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DEFECT STRUCTURE OF Co_3O_4 COBALT OXIDE

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Abstract – The deviation from stoichiometry, y, in the Co_3O_4 oxide has been studied as a function of temperature (973-1173 K) and oxygen pressure ($30\text{-}10^5$ Pa) using microthermogravimetric technique. It has been found that at low oxygen pressures, the deviation from stoichiometry decreases with increasing oxygen pressure, reaching zero value in intermediate oxygen pressure range and for higher pressures it starts to increase. This behaviour strongly suggests the presence of complex defect structure in the studied oxide. At very low oxygen pressures, close to the dissociation pressure of the oxide, interstitial cations are the predominant ionic defects, while at high pressures cation vacancies predominate. Using the obtained results of nonstoichiometry, the concentrations of predominant point defects in the studied oxide have been calculated as a function of temperature and oxygen pressure.

Résumé - Défauts dans les oxydes de cobalt Co_3O_4. L'écart à la stoéchiométrie, dans l'oxyde de cobalt Co_3O_4 a été étudié en fonction de la température (973-1173K) et de la pression ($30\text{-}10^5$ Pa) à l'aide d'une technique thermogravimétrique. A faible pression d'oxygène, l'écart de la stoéchiométrie diminue lorsque la pression d'oxygène augmente pour atteindre une valeur nulle dans une gamme de pression intermédiaire. Pour de plus fortes pressions, l'écart augmente. Ce comportement suggère la présence de défauts de structure complexes dans l'oxyde étudié. Pour de très faible pression d'oxygène, proche de la pression de dissociation de l'oxyde, des cations en position interstitielle sont les défauts prédominants, alors que ce sont des lacunes cationiques qui prédominent à haute pression. Les travaux présentés permettent de calculer la concentration des défauts prédominants en fonction de la pression partielle d'oxygène et de la température.

1. INTRODUCTION

Point defects are responsible for lattice diffusion, which determines or strongly influences at high temperatures such important processes as mass transport, solid state reactions, creep, phase transformations etc. [1-4]. Electronic defects, in turn, strongly related to ionic disorder, are responsible for semiconductive, thermoelectric, electro-optical and many other important properties of these compounds [1-2]. This is the reason why the concentration and the mobility of ionic and electronic defects in metal oxides are extensively studied for years. Consequently, the defect structure and transport properties of the majority of transition metal oxides are already known. In spite of this, the Co_3O_4 cobalt oxide makes an exception, because the defect structure in this

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material has never been studied systematically. Such a situation results mainly from considerable experimental difficulties in studying very low rate of the Co_3O_4 oxide formation, being a result of small concentration of predominant defects in this oxide. In addition, the homogeneity range of this oxide is relatively narrow.

Being active in this area of research for many years, we initiated rather long-term investigations on kinetics and mechanism of Co_3O_4 growth on the surface of CoO phase. As a consequence, using marker method and the precise oxidation rate measurements, controversial problem in the literature [5,6], concerning the type of predominant disorder in Co_3O_4 oxide, has definitely been solved [7]. It has been demonstrated that independently on temperature and oxygen pressure, cation sublattice of this oxide is predominantly disordered. In addition, it has been shown, analyzing the pressure dependence of the parabolic rate constant of CoO oxidation to Co_3O_4 [7], that the Co_3O_4 defect structure is rather complex. At very low oxygen pressures, namely, interstitial Co^{2+} and Co^{3+} cations are the predominant point defects, while at higher oxygen pressures, cation vacancies predominate. Thus, the hypothesis suggested by Dieckmann [8,9] concerning defect structure of the Co_3O_4 has been confirmed in indirect experimental way. It should be mentioned, however, that results obtained previously by us as well as Dieckmann considerations regarding defect structure of discussed cobalt oxide had only qualitative character and – as already mentioned – the defect concentration in Co_3O_4 still remained unknown. Therefore, the aim of the present work was to get quantitative information on the concentrations of cation interstitials and cation vacancies in the Co_3O_4 cobalt oxide in studies of nonstoichiometry of this material, using direct microthermogravimetric technique.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

High purity Co_3O_4 cobalt oxide (99.99 at.%) has been used as a starting material in this work. As already pointed out, the formation of Co_3O_4 oxide during the reaction of CoO with oxygen is very low. Consequently, it is impossible to obtain flat Co_3O_4 specimens with appropriate thickness of about 1 mm, sufficient for studying nonstoichiometry using direct microthermogravimetric technique, as a result of the oxidation process of cobalt sample in acceptable period of time. Thus, we used a Co_3O_4 powder material with the average grain size of 50 micrometers. Such Co_3O_4 powder sample with the mass of about 0.5 g was suspended in quartz crucible in reaction zone of the microthermogravimetric apparatus and next annealed in Ar-He-O_2 gas mixture at constant temperature and oxygen pressure till constant weight of the oxide sample has been reached. Then, the mass changes of the sample resulting from oxygen pressure or temperature changes were determined using microthermogravimetric aparatus with the sensitivity of 10^{-7} g. These data were used for calculation of deviation from stoichiometry in Co_3O_4 cobalt oxide and thereby the concentration of predominant ionic defects as a function of temperature and oxygen pressure.

The application of two carrier gases (He and Ar) was necessary to increase the accuracy of obtained results by elimination of Archimedes effect [10]. If only one carrier gas is used to obtain oxidizing gas mixture, the Archimedes effect is to be expected when the oxygen partial pressure in such binary gas mixture is changed. If, namely, the oxygen partial pressure in Ar-O_2 gas is decreased, the weight of the sample apparently decreases, because of the higher density of argon as compared to oxygen. As a consequence, the registered weight changes are lower than those resulting from the reaction. On the other hand, in He-O_2 atmosphere opposite effect should be observed. This problem may be an important source of inadequate results of nonstoichiometry measurements. In order to eliminate discussed systematic error the ternary gas mixture was used with such Ar/He ratio, that the density of this carrier gas mixture is exactly the same as that of oxygen. This method is described in details elsewhere [10].

3. RESULTS AND DISCUSSION

Figure 1 illustrates the results of Co_3O_4 mass measurements as a function of oxygen pressure for a several temperatures. As can be seen, at a given temperature the mass of Co_3O_4 oxide sample increases with increasing oxygen pressure in rather complex way. At lowest oxygen pressures, close to the dissociation pressure of Co_3O_4 oxide, the mass sample starts to increase with increasing pressure, reaching virtually a constant value and subsequently it is growing with oxygen pressure in highest pressure range. Such complicated behavior strongly confirms Dieckmann hypothesis on the defect structure in the oxide under discussion [8,9], as well as our previous considerations leading to the statement that in investigated oxide two different types of defects are present [7]. Next, data presented in *figure 1* have been used for calculation of deviation from stoichiometry, y, in the studied oxide, assuming that its chemical formula including nonstoichiometry can be written as $Co_{3-y}O_4$:

$$y = 3 - \frac{4 \cdot m_{Co} \cdot M_O}{m_O \cdot M_{Co}} \qquad (1)$$

where m_{Co} and m_O denote masses of cobalt and oxygen in a given sample, whereas M_{Co} and M_O are atomic masses of cobalt and oxygen, respectively.

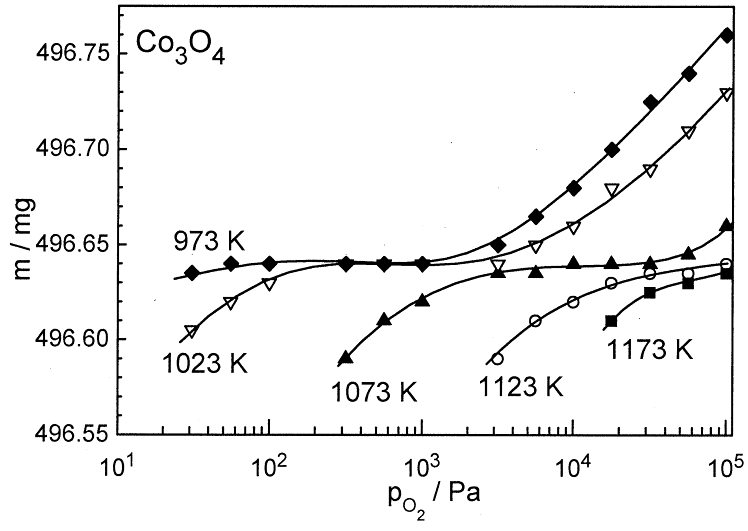

Figure 1. Pressure dependence of the mass of Co_3O_4 sample for several temperatures.

Unfortunately, as already stated the starting material was present in the form of powdered Co_3O_4 and thereby the mass of the cobalt in the oxide sample was unknown. Consequently, prior to use rather simple eq. 1, it was necessary to determine the mass of cobalt in investigated sample. The following procedure of determination of the mass of cobalt has been used. First, the total mass of oxide sample for the inflection point of the function $m = \ln p_{O_2}$ at a constant temperature, presented in *figure 1* was read. Next, the mass of the cobalt in oxide sample was calculated from eq. 1, because the Co_3O_4 is strictly stoichiometric (i.e.: y = 0) for the oxygen pressure related to the inflection point. Now, eq. 1 was used without any problems for calculations of deviation from stoichiometry, y, of the oxide being in equilibrium with gas phase at a given temperature and oxygen pressure. Certainly, the statement about the stoichiometric composition of Co_3O_4 oxide in inflection point needs some explanation.

To prove this thesis, it is necessary to show that two function: m = ln p_{O_2} and y = ln p_{O_2} have inflection point for the same value of oxygen pressure, for which the Co_3O_4 oxide is strictly stoichiometric (at constant temperature). The character of discussed functions is a result of the presence of two types of point defects in the studied cobalt oxide, i.e. cation interstitials ($Co_i^{8/3\bullet}$) and cation vacancies ($V_{Co}^{8/3'}$) [7]. The effective charge of these defects, being the result of the presence of Co^{2+} and Co^{3+} cations in the cation sublattice of the Co_3O_4 spinel oxide is equal to 8/3. The formation reactions of these defects can be written as follows (the Kröger-Ving notation is used throughout this paper [11]):

$$Co_3O_4 \Leftrightarrow 3Co_i^{8/3\bullet} + 8e' + 2O_2 \qquad (2)$$

$$2O_2 \Leftrightarrow 3V_{Co}^{8/3'} + 8h^{\bullet} + 4O_O^X \qquad (3)$$

It should be noted that according to Koch and Wagner [12], the Co_3O_4 oxide is intrinsic electronic semiconductor, what denotes that concentration of electronic defects is much higher than ionic defect concentration, resulting from nonstoichiometry. Taking into account this fact ($[e'] \cong [h^{\bullet}]$ = const) and applying mass conservation law and appropriate electroneutrality condition to defect equilibriums described by eqs. 2 and 3, the concentration of interstitial cations and cation vacancies can be presented by the following relationships:

$$\left[Co_i^{8/3\bullet}\right] = A \cdot p_{O_2}^{-2/3} \qquad (4)$$

$$\left[V_{Co}^{8/3'}\right] = B \cdot p_{O_2}^{2/3} \qquad (5)$$

where p_{O_2} is oxygen pressure normalized to 10^5 Pa, whereas A and B are constants.

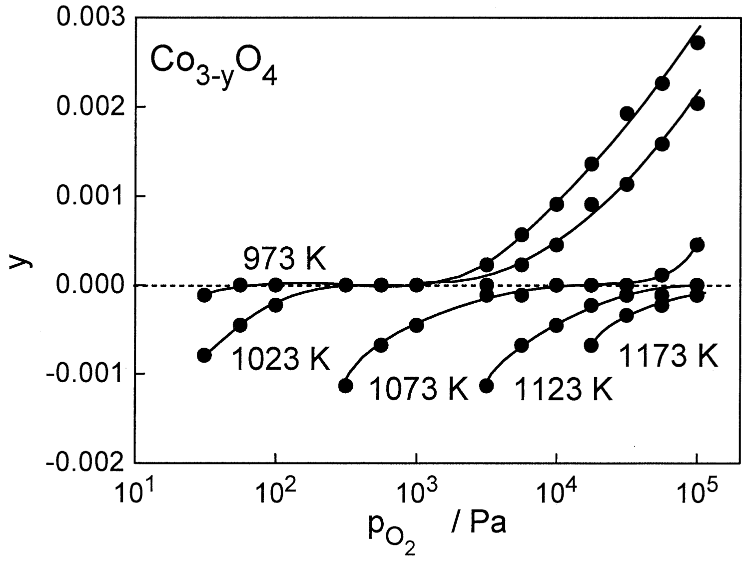

Figure 2. Pressure dependence of the deviation from stoichiometry, y, in the $Co_{3-y}O_4$ oxide for several temperatures.

Thus, the deviation from stoichiometry, y, in $Co_{3-y}O_4$ oxide can be presented in the following way:

$$y = \left[V_{Co}^{8/3'}\right] - \left[Co_i^{8/3\bullet}\right] = B \cdot p_{O_2}^{2/3} - A \cdot p_{O_2}^{-2/3} \qquad (6)$$

Using above equation, oxygen pressure, $p_{O_2}^*$, corresponding to stoichiometric composition of Co_3O_4 oxide (y=0) can be calculated:

$$p_{O_2} = p_{O_2}^* = (A/B)^{3/4} \qquad (7)$$

It is easy to demonstrate that the function y = ln p_{O_2} shows inflection point for $p_{O_2}^*$. It is necessary only to show that in the vicinity of the $p_{O_2}^*$ the second derivate of this function changes its sign and for $p_{O_2}^*$ it is equal to zero, what means that it has inflection point for $p_{O_2}^*$.

On the other hand, mass of the nonstoichiometric $Co_{3-y}O_4$ oxide sample (m), resulting from changes of oxygen partial pressure at constant temperature can be determined from the following relationship:

$$m = m_0 + (4/3) \cdot M_O \cdot B \cdot p_{O_2}^{2/3} - (4/3) \cdot M_O \cdot A \cdot p_{O_2}^{-2/3} \qquad (8)$$

where m_0 is the mass of the stoichiometric Co_3O_4 oxide sample. The mathematical analysis of the function m = ln p_{O_2} conducted in the similar way like analysis of the function y = ln p_{O_2} clearly indicates that this function has also inflection point for $p_{O_2}^*$.

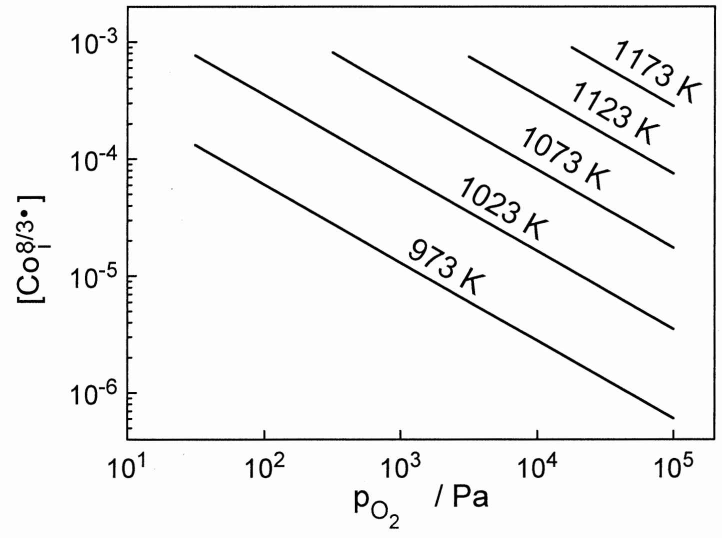

Figure 3. Pressure dependence of the concentration of interstitial cations in the studied cobalt oxide for several temperatures.

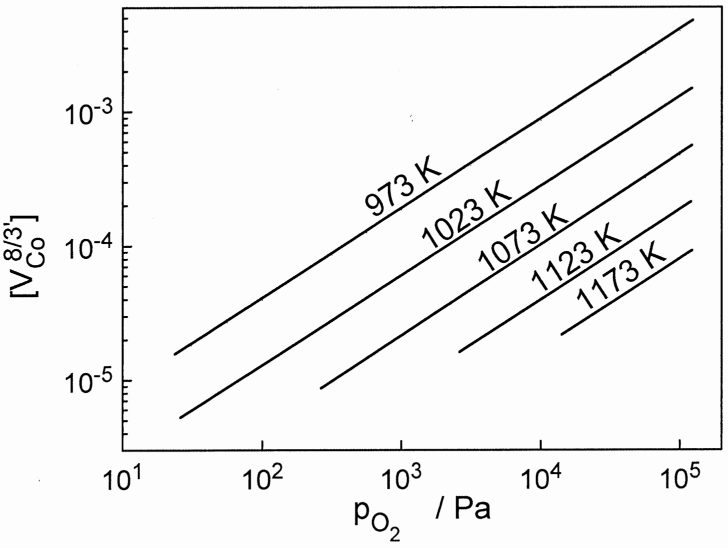

Figure 4. Pressure dependence of the concentration of cation vacancies in the studied cobalt oxide for several temperatures.

Thus, using experimental data presented in *figure 1* and mentioned above method of interpretation, the deviation from stoichiometry, y, in $Co_{3-y}O_4$ oxide has been calculated. The results of such calculations are presented in *figure 2*. These data, in turn, can be used for numerical determination of A and B parameters in eq. 6 for the studied temperatures, what allows for calculation of point defect concentration and thereby the deviation from stoichiometry, y:

$$\begin{aligned} y = \left[V_{Co}^{8/3'}\right] - \left[Co_i^{8/3\bullet}\right] &= 4.4\cdot 10^{-13}\cdot p_{O_2}^{2/3}\cdot \exp\left(\frac{185.3\ \mathrm{kJ/mol}}{RT}\right) \\ &- 2.8\cdot 10^{9}\cdot p_{O_2}^{-2/3}\cdot \exp\left(-\frac{291.7\ \mathrm{kJ/mol}}{RT}\right) \end{aligned} \quad (9)$$

The concentrations of predominant point defects in the studied cobalt oxide are presented in the graphical form in *figures 3 and 4*.

4. SUMMARY

The presented work definitely shows that the Co_3O_4 cobalt oxide has complex defect structure. At relatively low oxygen pressures, close to the dissociation pressure of this oxide, interstitial cations are the predominant ionic defects, while at high pressures cation vacancies predominate. The concentrations of these defects have been calculated as a function of temperature and oxygen pressure. Thus, the obtained results constitute the full quantitative description of point defect structure in the Co_3O_4 cobalt oxide.

5. ACKNOWLEDGMENTS

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