state of basic metal in its oxide. Thus, in this work the results of the oxidation kinetics determined as a function of temperature and oxygen pressure of two diluted binary Ni-1at.%Cr and

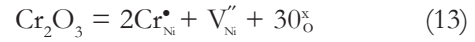
Ni-1at.%Li have been utilized [6]. The parabolic rate constants of the oxidation of these alloys ($k'_p(\text{Ni} - \text{Cr})$ and $k'_p(\text{Ni} - \text{Li})$) are the following functions of temperature and oxygen pressure, respectively:

$$k'_p(\text{Ni} - \text{Cr}) = 2.1 \cdot 10^{-4} \cdot \exp\left(-\frac{155\text{kJ/mol}}{RT}\right) \quad (11)$$

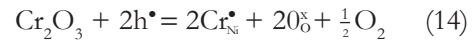
$$k'_p(\text{Ni} - \text{Li}) = 1.94 \cdot 10^3 \cdot p_{\text{O}_2}^{1/2} \cdot \exp\left(-\frac{410\text{kJ/mol}}{RT}\right) \quad (12)$$

As can be seen, during oxidation of both alloys different activation energies and different pressure dependence of parabolic rate constant have been obtained. In the case of the oxidation of the diluted Ni-Cr alloy, the scale consists of $\text{Ni}_{1-y}\text{O}-\text{Cr}_2\text{O}_3$ solid solution and its growth rate is considerably higher than that of Ni_{1-y}O scale on pure nickel and the oxidation rate does not depend on oxygen pressure. In addition, the activation energy of the diluted Ni-Cr alloy oxidation is lower than that observed in the case of pure nickel. Different situation is observed in the case of the oxidation of the diluted Ni-Li alloy. It has been found that the oxidation process of this alloy follows also parabolic kinetics, being thus diffusion controlled, but the rate of the reaction was lower and increased faster with increasing oxygen pressure than in the case of nickel oxidation. In addition, the activation energy of the reaction was higher. All these differences can satisfactorily be explained in terms of doping effect.

If, namely, one assumes that in the growing $\text{Ni}_{1-y}\text{O}-\text{Cr}_2\text{O}_3$ scale on diluted Ni-Cr alloy, doubly ionized cation vacancies and electron holes predominate and tri-valent chromium ions are substitutionally incorporated into the cation sub-lattice of the oxide, this process can be described by the following quasi-chemical reversible reactions:



and



where $\text{Cr}_{\text{Ni}}^{\bullet}$ denotes three-valent chromium ion incorporated substitutionally in the cation sub-lattice of Ni_{1-y}O .

It follows from these defect equilibria that the concentration of cation vacancies in chromium-doped Ni_{1-y}O oxide is higher (see eq. 13) than that in pure nickel oxide, and the concentration of electron holes is lower (eq. 14). Consequently, the growth rate of the oxide scale on the Ni-Cr alloy, composed of $\text{Ni}_{1-y}\text{O}-\text{Cr}_2\text{O}_3$ solid solution, should be higher than that of Ni_{1-y}O scale on pure nickel, because the parabolic rate constant of the reaction is directly proportional to the defect concentration.

The electroneutrality condition for such a $\text{Ni}_{1-y}\text{O}-\text{Cr}_2\text{O}_3$ solid solution is given by:

$$[\text{Cr}_{\text{Ni}}^{\bullet}] + [\text{h}^{\bullet}] = 2[V_{\text{Ni}}''] \quad (15)$$

Two limiting cases should be considered. If the concentration of dopant is too low to affect the intrinsic electronic and ionic disorder in Ni_{1-y}O ($[\text{Cr}^{\bullet}] \ll [\text{h}^{\bullet}]$), above electroneutrality condition reduces to the followed simplified form:

$$[\text{h}^{\bullet}] = 2[V_{\text{Ni}}''] \quad (16)$$

It follows from this relationship that the dopant does not influence on the native defect structure of nickel oxide and consequently, the oxidation rate of alloy, as dependent on oxygen pressure and temperature, should be the same as that of pure nickel (see eq. 2). On the other hand, when the dopant concentration is much higher than that of

electronic defects ($[Cr_{Ni}^{\bullet}] < [h^{\bullet}]$), the electroneutrality condition 15 assumes the following form:

$$[Cr_{Ni}^{\bullet}] = 2[V_{Ni}^{\prime\prime}] \quad (17)$$

indicating that in this case the extrinsic region of defect situation has been reached, in which the concentration of cation vacancies is fixed by the dopant on the constant level.

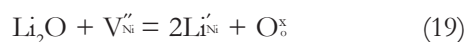
The results presented by eq. 11 show clearly that in the discussed case the amount of chromium ions incorporated in the oxide scale formed on Ni-Cr alloy was high enough to fix the concentration of cation vacancies in the $Ni_{1-y}O-Cr_2O_3$ solid solution on the constant level, i.e. that the simplified electroneutrality condition, described by eq. 17 was fulfilled. This is not surprising, because chemical analysis has shown that the concentration of chromium in this scale was equal 0.3 at %, while y in $Ni_{1-y}O$ at 1373 K is less than 10^{-3} % [22]. Consequently, the oxidation rate of alloy was higher than that of pure nickel and was pressure independent. In addition, from eq. 11 it follows also that the activation energy of alloy oxidation was lower than that of pure nickel. This important fact is also in agreement with theoretical predictions. From eqs. 4 and 7 it follows, namely, that the activation energy of pure nickel oxidation is the sum of 1/3 of enthalpy of defects formation and the activation enthalpy of their migration, because with increasing temperature, increase exponentially both, the defect concentration and their mobility. In the case of alloy oxidation, on the other hand, the concentration of cation vacancies is fixed by the dopant on the constant level (eq. 13) and consequently $\Delta H_f = 0$. Thus, the activation energy of alloy oxidation must be lower than that of pure nickel and simply equal to the activation enthalpy of defect migration,

ΔH_m . Consequently, theoretical relationship, describing the dependence of the parabolic rate constant of Ni-Cr alloy oxidation on temperature and oxygen pressure assumes the following form:

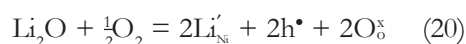
$$k'_p(Ni - Cr) = 3yD_v = \frac{3}{2}[Cr_{Ni}^{\bullet}] \alpha a_0^2 \chi v \exp\left(\frac{\Delta S_m}{R}\right) \exp\left(-\frac{\Delta H_m}{RT}\right) \quad (18)$$

because ΔS_f and ΔH_f are equal zero. From the comparison of above theoretical equation with empirical eq. 11 it follows clearly, that the activation energy of alloy oxidation equals enthalpy of defect migration $\Delta H_m = 155$ kJ/mol and $DS_m = 19.7$ J/mol K.

The results obtained during oxidation of diluted Ni-Li alloy may again be explained in terms of doping effect. Assuming, namely, that the univalent lithium ions are substitutionally incorporated into cation sub-lattice of nickel oxide, this process can be described by the following defect reactions:



and



where Li'_{Ni} denotes mono-valent lithium ion, incorporated substitutionally into cation sub-lattice of $Ni_{1-y}O$.

From these defect equilibriums it follows that - in contrast to chromium doping - the concentration of cation vacancies in lithium-doped nickel oxide should be lower and the concentration of electron holes higher, than those in pure nickel oxide.

The electroneutrality condition in the case under discussion assumes the form:

$$[Li'_{Ni}] + 2[V_{Ni}^{\prime\prime}] = [h^{\bullet}] \quad (21)$$

Two limiting cases should again be considered. If ($[Li'_{Ni}] \ll [V''_{Ni}]$), the electroneutrality condition reduces to the following simplified form:

$$2[V''_{Ni}] = [h^*] \quad (22)$$

which implies that the dopant concentration is too low to affect the intrinsic ionic and electronic disorder in $Ni_{1-y}O$. On the other hand, when the concentration of dopant is much higher than that of native defects ($[Li'_{Ni}] \gg [V''_{Ni}]$), the electroneutrality condition assumes the form:

$$[Li'_{Ni}] = [h^*] \quad (23)$$

This implies that the concentration of electronic defects in such $Ni_{1-y}O-Li_2O$ solid solution is higher than that in pure nickel oxide and fixed on the constant level. The concentration of cation vacancies, in turn, is much lower and increases more rapidly with increasing oxygen pressure than in the case of pure nickel oxide. This last conclusion results directly from replacing in equation 1 the electron hole by dopant and eliminating the equilibrium constant K by equation 3:

$$[V''_{Ni}] = \frac{1}{[Li'_{Ni}]^2} \cdot p_{O_2}^{1/2} \cdot \exp\left(\frac{\Delta S_f}{R}\right) \cdot \exp\left(-\frac{\Delta H_f}{RT}\right) \quad (24)$$

It follows from above relationship that the concentration of cation vacancies in $Ni_{1-y}O-Li_2O$ scale and thereby the oxidation rate of Ni-Li alloy must be lower than that in purely oxidizing atmospheres and should increase more rapidly with increasing oxygen pressure, what is in agreement with experimental results presented by eq. 12.

From the results shown in eq. 12, it follows clearly that the concentration of lithium in the oxide scale on Ni-Li alloy was high enough to reach the extrinsic region,

as the oxidation rate was lower than that of pure nickel and increased more rapidly with oxygen pressure, in agreement with theoretical equation 24. This conclusion could have been expected, because chemical analysis has demonstrated that the concentration of lithium in $Ni_{1-y}O-Li_2O$ scale, amounted to 0.1 at. %, being thus more than two orders of magnitude higher than that of native defects in pure $Ni_{1-y}O$ [22]. In addition, it has been found that the activation energy of nickel oxidation in Li_2O containing atmosphere was higher than that in purely oxidizing atmospheres (see eqs. 9 and 12). This difference is again in agreement with theoretical predictions. As already pointed out, the activation energy of nickel oxidation is the sum of one third of enthalpy of defect formation ($1/3 \Delta H_f$) and the activation enthalpy of their migration (ΔH_m) in the oxide scale on this metal. Such situation results from the fact that the concentration of both, ionic and electronic defects increase with increasing temperature and consequently, only one third of ΔH_f participates in the activation energy of cation self-diffusion and thereby in the activation energy of nickel oxidation. In lithium-doped nickel oxide, on the other hand, if dopant content is sufficiently high, the electron hole concentration is fixed on the constant level (eq. 20) and consequently, the temperature dependence of the concentration of ionic defects (cation vacancies) is described by eq. 24. It follows from this relationship that the concentration of cation vacancies in $Ni_{1-y}O-Li_2O$ solid solution must increase more rapidly not only with oxygen pressure, but also with temperature, because the whole value of ΔH_f participates in the activation energy of alloy oxidation:

$$k'_p(Ni-Li) = 3yD_V = \frac{3}{[Li'_{Ni}]^2} \alpha a_0^2 z v p_{O_2}^{1/2} \exp\left(\frac{\Delta S_f + \Delta S_m}{R}\right) \exp\left(-\frac{\Delta H_f + \Delta H_m}{RT}\right) \quad (25)$$

This theoretical relationship has been obtained by multiplying of eqs. 7 and 24.

Comparing further empirical eq. 12 with the theoretical relationship 25 and using already calculated values of ΔH_m and ΔS_m , as well as determined concentration of lithium in the scale, equal $[Li'] = 0.1$ at. %, the enthalpy and entropy of defect formation in nickel oxide have been calculated: $\Delta H_f = 255$ kJ/mol and $\Delta S_f = -35.5$ J/mol K.

In such a way, from the result of oxidation kinetics of two appropriate diluted binary alloys, the complete set of thermodynamic parameters (ΔH_f , ΔH_m , ΔS_p , ΔS_m) has been obtained. These parameters, in turn, can be applied for calculations of defect concentration and defect diffusion coefficient in nickel oxide as a function of temperature and oxygen pressure, using theoretical eqs. 4 and 7:

$$y = [V''_{Ni}] = \frac{1}{2}[h\bullet] = 0.152 \cdot p_{O_2}^{1/6} \cdot \exp\left(-\frac{85 \text{ kJ/mol}}{RT}\right) \quad (26)$$

$$D_v = 0.047 \cdot \exp\left(-\frac{155 \text{ kJ/mol}}{RT}\right) \quad (27)$$

These relationships do not differ virtually from those describing the results obtained in much more difficult and time consuming thermogravimetric experiments, presented by eqs. 5 and 6. The very good agreement between experimentally determined results and those calculated using proposed method is even better visible in Figures 1 and 2.

The results presented in this work enable to formulate the conclusion, that discussed method offers novel possibilities of indirect determination of concentration and mobility of point defects in transition metal oxides. This method is based on rather simple experimental procedure, consisting in oxidation rate measurements of diluted

binary alloys, from the results of which the defect concentration as well as the defect diffusion coefficient can be calculated as a function of temperature and oxygen pressure. In addition, proposed method allows to gain the correct results, completely independently on the disturbances caused by the presence of impurities in the studied oxides. Small amounts of such impurities in a number of oxides showing low native point defect concentration may dramatically disturb the results of investigation of concentration and mobility of defects, obtained with direct classical methods. On the other hand, in the case of indirect method proposed in this paper, the starting materials are diluted alloys, in which the concentration of alloying additions, playing the role of dopants is equal generally to about 1 at. %. Thus, the dopant concentration in a studied oxide is at least three orders of magnitude higher than the concentration of impurities, which consequently have not influence on the oxidation kinetics and thereby on correctness of conducted calculations.

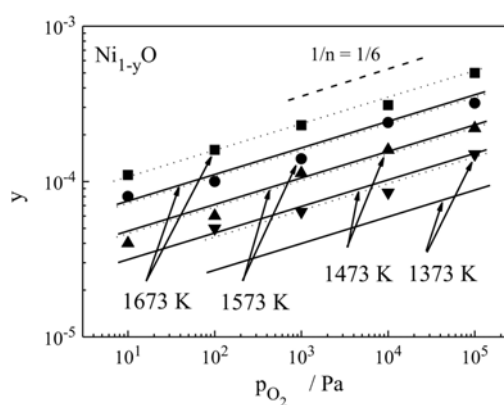


Figure 1. Pressure dependence of nonstoichiometry, y , in $Ni_{1-y}O$, determined in indirect way (solid lines) on the background of experimentally obtained data (symbols).

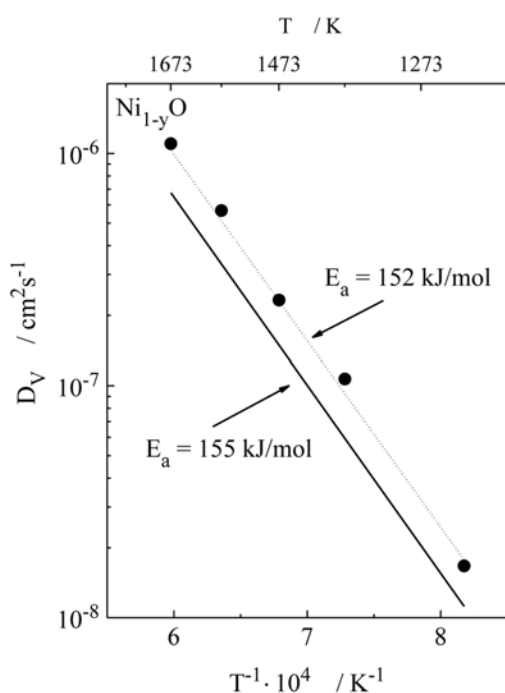


Figure 2. Temperature dependence of the vacancy diffusion coefficient in Ni_{1-y}O , determined in indirect way (solid line) on the background of experimentally obtained data (symbols).

Finally, the very important problem of errors and sensitivity of proposed method should be shortly discussed. The detailed considerations lead to the conclusion that generally error of determination of deviation from stoichiometry as well as the defect diffusion coefficient using proposed method is two times higher than in the case of application of direct gravimetric method. On the other hand, however, proposed method allow for determination of very low deviations from stoichiometry, impossible for detection using classical gravimetric method, up to the level of $2 \cdot 10^{-7}$. It means that sensitivity of proposed method is about 2 orders of magnitude better than that obtained using classical microthermogravimetry. This effect results from the fact that using direct gravimetric

method, the nonstoichiometry is calculated from mass changes of a given oxide sample during changes of temperature or oxidant pressure. In this case, the concentration changes of native point defects are responsible for mass changes of the oxide sample. For compounds with low defect concentration, such mass changes are relatively small and thereby the sensitivity of direct gravimetric method of determination of deviation from stoichiometry is not high. On the other hand, during determination of deviation from stoichiometry using proposed method, measured values of the parabolic rate constants are a result of mass changes of a given sample with time. In this case mass changes follow oxidant atoms incorporation by “all” metal atoms presented in substrate (i.e. “all” after appropriate long period of oxidation). Because the concentration of defects in oxides is orders of magnitude lower than the concentration of metal atoms in these materials, then the sensitivity of proposed method is higher than that observed in the case of direct gravimetric method.

CONCLUSIONS

The present paper describes the application of doping effect, observed during oxidation of diluted binary alloys, to indirect determination of concentration and mobility of native point defects in pure oxides. This possibility has been illustrated studying the influence of chromium and lithium dopants on the oxidation rate of nickel. Excellent agreement between calculated values of the concentration and the mobility of cation vacancies, being the predominant point defects in nonstoichiometric nickel oxide with those determined experimentally, strongly suggests that the indirect method proposed in this paper creates novel possibility for studying the defect structure and transport properties of transition metal oxides.

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