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***In Situ* XAFS Investigation on the Oxidation of Cu Foils at $T > 770$ K**

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Abstract. Serving as a model reaction for high temperature solid state investigations, the oxidation of copper metal foil to the corresponding oxides Cu_2O and CuO was studied for the first time by means of QEXAFS and DEXAFS spectroscopy. These techniques allow us to follow the solid state reaction in situ and time resolved, after changing the oxygen activity at elevated temperature ($770 \text{ K} < T < 1100 \text{ K}$). The overall reaction can be described by a two-step-mechanism with the Cu_2O -phase to be formed intermediately. XRD measurements performed ex situ at different reaction times coincide with these results. Involving a least-square refinement of the XANES-spectra the phase amounts of Cu , Cu_2O and CuO were determined with high accuracy to characterise the reaction kinetics.

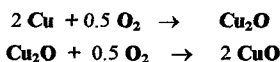
1. INTRODUCTION

In the early 30th C. Wagner [1] developed a theory for the oxidation of metals based on diffusion of ions. But as for XAS [2,3], most investigations on the kinetics of oxidation or reduction processes were carried out on samples quenched after equilibration at appropriate conditions. Through the increased availability of synchrotron radiation which is accompanied by a reduction in recording time, numerous new experimental techniques with improved time resolution were developed during the last 15 years. Especially on the field of XAS the QEXAFS [4] and DEXAFS [5] techniques were established. Applying these methods the data acquisition time can be reduced down to the second and subsecond scale. Combined with the fact that XAFS-measurements are not restricted to vacuum conditions, this offers the possibility to study the kinetics of chemical reactions in situ.

It is the main aim of this paper to demonstrate the applicability of the QEXAFS and DEXAFS technique for in situ studies of high temperature solid state reactions. For this purpose we report on first results on the oxidation of pure copper metal to tenorite, CuO :



Copper and its oxides, Cu_2O and CuO , have been the subject of numerous XAS studies for the last decades, and copper itself was often used as model substance to check the accuracy of new theoretical calculation routines. The phase transitions between these three compounds have not yet been investigated by means of a time resolved XAFS method under in situ conditions at $T > 700 \text{ K}$. Heating copper foils in a reducing atmosphere to the adequate temperature, we performed a systematic study, oxidising the metal to tenorite, CuO , in air. Considering the thermodynamics, during this reaction the monovalent copper oxide Cu_2O should be formed intermediately [6]. We attempted to check, in which temperature range one can subdivide the overall reaction (see above) into a stepwise mechanism:



2. EXPERIMENTAL

The investigations were performed on commercially available copper foils (GOODFELLOW, thickness: $7.8 \mu\text{m}$, light tested, ultra pure $> 99.99\%$). To fix the specimen (size: $8 \times 8 \text{ mm}^2$) a special $\text{Pt-Al}_2\text{O}_3$ -sample holder was constructed. The QEXAFS and DEXAFS experiments were carried out in a high temperature furnace ($770 \text{ K} < T < 1100 \text{ K}$) under continuous gas flow on beamlines X1.1 and X1.2 at HASYLAB. During the heating and equilibration period the conditions were established so that the copper remains in the

single phase field. The composition of the gas mixtures determines the oxygen activity. Either CO/CO₂ or Ar/H₂ gas mixtures were used. The metal oxidation was induced by increasing the oxygen activity to 0.21 (air). The reduction of CuO to metal after an oxidation run was also analysed.

For data reduction and analysis the software packet WinXAS (© Th.Ressler [7]) based on standard XAFS-routines [8] was used. Further analysis was performed using a C++-code [9] including a spline-interpolation of the data and a least-square-refinement to determine the phase composition.

3. RESULTS AND DISCUSSION

To follow the oxidation of copper at the Cu-K-edge the QEXAFS data acquisition was optimised to 30 s recording time per spectrum. The spectral range covered during one scan amounts to 1.1 keV and a good signal-to-noise-ratio was obtained. Thus, information can be extracted either by XANES or EXAFS-analysis. One series of XANES-spectra is depicted in fig. 1. For purpose of clearness, only every 10th spectrum is presented within 90 minutes of experimental time. The first spectrum represents copper, the final one the reaction product tenorite, CuO. Their XANES are plotted in a different line width.

In a temperature interval between 770 and 1100 K different states during the oxidation can be observed, indicated by strong changes in the absorption coefficient clearly visible in the XANES region. The overall reaction can be described using two time scales. Within the first, short reaction period the pre-edge peak intensity at 8.9835 keV increases. This process is accompanied by a smearing out of the two absorption maxima of bulk copper and is characteristic for the formation of the monovalent copper oxide, Cu₂O. The further oxidation is dominated by a subsequent, but slower decrease of the pre-edge peak intensity, while the white line of CuO develops.

Simultaneously the edge position E_0 , described by the first inflection point in the edge jump, shifts to higher energies indicating the increase in the effective charge of copper. The time evolution of the edge follows a S-shape curve as shown in fig. 2 for two temperatures. After 15 min of air exposition at $T = 873$ K a nearly constant value of E_0 was obtained. Relative to the copper metal the edge E_0 is shifted by 1.2 eV indicating that the intermediate product mainly consists of Cu₂O. This was confirmed by comparing the first two derivatives of the XANES spectra with those of Cu, Cu₂O and CuO standards and by XRD measurements on quenched samples (fig. 3). The first reaction interval was further characterised by applying the DEXAFS technique as discussed in [10].

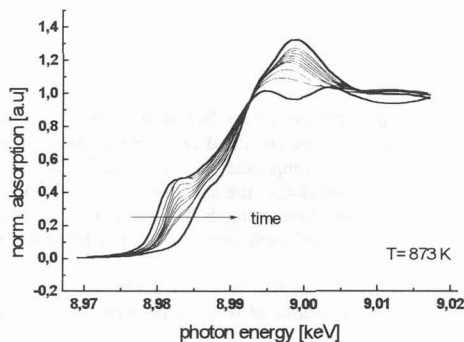


figure 1 Time evolution of the Cu-K-XANES during the oxidation of Cu to CuO

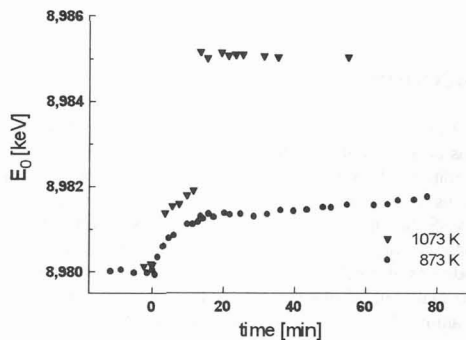


figure 2 Temperature dependence of the Cu oxidation kinetics indicated by the shift of the edge position E_0 with time

As the reaction kinetics is temperature dependent (see fig.2) the described changes are most clearly resolved at low reaction temperature and smeared out as T increases. Thus, the intermediate occurrence of Cu₂O, formed in the fast reaction step, is not unequivocally identified via the XANES-shape and edge position. Therefore an analysing routine was developed to further characterise the chemical reaction on the basis of XANES-spectra. A quantitative picture of the reaction path can be obtained by determining the amounts of the three phases detected during the oxidation. In a first approximation, the absorption coefficients μ_i of the different phases - Cu, Cu₂O and CuO - can be assumed to be additive and the phase composition can be obtained by refining the measured absorption coefficient μ_{exp} in the XANES regions according to:

$$\mu_{exp} = \sum_i x_i \cdot \mu_i \quad i = \text{Cu, Cu}_2\text{O, CuO} \quad (1)$$

As the overall copper content in the compounds remains constant, additionally, the copper balance

$$I = \sum_i x_i \quad (2)$$

has to be fulfilled during the refinement. The amount of copper x_i in phase i obtained for the kinetics at $T = 873$ K is depicted in figure 4. The deduced two-step-mechanism, involving a fast formation of cuprite followed by its reaction to tenorite, was confirmed. The time evolution of the Cu_2O phase can be described by a parabolic rate law. In addition, a layer growth was observed via REM-analysis for a sample quenched after 5 min of air exposition. Thus, a bulk diffusion transport mechanism should mainly determine the atomistic processes. Based on this refinement, the formation and dissolution of Cu_2O can be observed even at $T = 1073$ K.

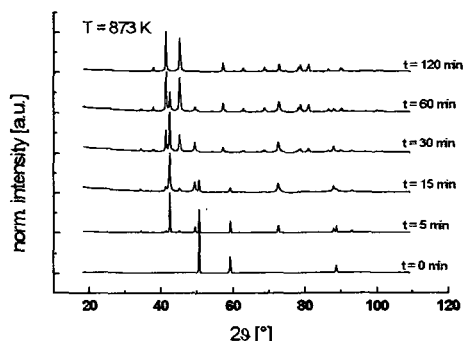


figure 3 ex situ XRD-measurement on oxidised Cu-foils
 $t = 0$ min: pure Cu-foil, $t = 5$ -15 min: main compound Cu_2O
 $t = 120$ min: main compound CuO

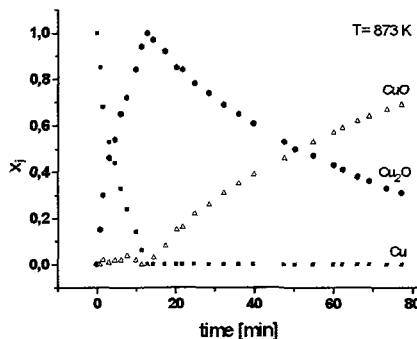


figure 4 Phase composition changes obtained by XANES analysis

Focusing on the time evolution of the Fourier transform of the k^3 -weighted EXAFS-function (not shown here), the two-step-mechanism can also be resolved. First, the peak corresponding to the nearest-neighbour Cu-Cu distance in bulk copper diminishes and the Cu-O first distance peak of Cu_2O is formed at ~ 200 pm. The transformation to CuO can be observed by the increase of this Cu-O peak due to a change in co-ordination number from 2 to 4+2. Simultaneously, the peak shifts to higher distances values, as expected from the crystallographic structure of Cu_2O and CuO. As a multiple shell fit is required for EXAFS-analysis, the reliability of the information has to be checked thoroughly. The results will be discussed in a forthcoming paper.

Acknowledgements

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