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Oxidation Mechanism of Cu_2O and Defect Structure of CuO at High Temperatures

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Abstract. Kinetics and mechanism of Cu_2O oxidation have been studied as a function of temperature (973–1273 K) and oxygen pressure (1–10^5 Pa), using microthermogravimetric and marker techniques. It has been found that in early stages not exceeding 30 hours, CuO formation follows approximately cubic rate law and in later stages, the process can be described by parabolic kinetics with the rate being independent of Cu_2O pretreatment. Marker experiments, confirmed by two-stage oxidation studies, have demonstrated that the growth process of CuO layer on the surface of Cu_2O proceeds by the outward diffusion of cations, clearly indicating that the cation sublattice of CuO is predominantly defected. These results together with kinetic and nonstoichiometry data strongly suggest that in addition to intrinsic electronic disorder (i.e. electron holes and quasi-free electrons), doubly ionized cation vacancies are the prevailing ionic defects in this oxide.

Keywords. CuO, mechanism of the reaction, kinetics, defect structure.

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1 Introduction

First experimental proof of Wagner's theory of metal oxidation [1–3] has been obtained more than 60 years ago in studying the kinetics and mechanism of copper oxidation [4–7]. In agreement with this theory it has been found that the metal deficient cuprous oxide scale ($Cu_{2-y}O$) on this metal is growing by the outward volume diffusion of cations and electrons via cation vacancies and electron holes, the parabolic rate constant of this reaction being in quantitative agreement with that calculated from the self-diffusion coefficient of copper in $Cu_{2-y}O$ [8–15]. These pioneering results are considered in the literature as the starting point of the rapid development of not only the theory of gas corrosion of metallic materials [2, 3, 16, 17], but also of thermodynamics and kinetics of point defects in transition metal oxides and sulfides [8, 18, 19]. However, in those times virtually no information was available on the mechanism of the second copper oxide (CuO) formation, because of extremely low rate of this process. It is interesting to note that in last 10 years the interest in physico-chemical properties of cupric oxide, CuO, has shown great revival in connection with its specific applications in solar cells [20], gas sensors [21–23], magnetic storage media [24, 25], semiconductors [26], catalysis [27–29] and high temperature superconductors [30, 31]. Apart from the above mentioned applications, there are many reports about the preparation of CuO nanomaterials, in the form of nanorodes [32], nanowires [33], shuttle-like structures [34], nanoribbons [35] and nanoparticles [36, 37]. In addition, due to low cost of production, both copper oxides constitute important candidates for mass market applications. However, in all possible applications of copper oxides, detailed knowledge of their defect structure and transport properties is urgently needed.

As far as Cu_2O is concerned, these properties have been almost satisfactorily understood [9, 14, 15]. On the other hand, little information is still available on the kinetics and thermodynamics of point defects in CuO, in spite of the fact that from practical point of view this oxide is even more important than Cu_2O. In addition, available literature data are highly controversial. For instance, Carel et al. [31] and Ettorche et al. [38] postulate that CuO shows rather large deviation from stoichiometry, resulting either from cation vacancies ($Cu_{1-y}O$) or from interstitial anions (CuO_{1+x}), while Tretyakov et al. [11] claim that nonstoichiometry in CuO (if any) is very low. Finally, considerable disagreement is observed between the results reported by different authors concerning the kinetics of Cu_2O to CuO oxidation. Some authors [38–40] suggest that this process at moderate and high temperatures follows cubic or even logarithmic kinetics [41] and others [39, 42] postulate that at moderate temperatures this reaction may proceed rather in agreement with familiar parabolic rate law. However, all these results have been obtained in rather short oxidation times, not exceeding 30 hours and consequently they can not be considered as a rational basis for describing the mechanism of CuO formation under steady-state conditions and in particular, for the formulation of some conclusions concerning defect structure and transport properties of this oxide.

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Detailed analysis of all available literature data [11, 31, 38–43] strongly suggests that one of the main reasons of disagreements observed in the literature concerning the mechanism of CuO formation and the type of defect structure in this oxide result first of all from insufficient purity and care in the preparation of starting material (Cu_2O for oxidation kinetics and CuO for determination of nonstoichiometry) as well as from inadequate experimental procedure. Thus, the present paper is an attempt to get the reliable information on the influence of the history of starting material (Cu_2O) on the kinetics and mechanism of CuO formation, in precise long-term microthermogravimetric oxidation studies and to explain the type of predominant ionic disorder in CuO using marker [44, 45] and two-stage oxidation techniques [46, 47].

2 Materials and Experimental Procedure

In order to eliminate – as much as possible – the impurities in Cu_2O starting material, high purity copper (99.9999 at. %) in the form of rectangular plates (1.5×2.5 cm^2) with the thickness of 0.02 cm and mirror-like surfaces have been completely oxidized at 1273 K in Ar-He-O_2 gas mixture with the partial pressure of oxygen lower than the dissociation pressure of CuO. Cu_2O samples obtained in this way were coarse-grained (Figure 1) and showed virtually theoretical density, as well as the total concentration of impurities in this material was lower than 10^{-5} %. Oxidation rate measurements of these Cu_2O specimens have been carried out as a function of temperature (973–1273 K) and oxygen pressure (1–10^5 Pa) – Figure 2 – in the microthermogravimetric apparatus described elsewhere [48]. The weight gains of the oxidized samples were followed continuously as a function of time at constant temperature and oxygen pressure with the accuracy of the order of 10^{-6} g. The partial pressure of oxygen in ternary Ar-He-O_2 gas mixture, flowing with the constant rate (50 ml/min) through the reaction chamber, was obtained by suitable composition of this atmosphere of the total pressure of 10^5 Pa.

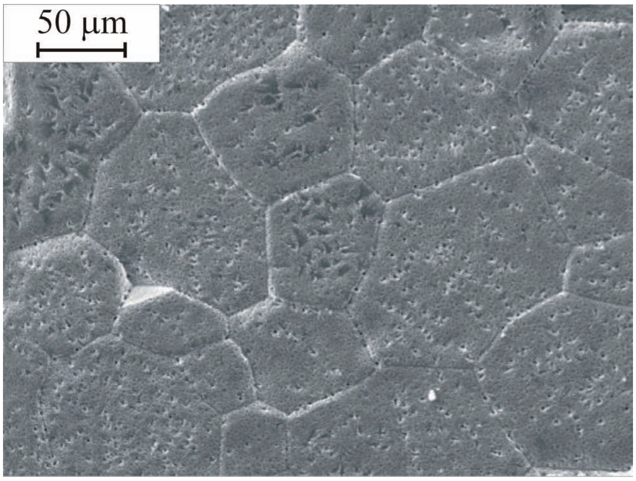

Figure 1. SEM image of the surface of Cu_2O sample obtained after oxidation of copper in Ar-He-O_2 atmosphere at 1273 K and oxygen pressure 10^3 Pa.

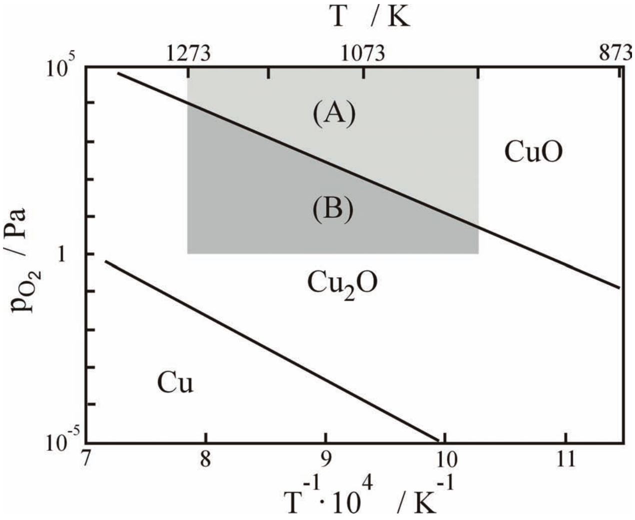

Figure 2. Phase diagram of Cu-O_2 system. A – temperature-pressure range of oxidation rate measurements of Cu_2O to CuO, B – temperature-pressure range of $Cu_{2-y}O$ pretreatments before oxidation.

The application of two carrier gases (helium and argon) needs some explanation. If only one carrier gas is used (as usual) to obtain oxidizing gas mixture, the Archimedes effect is to be expected when the oxygen partial pressure in such mixture is changed [49]. If, namely, the oxygen pressure in Ar-O_2 gas mixture 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 gains of the oxidized sample are lower than those resulting from the oxidation process. On the other hand, in He-O_2 atmosphere opposite effect should be observed. This problem has not been taken into account in previous works published in the literature and can be considered as an important source of inadequate results of nonstoichiometry studies of CuO and of the oxidation kinetics of Cu_2O, in addition to impurity effect. In order to eliminate this systematic error, the Ar/He ratio was chosen in such way that the density of this carrier gas mixture was exactly the same as that of oxygen.

In order to prove the possible influence of the history of Cu_2O sample on the kinetics of CuO formation, the starting material was equilibrated before successive kinetic runs at different oxygen pressures, ranging from the very low one, close to the dissociation pressure of Cu_2O up to the Cu_2O-CuO equilibrium (see Figure 2). As the predominant defects in metal deficient $Cu_{2-y}O$ are cation vacancies and electron holes [9, 14, 15], the above mentioned procedure enabled to start the oxidation process with highly different defect concentrations in the starting material. These differences may be reflected in different influence of field transport [39] of ions through the growing CuO layer in early stages of the reaction when CuO layer is very thin (< 1000 Å). In later stages of the reaction, this influence should gradually disappear and the oxidation process should follow familiar parabolic kinetics, being independent of the history of Cu_2O starting material. In fact, from available literature data it follows that in early stages of the reaction, oxidation process may follow cubic [39, 40] or even logarithmic [41] kinetics, but long-term oxidation studies have not been carried out, at all. These short-term oxidation data were interpreted in terms of field transport [39] or aging effect [40] but not convincing conclusions have been formulated concerning the mechanism of Cu_2O oxidation and in particular on the defect structure of CuO. To get more inside into these problems, systematic long-term oxidation rate measurements of Cu_2O to CuO have been carried out as a function of temperature and oxygen pressure. Further, marker and two-stage oxidation techniques were applied in order to explain, which sublattice of CuO is predominantly defected and finally the stoichiometric composition of this oxide has been studied as a function of temperature and oxygen pressure. Basing on all these results, defect structure model of CuO has been elaborated and self-diffusion coefficient of copper in this oxide was calculated.

3 Experimental

3.1 Kinetic Results

Long-term oxidation rate measurements have been carried out, as a function of defect concentration in $Cu_{2-y}O$. Figure 3 illustrates kinetic runs, presented in parabolic plot, obtained at 1273 K on Cu_2O samples equilibrated under different oxygen pressures. As can be seen, in early stages of the reaction, oxidation process does not follow parabolic rate law and depends slightly on the history of the starting material, but in later stages, exceeding 30 hours, exact parabolic behavior is observed. It is important to note, that as expected, under steady state conditions parabolic rate constants of Cu_2O oxidation do not depend on the history of starting material, at all (Figure 3). Figure 4, in turn, illustrates the results of early stages of oxidation, presented in cubic system of coordinates. It follows from this plot that the oxidation process of Cu_2O specimens, equilibrated at three different oxygen pressures (curves 1, 2 and 3) can be described by cubic rate law, but the rate of the reaction depends slightly on the history of starting material. It

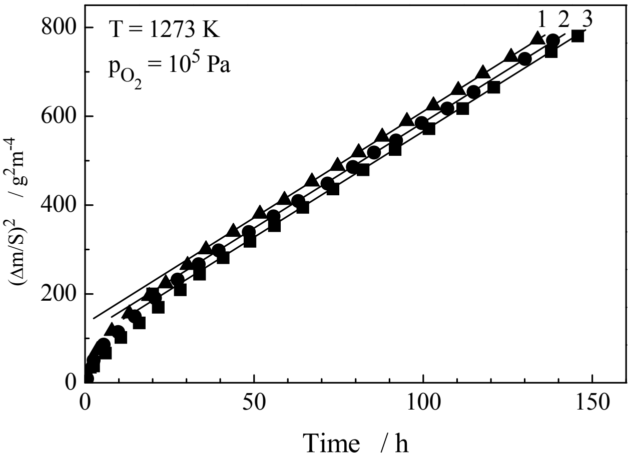

Figure 3. Long-term oxidation kinetics of $Cu_{2-y}O$ at 1273 K and $p_{O_2} = 10^5$ Pa, equilibrated before the reaction at different oxygen partial pressures: 1 – 10^4 Pa, 2 – 10^3 Pa. 3 – 10 Pa. Parabolic system of coordinates.

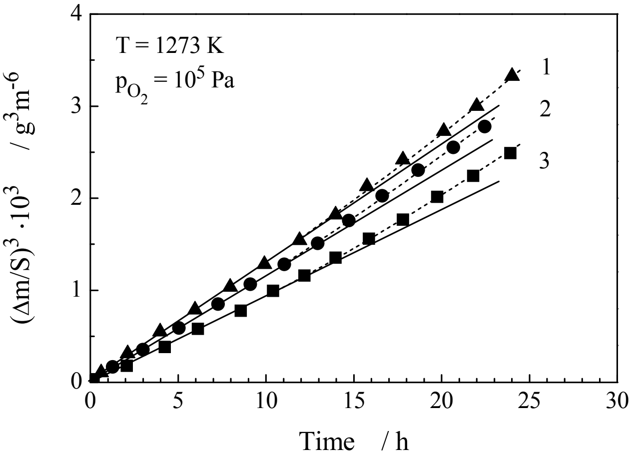

Figure 4. Early stages of oxidation kinetics of $Cu_{2-y}O$ at 1273 K and $p_{O_2} = 10^5$ Pa, equilibrated before the reaction at different oxygen partial pressures: 1 – 10^4 Pa, 2 – 10^3 Pa, 3 – 10 Pa. Cubic system of coordinates.

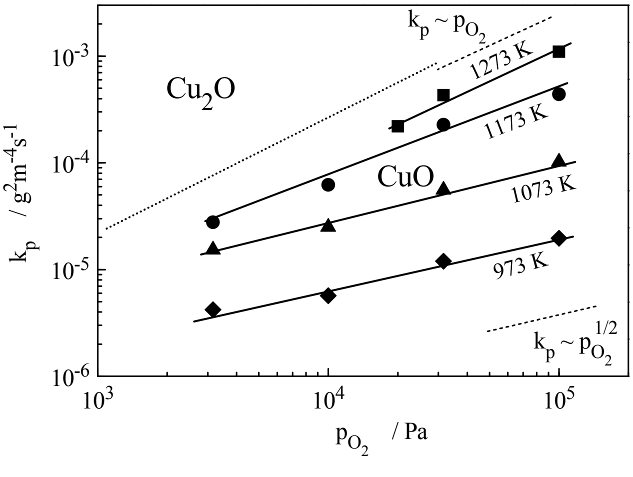

Figure 5. Pressure dependence of the parabolic rate constant of $Cu_{2-y}O$ oxidation, presented in double logarithmic plot.

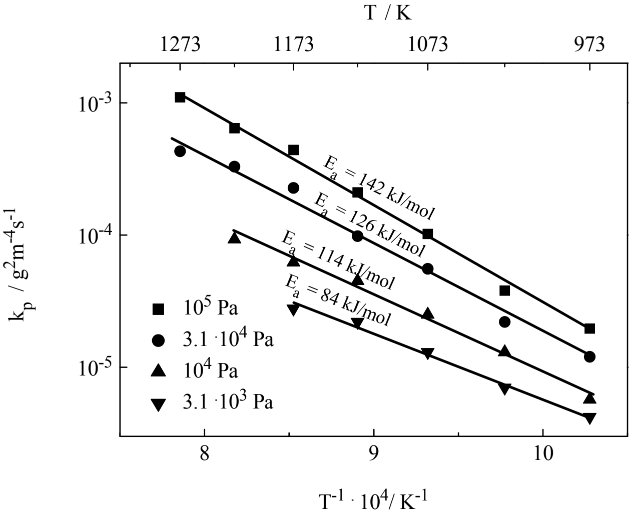

Figure 6. Temperature dependence of the parabolic rate constant of $Cu_{2-y}O$ oxidation for several oxygen pressures, presented in Arrhenius plot.

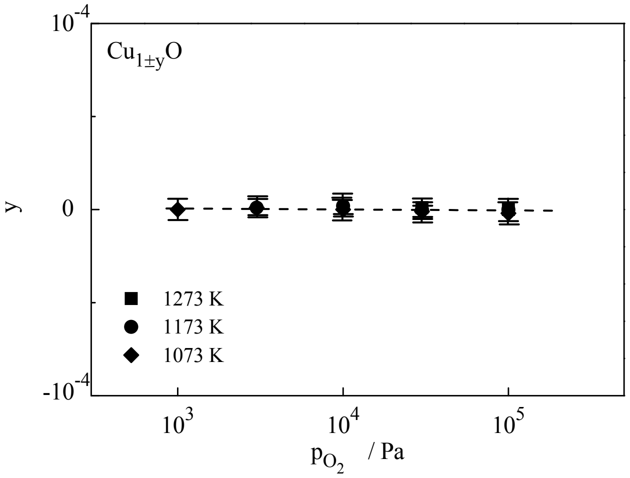

Figure 7. Stoichiometric composition of $Cu_{1\pm y}O$ determined in situ thermogravimetric measurements, as a function of equilibrium oxygen pressure for several temperatures.

may be then concluded that reasonable information on the steady state growth mechanism of CuO on the surface of Cu_2O may only be obtained from long-term oxidation studies. Following this type of reasoning, parabolic rate constants of Cu_2O oxidation, calculated from the results obtained under such conditions, are shown in Figures 5 and 6, as dependent on oxygen pressure and temperature, respectively. These results will be utilized later in connection with those of marker and two-stage oxidation, as well as nonstoichiometry data in explaining the defect structure and transport properties of the discussed oxide.

3.2 Nonstoichiometry Studies

In order to get a direct information about possible deviations from stoichiometry of CuO, the following experiments have been carried out. High purity copper sample with the weight determined with the accuracy of the order of 10^{-6} g, was suspended in the microthermogravimetric apparatus and completely oxidized to CuO at 1273 K and oxygen pressure 10^5 Pa. When constant weight of the oxide sample has been reached, i.e. when the thermodynamic equilibrium in CuO-O_2 system was established, the Cu/O atomic ratio was calculated from the weight of Cu sample and its increases due to oxidation. Subsequently, the partial pressure of oxygen in ternary Ar-He-O_2 gas mixture has been changed, step by step to lower values, annealing the sample after each step during 24 hours to get every time thermodynamic equilibrium. No change of the sample mass has been recorded. This procedure has been repeated several times at lower and lower temperatures in order to determine the possible influence of temperature on Cu/O ratio. It has been found, rather surprisingly, that in the whole temperature and oxygen pressure range studied, CuO does not show any measurable deviation from stoichiometry (Figure 7), because Cu/O atomic ratio was still equal to unity. Taking into account the accuracy of our thermogravimetric experiments (10^{-6} g), the deviation from stoichiometry, if any, of the studied oxide is lower than 10^{-5}. These results are in agreement with data, obtained by Tretyakov et al. [11], which suggest very low, but still measurable deviation from stoichiometry of CuO of the order of 10^{-5}. On the other hand, these results as well as those obtained in the present work do not confirm information, reported by Milliken and Cordaro [43], and Ettorche et al. [38], which claim, that CuO shows much higher departures from stoichiometry. This distinct disagreement of the literature data may result from inadequate methods utilized in determination of Cu/O ratio. The data of Ettorche [38] and Milliken [43] have, namely, been obtained not in situ thermogravimetric experiments, but on quenched samples. Tretyakov data [11], on the other hand, can be considered as obtained in situ experiments, because he studied equilibrium states between CuO and oxygen in a solid electrolyte galvanic cell. Consequently, these data may be considered as most reliable, which in fact – in agreement with our results – suggest extremely low, if any, deviation from stoichiometry in CuO.

3.3 Marker Experiments

Marker method [44,45] widely used in studying the mechanism of metal oxidation consists in the oxidation of a given metal sample, "marked" before the reaction by an inert substance (e.g. gold or platinum) and after terminating the reaction, in determining the position of such a marker in the layer of reaction product (scale). If the marker is found at the metal-scale interface, it clearly indicates that the scale was growing by the outward diffusion of cations, and thereby that the cation sublattice of the oxide forming the scale is predominantly defected. On the other hand, if the marker is located on the scale-gas interface, it means that the scale was growing by the inward diffusion of oxidant, indicating that the anion sublattice is predominantly disordered. It should be noted that reliable information from this method can only be obtained if the thickness of the reaction product is at least one order of magnitude higher than that of the marker.

During last 60 years the application of this method greatly contributed to the better understanding of the mechanism of high temperature corrosion of metallic materials, and in particular in explaining the type of predominant defects in the number of transition metal oxides and sulphides. However, in few cases only this method has been used in studying the mechanism of oxide oxidation. For instance, it has been shown using this method that the growth process of Co_3O_4 on the surface of CoO proceeds by the outward diffusion of cations and consequently, that the cation sublattice in Co_3O_4 is predominantly defected [50].

In order to get direct information on the type of predominant disorder in studied cupric oxide, thin gold film of about 1 µm in thickness was used as a marker. This gold film was vacuum evaporated onto the surface of Cu_2O sample through copper mesh, what resulted in the formation of small islands of gold spread on the specimen surface. The Cu_2O sample marked in this way was then oxidized at 1273 K under oxygen pressure equal 10^5 Pa. After terminating the reaction, a cross-section of the sample have been made in order to determine the position of the marker in the CuO layer. Figure 8 shows BSE micrograph of metalographic cross-section of such a sample, illustrating the position of the gold markers in the interior of the reaction product. Such a position of the marker in the middle of the total CuO thickness, clearly indicates that cation sublattice in CuO is predominantly defected. This conclusion follows from the fact that in contrast to metal oxidation, CuO layer is growing simultaneously on both its surfaces, as illustrated by the model shown schematically in Figure 9. Outward diffusion of cations and electrons leads to the formation above the markers of the outer CuO layer, growing at the outer CuO-O_2 interface:

$$Cu^{+2} + 2e' + \frac{1}{2}O_2 \rightarrow CuO. \qquad (1)$$

Simultaneously, beneath the marker, the inner CuO layer is being formed due to the following reaction:

$$Cu_2O \rightarrow CuO + Cu^{+2} + 2e'. \qquad (2)$$

On the other hand, if CuO layer would grow by the inward diffusion of oxygen, the markers should be located at the outer CuO surface, because the oxidation product would form at the inner Cu_2O-CuO interface, only.

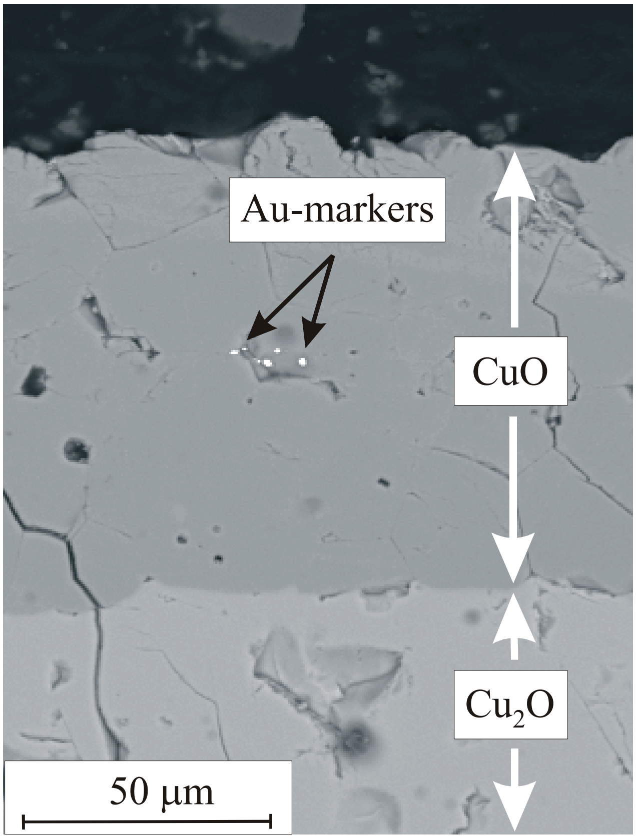

Figure 8. Metalographic cross-section of the $Cu_{2-y}O$ sample after partial oxidation at 1273 K and oxygen pressure 10^5 Pa, illustrating the position of Au-markers in the interior of the CuO layer.

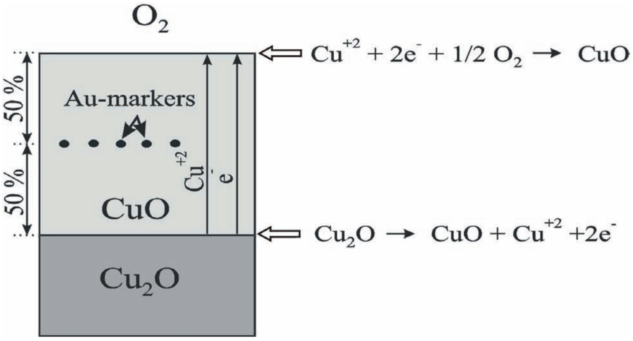

Figure 9. Schematic representation of the growth mechanism of CuO on the surface of Cu_2O.

3.4 Two-stage Oxidation Experiments

In order to confirm the above described results, obtained with the use of marker method, two-stage oxidation technique has been applied, constituting in the oxidation in the first stage the Cu_2O sample in oxygen ^{16}O and subsequently – without breaking the reaction – in oxygen ^{18}O. After terminating the reaction, distribution of oxygen isotopes in the CuO product layer has been determined by Sec-

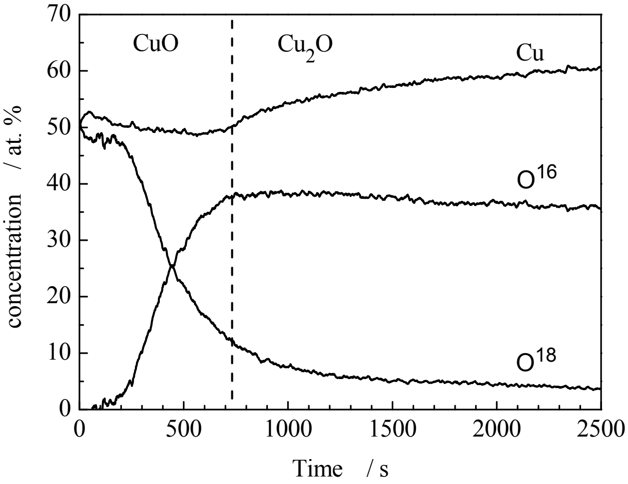

Figure 10. The concentration profiles of Cu, ^{16}O and ^{18}O isotopes in the interior of CuO layer, formed at 1273 K and oxygen pressure 10^5 Pa in two-stage oxidation experiments.

ondary Neutrals Mass Spectrometry (SNMS). Concentration profiles of both oxygen isotopes in the interior of CuO layer, obtained at 1273 K under total oxygen pressure 10^5 Pa are shown in Figure 10. As can be seen, oxygen ^{18}O introduced to the reaction chamber in the second stage of the reaction is concentrated in the outer part of CuO layer, univocally confirming the results obtained with the use of marker method, i.e. that CuO layer is growing by the outer diffusion of cations [51, 52] and consequently that cation sublattice of this oxide is predominantly defected.

4 Discussion

Experimental results described above enable some new conclusions to be formulated, concerning the mechanism of Cu_2O oxidation and, in particular, the defect structure and transport properties of cupric oxide. Long-term oxidation rate measurements have shown that after incubation period, the process of CuO formation under steady-state conditions follows strictly familiar parabolic kinetics, being thus diffusion controlled. From Figures 5 and 6 it follows that the apparent activation energy of oxidation changes with oxygen pressure and the pressure dependence of the oxidation rate, in turn, changes also with temperature. This peculiar phenomenon will be explained later on the basis of defect structure model of CuO, presented in this paper.

The first problem to be solved in this respect is to decide, which kind of point defects in CuO predominates. From marker and two-stage oxidation experiments it follows clearly that cation sublattice is predominantly defected. Thus, the main problem on the beginning of this discussion consists in deciding whether cation vacancies or interstitial cations are the predominant point defects. This problem could immediately be solved from the pressure dependence of nonstoichiometry of CuO at high temperatures. If, namely, cation vacancies and electron holes would predominate, the metal deficit and thereby nonstoichiometry in CuO should increase with oxygen pressure. On the other hand, if interstitial cations and quasi-free electrons would be the predominant defects, the nonstoichiometry and thereby defect concentration would decreased with oxygen pressure. Unfortunately, in the case under discussion, this problem could not be solved in this way, because – as shown in Figure 7 – the nonstoichiometry in CuO was to low, to be determined experimentally. However, there is still another possibility to decide which kind of point defects prevails in cation sublattice of CuO. Different pressure dependence of the oxidation rate of Cu_2O is, namely, to be expected for two different types of point defects in CuO. If cation vacancies would be the prevailing defects, parabolic rate constant of Cu_2O oxidation should increase with oxygen pressure. This conclusion follows from the fact that this type of defects is being created at the outer CuO-O_2 interface and consequently, their concentration is there much higher than that at the inner Cu_2O-CuO phase boundary, where these defects are annihilated, as schematically depicted in Figure 11a). Thus, the con-

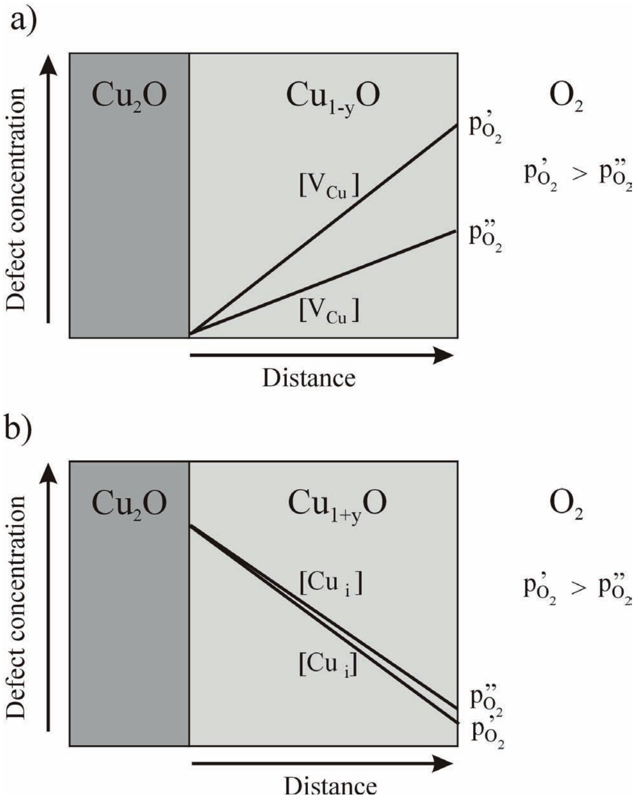

Figure 11. Concentration gradients of points defects in the CuO layer, growing on $Cu_{2-y}O$ by the outward diffusion of cations. a) cation vacancies predominate, b) interstitial cations predominate.

centration gradient of defects in CuO layer, determining its growth rate increases with increasing oxygen pressure and, consequently, the parabolic rate constant of the oxidation increases with the oxygen pressure. On the other hand, if interstitial cations would be the predominant point defects, their concentration at the inner Cu_2O-CuO interface, where these defects are generated, is much higher than that at the outer CuO-O_2 interface, where they are annihilated (Figure 11b)). Consequently, concentration gradient of defects in the growing CuO layer and thereby the oxidation rate must be in this case virtually pressure independent, because extremely low defect concentration at the outer CuO surface does not virtually change with oxygen pressure. It should be noted, however, that these differences can be observed only when the oxidation process is carried out at oxygen pressures several orders of magnitude higher than the dissociation pressure of CuO. At very low oxygen pressures, on the other hand, near the dissociation pressure of CuO, very small defect concentration gradients will change in both cases, i.e., when cation vacancies or interstitial cations predominate. Thus, in order to decide which type of point defects predominates, the pressure dependence of the oxidation rate must be studied at pressures several orders of magnitude higher than the dissociation pressure of CuO. From Figure 5 it follows that at temperatures not exceeding 1073 K and oxygen pressures higher than 10^4 Pa, i.e. at pressures more than 3 orders of magnitude higher than the dissociation pressure of CuO (see Figure 2), the oxidation rate increases definitively with increasing oxygen pressure. It may be then concluded that the predominant defects in cupric oxide are cation vacancies and electron holes, but not interstitial cations and quasi-free electrons. Thus, cupric oxide must show in fact very low metal deficit (nonstoichiometry) and consequently stoichiometric formula should be written as $Cu_{1-y}O$.

However, the problem of defect ionization degree remained unclear. Nevertheless, taking into account the fact that the concentration of point defects in CuO is extremely low, it is reasonable to assume with high probability that cation vacancies are completely, i.e. doubly ionized. Thus, the formation of these defects may be described by the following quasi-chemical reaction (Kröger–Vink notation of defects is used throughout of this paper [53]):

$$\frac{1}{2}O_2 \leftrightarrow V''_{Cu} + 2h^\bullet + O_O. \qquad (3)$$

Applying to this defect equilibrium the mass action law, one obtains the following relationship:

$$K = [V''_{Cu}] \cdot [h^\bullet]^2 \cdot p_{O_2}^{-1/2}. \qquad (4)$$

In order to describe the defect structure model of the discussed oxide, it is necessary to consider the fact that CuO is an intrinsic electronic semiconductor [54], i.e. that the concentration of electronic defects (electron holes and quasi-free electrons) is rather high and only temperature dependent. Consequently, the formation of these defects can be described by the following quasi-chemical reaction:

$$\text{zero} \leftrightarrow h^\bullet + e' \qquad (5)$$

with the equilibrium constant given by:

$$K_e = [h^\bullet] \cdot [e']. \qquad (6)$$

Consequently, general electroneutrality condition assumes the form:

$$2[V''_{Cu}] + [e'] = [h^\bullet]. \qquad (7)$$

As the concentration of quasi-free electrons is much higher than that of cation vacancies ($[e'] \gg [V''_{Cu}]$), general electroneutrality condition assumes the following simplified form:

$$[e'] = [h^\bullet]. \qquad (8)$$

Thus, considering eqs. (4), (6) and (8), the pressure dependence of cation vacancy concentration in CuO is described by the following relationship:

$$[V''_{Cu}] = K \cdot K_e^{-1} \cdot p_{O_2}^{1/2}. \qquad (9)$$

From Wagner's theory [17] it follows simply that the parabolic rate constant of Cu_2O oxidation, k_p, determined at pressures highly exceeding dissociation pressure of CuO should depend in the same way on oxygen pressure as the concentration of ionic defects (cation vacancies) in the oxidation product (CuO):

$$k_p = \text{const}' \cdot [V''_{Cu}] = \text{const} \cdot p_{O_2}^{1/2}. \qquad (10)$$

From Figure 5 it follows clearly that at pressures highly exceeding dissociation pressure of CuO (see Figure 2), parabolic rate constant of Cu_2O oxidation increases with oxygen pressure exactly in the same way, as predicted by theoretical equation (10). This agreement may then be considered as the first important proof of the validity of the proposed defect structure model of CuO. Thus, the results of oxidation rate measurements of Cu_2O, obtained at oxygen pressures much higher than dissociation pressure of CuO may be utilized in calculation of the self-diffusion coefficient of copper in cupric oxide as a function of temperature and oxygen pressure. In the discussed oxygen pressure range, namely, the pressure dependence of parabolic rate constant of Cu_2O oxidation does not change with the temperature and activation energy of this reaction does not change with the oxygen pressure (Figure 5). Consequently, parabolic rate constant of Cu_2O oxidation (expressed in

$g^2m^{-4}s^{-1}$) may be described by the following empirical equation:

$$k_p = 1.4 \cdot 10^3 \cdot p_{O_2}^{1/2} \cdot \exp\left(-\frac{147\ \mathrm{kJ/mol}}{RT}\right) \qquad (11)$$

enabling the self-diffusion coefficient of copper in cupric oxide, D_{Cu}, to be calculated as a function of oxygen pressure and temperature. This possibility follows directly from Wagner's theory of metal oxidation [17, 18]. However, in order to use equation (11) in these calculations, parabolic rate constant, k_p, expressed in $g^2\,m^{-4}\,s^{-1}$, must be recalculated into k'_p, utilized in Wagner's theory of metal oxidation and expressed in $m^2\,s^{-1}$. As the k_p determined thermogravimetrically is the measure of oxygen uptake in the outer CuO layer, recalculation of this constant into k'_p, describes directly the growth rate of this layer, in agreement with Tamman's parabolic rate law:

$$x^2 = 2k'_p t + C, \qquad (12)$$

where x is the thickness of the outer CuO layer after time t and C is a constant. From Wagner's theory [17] it follows that if the concentration of defects in the growing oxide layer is low and their mobility is concentration independent, the parabolic rate constant k'_p is related to the self-diffusion coefficient of migrating species (in our case of cations), by the following simple relationship [2, 3]:

$$k'_p = (1 + |p|) \cdot D_{\mathrm{Cu}}, \qquad (13)$$

where p is the degree of defect ionization.

In the case under discussion, all simplified assumptions made by Wagner in deriving equation (13) are fullfiled, because the concentration of point defects in CuO is extremely low and consequently, their mobility must be concentration independent. Finally, in the case of such a low defect concentration, they obviously must be fully ionized ($p = -2$). Summing up this short discussion, it may be then concluded that simplified equation (13) can be utilized in calculating the self-diffusion coefficient of copper in CuO. The results of these calculations may be summarized in equation (14), describing this coefficient as a function of temperature and oxygen pressure:

$$D_{\mathrm{Cu}} = 1.5 \cdot 10^{-10} \cdot p_{O_2}^{1/2} \cdot \exp\left(-\frac{147\ \mathrm{kJ/mol}}{RT}\right)\ m^2\,s^{-1}. \qquad (14)$$

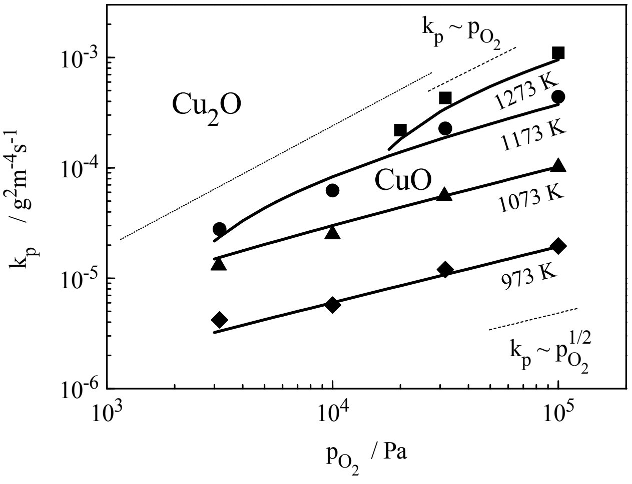

Figure 12. Pressure dependence of the parabolic rate constant of Cu_2O oxidation, presented in double logarithmic plot: solid line – calculated from empirical equation (15), points – experimental data.

It is important to note that the defect structure model of CuO, presented in this work is not restricted to oxygen pressures much higher from dissociation pressures of CuO, but also valid at lower pressures, close to the dissociation pressure of CuO. This conclusion follows again from the application of Wagner's equation but in its general form, taking into account not only the oxygen pressure at the outer phase boundary, p_{O_2}, but also equilibrium oxygen pressure at the inner interface, p'_{O_2}, equal to the dissociation pressure of the growing oxide layer. In the case under discussion, this equation assumes the following form:

$$k_p = 1.4 \cdot 10^3 \cdot (p_{O_2}^{1/2} - p_{O_2}'^{1/2}) \cdot \exp\left(-\frac{147\ \mathrm{kJ/mol}}{RT}\right). \qquad (15)$$

This relationship has been used in calculating the parabolic rate constant of Cu_2O oxidation over the whole oxygen pressure range studied. The results of these calculations are shown in the form of solid lines in Figure 12, on the background of experimental data, obtained in the present study. As can be seen, very good agreement between calculated and experimentally obtained data is observed over the whole pressure and temperature range studied, confirming the validity of defect structure model of CuO.

In order to compare calculated values of the self-diffusion coefficient of copper in CuO with analogous data for other transition metal oxides available in the literature, the temperature dependence of D_{Cu} in CuO, calculated for oxygen pressure equal 10^5 Pa, is shown in Figure 13 on the background of other self-diffusion data. As can be seen, our diffusion data are located in the interior of the area, covered by lines representing temperature dependence of self-diffusion coefficients in a number of transition metal oxides. It is important to note, that not only absolute values of D_{Cu}, but also activation energy of copper diffusion in CuO is comparable with the activation energy of diffusion in other oxides. Following this line of speculation, one may calculate the concentration of point defects (cation vacancies) in the studied oxide by assuming an average value of chemical diffusion coefficient, $\widetilde{D}$, typical for all transition

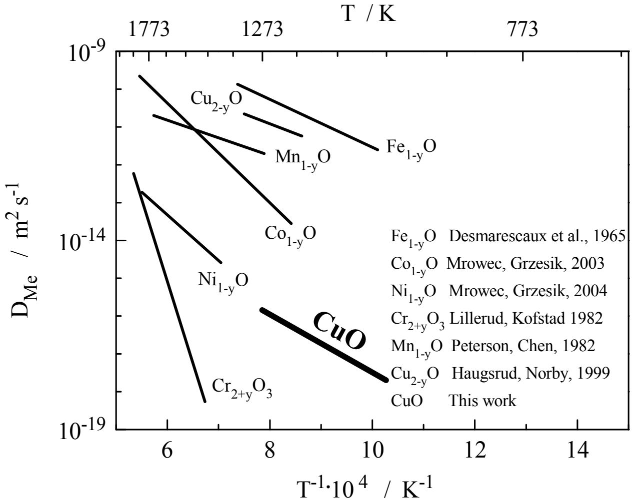

Figure 13. Temperature dependence of the calculated self-diffusion coefficient of cations in CuO on the background of the analogous dependence for a number of transition metal oxides.

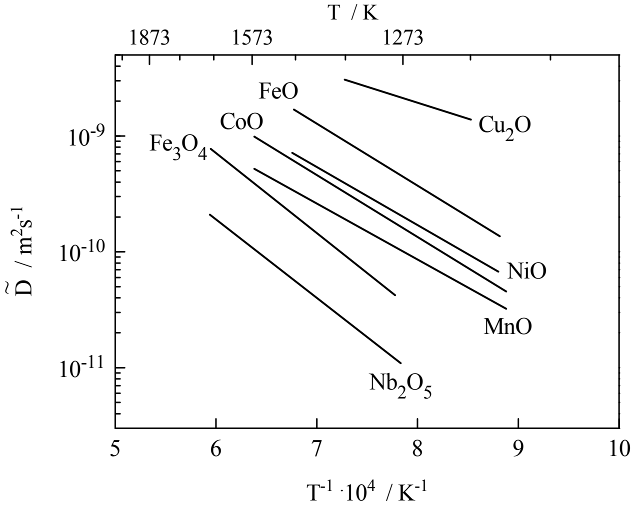

Figure 14. Collective plot of the temperature dependence of the chemical diffusion coefficients in a number of transition metal oxides.

metal oxides. From the diagram presented in Figure 14, it follows that the chemical diffusion coefficients in transition metal oxides do not differ considerably, maximum differences do not exceed one order of magnitude. Thus, an average value of the chemical diffusion coefficient at 1273 K may be assumed to be equal 10^{-10} $m^2\,s^{-1}$. The self-diffusion coefficient of copper in CuO, in turn, in the same temperature is equal $1.6 \cdot 10^{-16}$ $m^2\,s^{-1}$. Both these parameters are related with the defect concentration by the following equation [8, 18]:

$$[V''_{Cu}] \cdot \widetilde{D} = (1 + |p|) \cdot D_{Cu}. \qquad (16)$$

Using this relationship and above mentioned values of the chemical and self-diffusion coefficients, the defect concentration expressed in mole fraction in CuO has been calculated: $\approx 10^{-6}$. This estimated value of point defects concentration in cupric oxide may be considered as being in agreement with our results of deviation from stoichiometry in CuO and those reported by Tretyakov et al. [11], from which it follows that the defect concentration in CuO is lower than 10^{-5}.

5 Conclusions

The results described in the present paper enable the following conclusions to be formulated.

In early stages of Cu_2O to CuO oxidation, not exceeding 30 hours, the process follows approximately cubic rate law and the reaction rate depends slightly on the substrate pretreatment, i.e. on the defect concentration in $Cu_{2-y}O$ phase. In later stages, during long-term oxidation, lasting hundreds of hours, the formation of CuO layer on the surface of $Cu_{2-y}O$ substrate proceeds strictly in agreement with familiar, diffusion controlled parabolic kinetics and the reaction rate becomes independent on the substrate history. Cubic kinetics observed in early stages of the reaction, when the thickness of CuO layer does not exceed about 10^{-7} m may results from the influence of electrical field on diffusion in this layer, as suggested for the first time by Hauffe and Kofstad [39].

From marker and two-stage oxidation experiments it follows clearly that under steady state conditions, a "thick" CuO layer is growing by the outward diffusion of cations. This result may be considered as a first experimental proof that the cation sublattice of CuO is predominantly disordered. From the pressure dependence, in turn, of the parabolic rate constant of Cu_2O oxidation it follows, that the disorder in cation sublattice in CuO results from cation vacancies and not from interstitial cations. Theoretical analysis of all these results in terms of point defect thermodynamics leads to the conclusion that doubly ionized cation vacancies are the predominant point defects in CuO lattice. Basing on these results and considering the fact, that CuO is an intrinsic electronic semiconductor, the defect structure model for cupric oxide has been elaborated. Using this model and the results of oxidation rate measurements, the self-diffusion coefficient of copper in CuO has been calculated as a function of temperature and oxygen pressure.

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References

[1] C. Wagner, Beitrag zur Theorie des Anlaufvorgangs, *Z. physik. Chem.* **B2** (1933), 25.

[2] P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, London and New York, 1988, p. 163.

[3] S. Mrowec, *An Introduction to the Theory of Metal Oxidation*, National Bureau of Standards and National Science Foundation, Washington D.C., 1982, p. 161.

[4] J. Gundermann, K. Hauffe, C. Wagner, Conductivity measurements on couprous oxide, *Z. phys. Chem.* **B37** (1937), 148.

[5] C. Wagner, K. Grünewald, Theory of the tarnishing processes, *Z. phys. Chem.* **B40** (1938), 455.

[6] W. J. Moore, B. Selikson, The diffusion of copper in cuprous oxide, *J. Chem. Phys.* **19** (1951), 1539.

[7] W. J. Moore, B. Selikson, Erratum: The diffusion of copper in cuprous oxide, *J. Chem. Phys.* **20** (1952), 927.

[8] P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides*, J. Wiley, New York, 1972.

[9] S. Mrowec, A. Stoklosa, K. Godlewski, Thermodynamics and kinetics of point-defects in couprous-oxide, *Cryst. Latt. Def.* **5** (1974), 239.

[10] N. L. Peterson and C. L. Wiley, Diffusion and point defects in Cu_2O, *J. Phys. Chem. Solids* **45** (1984), 281.

[11] Y. D. Tretyakov, V. F. Komarov, N. A. Prosvirnina and I. B.Kutsenok, Nonstoichiometry and defect structures in copper oxides and ferrites, *J. Solid State Chem.* **5** (1972), 157.

[12] O. Porat and I. Riess, Defect chemistry of $Cu_{2-y}O$ at elevated temperatures. Part I: Non-stoichiometry phase width and dominant point defects, *Solid State Ionics* **74** (1994), 229.

[13] S. Mrowec and A. Stoklosa, Oxidation of copper at high temperatures, *Oxid. Met.* **3** (1971), 291.

[14] R. Haugsrud and T. Norby, Dermination of thermodynamics and kinetics of point defects in Cu_2O using the Rosenburg method, *J. Electrochem. Soc.* **146** (1999), 999.

[15] J. Xue and R. Dieckmann, The non-stoichiometry and the point defect structure of cuprous oxide ($Cu_{2-\delta}O$), *J. Phys. Chem. Solids* **51** (1990), 1263.

[16] N. Birks and G. H. Meier, *Introduction to High temperature Oxidation of Metals*, Edward Arnold, 1983.

[17] C. Wagner, Diffusion and high temperature oxidation of metals, *Atom Movements*, ASM Cleveland Ohio, 1951 p.153.

[18] S. Mrowec, *Defects and Diffusion in Solids*, Elsevier, Amsterdam – Oxford – New York, 1980.

[19] R. Dieckmann, Point defects and transport in non-stoichiometric oxides: Solved and unsolved problems, *J. Phys. Chem. Solids* **59** (1998), 507.

[20] B. Balamurugan, B. R. Mehta, D. K. Avasthi, F. Singh, A. K. Arora, M. Rajalakshmi, G. Raghavan, A. K. Tyagi, S. M. Sivaprasad, Modifying the nanocrystalline characteristics – structure, size, and surface state of copper oxide thin films by high-energy heavy-iron irradiation, *J. Appl. Phys.* **92** (2002), 3304.

[21] N. Serin, T. Serin, S. Horzum, Y. Celik, Annealing effects on the properties of copper oxide thin films prepared by chemical deposition, *Semicond. Sci. Technol.* **20** (2005), 398.

[22] R. Tongpool, C. Leach, R. Freer, Temperature and microstructural dependence of the sensitivity of heterocontacts between zinc oxide and copper oxide in reducing environments, *J. Mater. Sci. Lett.* **19** (2000), 119.

[23] T. Ishihara, M. Higuchi, T. Takagai, M. Ito, H. Nishiguchi, T. Takita, Preparation of CuO thin films on porous $BaTiO_3$ by self-assembled multibilayer film formation and application as a CO_2 sensor, *J. Mater. Chem.* **8** (1998), 2037.

[24] Z. H. Gan, G. Q. Yu, B. K. Tay, C. M. Tan, Z. W. Zhao, Y. Q. Fu, Preparation and characterization of copper oxide thin films deposited by filtered cathodic vacuum arc, *J. Phys. D: Appl. Phys.* **37** (2004), 81.

[25] R. A. Borzi, S. J. Stewart, R. C. Mercader, G. Punte, F. Garcia, Magnetic behavior of nanosized cupric oxide, *J. Magn. Magn. Mater.* **226-230** (2001), 1530.

[26] H. Wang, J. Z. Xu, J. J. Zhu, H. Y. Chen, Preparation of CuO nanoparticles by microwave irradiation, *J. Cryst. Growth* **88** (2002), 244.

[27] E. R. Kari Brown, K. Choi, Electrochemical synthesis and characterization of transparent nanocrystalline Cu_2O films and their conversion to CuO films, *Chem. Commun.* 3311 (2006).

[28] W. Wang, Z. Liu, Y. Liu, C. Xu, C. Zheng, G. Wang, A simple wet-chemical synthesis and characterization of CuO nanorods, *Appl. Phys.* **A76** (2003), 417.

[29] A. Bellaloui, J. Varloud, P. Meriaudeau, V. Perrichon, E. Lox, M. Chevrier, C. Gauthier, F. Mathis, Low temperature diesel soots combustion using copper based catalysts modified by niobium and potassium promoters, *Catalysis Today* **29** (1996), 421.

[30] A. D. Berry, K. D. Gaskill, T. T. Holm, E. J. Cukauskas, R. Kaplan, R. L. Henry, Formation of high T_c superconducting films by organometallic chemical vapor deposition, *Appl. Phys. Lett.* **52** (1988), 1743.

[31] C. Carel, M. Mouallem-Bahout, J. Gaude, Re-examination of the non-stoichiometry and defect structure of copper(II) oxide or tenorite $Cu_{1+-z}O$ or $CuO_{1+-\eta}$: A short review, *Solid State Ionics* **117** (1999), 47.

[32] W. Z. Wang, Y. J. Zhan, G. H. Wang, One-step, solid-state reaction to the synthesis of copper oxide nanorods in the presence of a suitable surfactant, *Chem. Commun.* 8 (2001), 727.

[33] C. H. Lu, L. M. Qi, J. H. Yang, D. Y. Zhang, N. Z. Wu, J. M. Ma, Simple template-free solution route for the controlled synthesis of $Cu(OH)_2$ and CuO nanostructures, *J. Phys. Chem. B* **108** (2004), 17925.

[34] D. Chen, G. Z. Shen, K. B. Tang, Y. T. Qian, Large-scale synthesis of CuO shuttle-like crystals via a convenient hydrothermal decomposition route, *J. Cryst. Growth* **254** (2003), 225.

[35] B. Liu, H. C. Zeng, Mesoscale organization of CuO nanoribbons: Formation of “dandelions”, *J. Am. Chem. Soc.* **126** (2004), 8124.

[36] H. Wang, J. Z. Xu, J. J. Zhu, H. Y. Chen, Formation of stable Cu_2O from reduction of CuO nanoparticles, *J. Cryst. Growth* **244** (2002), 88.

[37] R. V. Kumar, R. Elgamiel, Y. Diamant, A. Gedanken, Sonochemical preparation and characterization of nanocrystalline copper oxide embedded in poly(vinyl alcohol) and its effect on crystal growth of copper oxide, *Lanmuir* **17** (2001), 1406.

[38] M. L. Ettorche, C. Carel, G. Peslerbe, Etude thermodynamique dans le diagramme de phase cuivre-oxygene, *Bull. Soc. Sci. Bretagne* **65** (1994), 71.

[39] K. Hauffe and P. Kofstad, Über den Mechanismus der Oxydation von Cu_2O bei hohen Temperaturen, *Z. Electrochemie* **59** (1955), 399.

[40] J. L. Meijering and M. L. Verheijke, Oxidation kinetics in the case of ageing oxide films, *Acta Metall.* **7** (1959), 331.

[41] Y. Zhu, K. Mimura, M. Isshiki, Oxidation mechanism of Cu_2O to CuO at 600–1050°C, *Oxid. Met.* **62** (2004), 207.

[42] W. McKewan and W. M. Fassell, High pressure oxidation rate of metals – copper in oxygen, *J. Metals* **5** (1953), 1127.

[43] E. C. Milliken, J. F. Cordaro, Influence of oxygen atmosphere on the crystal growth of copper(II) oxide, *J. Mater. Res.* **5** (1990), 53.

[44] P. Kofstad, *High Temperature Corrosion*, Elsevier Applied Science, London and New York, 1988, p. 207.

[45] S. Mrowec, *An Introduction to the Theory of Metal Oxidation*, National Bureau of Standards and National Science Foundation, Washington D. C., 1982, p. 399.

[46] S. N. Basu, J. W. Halloran, Tracer isotope distribution in growing oxide scales, *Oxid. Met.* **27** (1987), 143.

[47] W. J. Quadakkers, H. Holzbrecher, K. G. Briefs, H. Beske, Differences in growth mechanisms of oxide scales formed on ODS and conventional wrought alloys, *Oxid. Met.* **32** (1989), 67.

[48] S. Mrowec, Z. Grzesik, Oxidation of nickel and transport properties of nickel oxide, *J. Phys. Chem. Solids* **65** (2004), 1651.

[49] Z. Grzesik, Experimental errors in studying the defect mobility in nonstoichiometric metal oxides, *Defect and Diffusion Forum* **237–240** (2005), 139.

[50] K. Przybylski and W. W. Smeltzer, High temperature oxidation of CoO to $Co3O_4$, *J. Electrochem. Soc.* **128** (1981), 897.

[51] W. J. Quadakkers, A. Elschner, W. Speier, H. Nickel, Composition and growth mechanisms of alumina scales on FeCrAl-based alloys determined by SNMS, *Appl. Surf. Sci.* **52** (1991), 271.

[52] J.-P. Pfeifer, H. Holzbrecher, W. J. Quadakkers, U. Breuer, W. Speier, Quantitative analysis of oxide films on ODS-alloys using Mcs^+-SIMS and e-beam SNMS, *J. Anal. Chem.* **346** (1993), 186.

[53] F. Kröger, *The Chemistry of Imperfect Crystals*, North Holland, Amsterdam, 1964.

[54] J. H. Park and K. Natesan, Oxidation of copper and electronic transport in copper oxides, *Oxid. Met.* **39** (1993), 411.