1. Introduction

Magnesium is the eight most abundant element within the earth crust (~ 2.5 % of its total composition; the sixth most abundant metal) and the third most abundant element dissolved within the sea water (~ 0.14 %) [1]. It can be extracted from carbonates like dolomite ($(Mg,Ca)CO_3$) and magnesite ($MgCO_3$), from salt minerals like carnallite ($(Mg,K)Cl{\cdot}6H_2O$), bischofite ($MgCl_2{\cdot}6H_2O$) and tachyhydrite ($CaMg_2Cl_6 \cdot 12H_2O$) or from sea water. Two principal production methods are normally used: Electrolysis of molten magnesium chloride and thermal reduction of magnesium oxide.

Being the lightest metal after Li and Be, magnesium is of great interest for application in industry, especially in automobile and aerospace application. The expected global increase in use of Mg in automobile industry is projected to be ~ 15 % to 20 % each year and ~ 5 % annually in other industries [2]. Its direct competitor is aluminium. The weight of Mg is ~35% lower than that of Al and shows superior vibration characteristics resulting from its high strength-to-weight ratio. However, prices are still ~ 50 % higher than for Al [2] which is due to reasons of exploitation output and processing costs. Mg is most commonly added as an alloying element to other metals, especially to Al (~50 % of the primary Mg production) increasing both hardness and corrosion resistance of the alloy and it has a wide application in high-pressure die-cast products.

In the past, a major technical reason for the limited application of pure Mg or Mg rich alloys, as compared to Al and its alloys, was its poor oxidation and corrosion resistance, especially at elevated temperatures and in moisture ambience. However, in recent years new high purity alloys offer corrosion resistance better than carbon, steel and some aluminium alloys [1]. However, fundamental research yielding an enhanced understanding of the mechanisms of oxidation of pure Mg has been little performed and is still required for the optimisation of properties of technical Mg alloys.

Besides the interest in the oxidation behaviour of magnesium with regard to the application of magnesium as a construction metal, thin magnesium oxide layers are of interest for use as insulating layers in semiconductor industry.

1.1. Oxidation of magnesium – from the past to today

Oxidation of magnesium has been a subject of research since the early 1920s. Early investigations were made at elevated temperatures in air where Mg exhibits a non-protective behaviour against oxidation [3-5], i.e. Mg oxidises at a constant rate due to cracks in the oxide

caused by stress due to the smaller volume of Mg-oxide in comparison to that of pure Mg metal. This enables a continuous supply of oxygen directly to the metal surface and thus the rate of oxidation depends only on the reaction speed between oxygen and Mg [3]. In the 1930s a linear oxidation behaviour was suggested to be common to this kind of metal-oxygen interface reactions [4]. At that time weight measurements on microbalance systems were usually used to monitor the oxidation rate [6]. This way oxide layer thicknesses in a range of ~ 50 nm up to 10 μm could roughly be measured.

Apart from the linear oxidation kinetics at elevated temperatures a significant enhancement of the oxidation rate due to oxygen saturated with water and a macroscopic inhomogeneous oxide growth from grain to grain were reported in those early days [6]. It was also found that for temperatures ≤ 725 K in air an initial growth of a 'protective' oxide layer was reported, where oxide layer growth was denoted 'protective' when the oxidation rate decreased with time, i.e. linearity has been lost [6]. From oxidation experiments of other authors on other metals a general theory of protective oxidation was assumed. In this theory the oxidation behaviour was stated to be controlled by diffusion of one of the species through the developing oxide. Increasing oxide thickness thereby causes increasing diffusion paths. Thus oxidation slows down, according to a parabolic rate law. For Mg oxidised at low temperatures an almost parabolic rate of oxidation could be confirmed [7]. Up to a critical thickness thin oxide films were assumed to withstand the tensile stress necessary to adapt it to the metal lattice such that no cracks are produced. This state is then followed by rupturing of the protective film and linear growth.

In the 1960s weight measurements were improved and extended to the first ultra-high vacuum (UHV) microbalance systems. It could be verified that the growth of a 'protective' oxide layer follows a parabolic oxide growth mechanism [8-10] for oxide layers in a thickness range between ~ 5 nm and ~100 nm [8]. Also a pressure dependence of the oxidation kinetics was observed [8,9]. The parabolic rate constant was found experimentally to be proportional to almost $p^{1/6}$. On the basis of Fick's first law, an expression for the oxide thickness as a function of time was suggested [10]. It is based on the cation vacancy diffusion controlled model, first suggested by Wagner [11] and later extended by Wagner-Hauffe [12] and it correctly predicts the experimental findings at an 'intermediate' temperature range (~ 700 K) and oxygen partial pressures between $1.3 \cdot 10^{-2}$ mbar and ~ $1.3 \cdot 10^{2}$ mbar. Below an oxide thickness of ~ 5 nm the volume diffusion model might not be applicable. In Refs. [9,13,14] an exponential decrease of oxidation rate up to a thickness of ~ 2.5 nm was found. With the weight measurement method,

however, the initial oxidation stage below oxide thicknesses of 5 nm, which occur at low temperatures and/or low oxygen partial pressures, could not be clarified.

From the 1970s on oxidation research of this initial oxidation regime became accessible after improvement of the necessary UHV techniques in combination with invention and spread of the electron spectroscopy methods, like X-ray and ultraviolet photoelectron spectroscopy (XPS, UPS), Auger electron spectroscopy (AES) and electron energy loss spectroscopy (EELS) [15-38], as well as other methods like low energy electron diffraction (LEED) [20,22,23,32,33,37], ellipsometry [37,39], work function measurements [22,26,37,40,41] and others [24,26,27,42-44]. These techniques are suitable to probe the first few nanometers of a material only and due to continuous improvement of these techniques a large amount of information concerning the initial oxidation range for Mg could be gained up to the present time.

In spite of the above, the number of investigations on Mg as compared to other metals is still low and the kind of information given within a considerable part of these investigations is more of a descriptive nature. There are findings common to a considerable amount of investigations, e.g. the incorporation of oxygen below the surface [23,31,40,41,45], the growth of oxide by island formation [20-22,29,31,32,37,39,44,45] or the strong drop of the oxidation rate after an initial fast oxidation stage [17,26,29,36]. However, quantitative modelling of the initial Mg-oxidation kinetics (in the range of low temperatures and oxygen partial pressures) has not been done to a large extend (e.g. Ref. [29]). Also information about the composition [28,32-34,41,44] and the structure of the early oxide [42] is scarce. The quantitative data that is available concerning the early oxidation stage scatter considerably, probably due to the different experimental and instrumental conditions. Furthermore, in recent publications the idea of an initial oxide with a composition and electronic properties more similar to a metal than to an insulator came up [44,46], but data supporting this assumption is lacking. Thus, there is still a demand for more (quantitative) work on the initial oxidation of Mg.

1.2. Quantitative analysis of thin oxide layers with X-ray photoelectron spectroscopy

One of the methods that is most suitable for obtaining (quantitative) information about thin oxide layers is X-ray photoelectron spectroscopy (XPS). Since most of the investigations in the present work have been carried out with XPS, its basic principles are noteworthy to mention here in more detail.

In 1887 Hertz discovered the photoelectric effect which forms the basis of XPS. Thereby electromagnetic radiation (X-rays in the case of XPS) is interacting with the electrons in an atom, leading to the ejection of an electron out of its shell with a kinetic energy characteristic for the particular atom. From the kinetic energy of the electron the binding energy of the electron in the atom can be calculated with

$$E_{bdg} = h\nu - E_{kin} - \phi_S \tag{1.1}$$

Thereby, $h\nu$ is the energy of the X-radiation used (usually Al K_α or Mg K_α), E_{kin} is the kinetic energy of the electron after the interaction with the X-ray photon, E_{bdg} is the binding energy of the electron before the interaction and ϕ_s is the spectrometer work function, a value depending both on the spectrometer as well as on the material under investigation.

Chemical information can be gained from the shift in energy of a certain XPS line. Those so-called chemical shifts, which are typically of the order of a few tenths of an electron volt, are caused by the changes of the binding energy of the valence electrons due to their particular chemical environment or formal charge state. For example, a core level electron in a Mg atom in Mg metal (Mg^0) has a lower binding energy than a core level electron in Mg in MgO (Mg^{2+}). This is because the highly ionic kind of binding in MgO pulls away the valence electrons from the Mg atom and due to the lower electron charge density the positive electric field of the nucleus is shielded less by the remaining electrons and thus the attraction of the inner shell electrons to the nucleus enhances.

Although the penetration depth of the X-rays and thus the depth of ionisation of atoms is of the order of many micrometers, only photoelectrons of the first few nanometers will manage to escape from the sample because of the energy loss due to inelastic interactions. Only photoelectrons with trajectories within the material that are shorter than 3-5 times the inelastic mean free path (i.e. the mean distance a photoelectron can travel without an inelastic interaction; for details see Appendix of chapter 3) might escape from the sample. This is the reason why XPS is a surface sensitive technique.

Because of the energy loss processes that occur when an electron travels through a material, the intensity of a measured XPS spectrum is composed of an intrinsic part and an extrinsic part. The intrinsic part is inherent to the excitation of the core electrons itself (containing also intrinsic plasmon excitations and/or other intrinsic effects), whereas the extrinsic part contains the background composed of all inelastically scattered electrons, i.e. electrons that suffered an energy loss (e.g. due to extrinsic plasmon excitation) while passing through the material, but also secondary electrons and photoelectrons excited by Bremsstrahlung (if non-monochromatic X-rays are used). For the removal of this background

from the spectrum Tougaard and co-workers developed a method [47-50], which has also been used in this work (see chapter 1 and 2).

From the integrated intensity of the background subtracted spectrum quantitative information about a sample can be obtained. Generally, the intensity of the spectrum of an element A is given by (see e.g. chapter 5 of Ref. [51] and Ref. [49]):

$$I_A = F(\gamma, E_A) \cdot \sigma_A(h\upsilon) \int_{z=0}^{\infty} C_A(z) \cdot \exp\left[- \int_{z'=0}^{z} \frac{dz'}{\lambda_M(z, E_A) \cdot \cos(\Theta)} \right] dz \qquad (1.2)$$

Thereby, $F(\gamma,E_A)$ is an instrument factor depending on the angle γ between the incoming X-rays and outgoing photoelectrons and the energy E_A of the electron originating from a specific core level of element A, σ_A $(h\nu)$ is the cross section for emission of an electron from the atom of the element A in the sample by a photon of energy $h\nu$, $C_A(z)$ is the atom density of A atoms at depth z, $\lambda_M(z,E_A)$ is the inelastic mean free path (IMFP) of an photoelectron with energy E_A at depth z and Θ is the angle between the sample normal and the outgoing photoelectrons. For the derivation of Eq. (1.2) it is assumed that there are no lateral concentration variations, i.e. Eq. (1.2) is independent of x and y coordinates, and that elastic scattering of electrons can be neglected, i.e. electrons are assumed to move in a straight line from their point of excitation to the sample surface.

If a sample is homogeneous, i.e. $C_A(z) = C_A$, Eq. (1.2) reduces to:

$$I_A = \sigma_A(h\nu) \cdot C_A \cdot \lambda_A(E_A) \cdot F(\gamma, E_A) \qquad (1.3)$$

Since quantitative evaluation, e.g. of the sample composition, can be carried out referring to a standard reference sample with known composition the instrumental factor in Eq. (1.3) can be ignored as long as all intensities have been measured with the same XPS system and measurement conditions.

In this work, the following model for the oxidised samples has been used for quantitative analysis of the XPS spectra: A substrate of the pure metal M covered with an overlayer of oxide homogeneous in composition and thickness. The intensity of the metal, for an overlayer with thickness z, is given by:

$$I_M = F_M(\gamma, E_M) \cdot \sigma_M(h\nu) \cdot C_M \cdot \lambda_M(E_M) \cdot \exp\left[- \frac{z}{\lambda_M^{ox}(E_M) \cdot \cos\theta} \right] \qquad (1.4)$$

where λ_M^{ox} is the IMFP in the oxide and λ_M is the IMFP in the metal of electrons originating from metal atoms. Correspondingly for the (oxide) overlayer one gets:

$$I_M^{ox} = F_M^{ox}(\gamma, E_M) \cdot \sigma_M^{ox}(h\nu) \cdot C_M^{ox} \cdot \lambda_M^{ox}(E_M) \cdot \left(1 - \exp\left[- \frac{z}{\lambda_M^{ox}(E_M) \cdot \cos\theta} \right] \right) \qquad (1.5)$$

where the subscript M now refers to metal ions in the oxide. The intensities of a pure metal and a pure oxide (reference) sample I_M^{∞} and $I_M^{ox,\infty}$, respectively, are obtained from Eqs. (1.4) and (1.5) for $z = 0$ (analogous to Eq. (1.3)).

From the ratio of the signals of a clean metal reference and the covered substrate one can determine the thickness of the overlayer as long as both measurements have been measured with the same $F(\gamma, E_M)$, i.e. on the same instrument with the same measurement conditions:

$$I_M = I_M^{\infty} \cdot \exp\left[-\frac{z}{\lambda_M^{ox}(E_M)\cdot\cos\theta}\right] \tag{1.6a}$$

and thus:

$$z = -\lambda_M^{ox}(E_M)\cdot\cos\theta\cdot\ln\left(\frac{I_M}{I_M^{\infty}}\right) \tag{1.6b}$$

An equation analogue to Eqs. (1.6) holds for the ratio of the signals of an oxide reference and the oxide overlayer:

$$I_M^{ox} = I_M^{ox,\infty}\cdot\left(1-\exp\left[-\frac{z}{\lambda_M^{ox}(E_M)\cdot\cos\theta}\right]\right) \tag{1.7a}$$

and thus:

$$z = -\lambda_M^{ox}(E_M)\cdot\cos\theta\cdot\ln\left(1-\frac{I_M^{ox}}{I_M^{ox,\infty}}\right) \tag{1.7b}$$

Since it is not always possible to measure an reference sample another possibility to determine the (oxide) overlayer thickness is given from the ratio of Eqs. (1.4) and (1.5):

$$\frac{I_M^{ox}}{I_M} = \frac{C_M^{ox}\cdot\lambda_M^{ox}(E_M)}{C_M\cdot\lambda_M(E_M)}\cdot\left(\exp\left[\frac{z}{\lambda_M^{ox}(E_M)\cdot\cos\theta}\right]-1\right) \tag{1.8a}$$

where it has been assumed that $\sigma_M^{ox}(h\nu) = \sigma_M(h\nu)$ and $F_M^{ox}(\gamma, E_M) = F_M(\gamma, E_M)$. Thus:

$$z = \lambda_M^{ox}(E_M)\cdot\cos\theta\cdot\ln\left(\frac{I_M^{ox}\cdot C_M\cdot\lambda_M(E_M)}{I_M\cdot C_M^{ox}\cdot\lambda_M^{ox}(E_M)}+1\right) \tag{1.8b}$$

The calculation of the atom densities C_M^{ox} and C_O^{ox} of the metal and oxygen atoms in the oxide layer, respectively, can be executed as follows. From the ratio of Eq.(1.5) to the intensity of the clean metal (Eq.(1.4) with $z = 0$) one can determine C_M^{ox}:

$$C_M^{ox} = C_M\cdot\frac{I_M^{ox}\cdot\lambda_M(E_M)}{I_M^{\infty}\cdot\lambda_M^{ox}(E_M)}\cdot\left(1-\exp\left[-\frac{z}{\lambda_M^{ox}(E_M)\cdot\cos\theta}\right]\right)^{-1} \tag{1.9}$$

Thereby, again $\sigma_M^{ox}(h\nu)=\sigma_M(h\nu)$ and $F_M^{ox}(\gamma,E_M)=F_M(\gamma,E_M)$. The intensity from oxygen within the oxide layer I_O^{ox} can be calculated analogous to Eq. (1.5):

$$I_O^{ox}=F_O(E_O)\cdot\sigma_O\cdot C_O^{ox}\cdot\lambda_O^{ox}(E_O)\cdot\left(1-\exp\left[-\frac{z}{\lambda_O^{ox}(E_O)\cdot\cos\theta}\right]\right) \tag{1.10}$$

with λ_O^{ox} being the IMFP within the oxide of electrons originating from oxygen atoms. From the ratio of Eqs. (1.5) and Eq.(1.10) and inserting Eq. (1.9) for C_M^{ox} one can determine C_O^{ox}:

$$C_O^{ox}=C_M\cdot\frac{I_O^{ox}\cdot\lambda_M(E_M)\cdot\sigma_M\cdot F_M(E_M)}{I_M^{\infty}\cdot\lambda_O^{ox}(E_O)\cdot\sigma_O\cdot F_O(E_O)}\cdot\left(1-\exp\left[-\frac{z}{\lambda_O^{ox}(E_O)\cdot\cos\theta}\right]\right)^{-1} \tag{1.11}$$

1.3. The scope of this thesis

The aim of this work was the investigation of the initial oxidation of magnesium, i.e. the development of the first nanometers of oxide on the metal during exposure to oxygen. Since the oxide layer thicknesses one is dealing with at this stage are that small, a deviation of results by ~ 0.1 nm to 0.2 nm is not negligible anymore. Therefore evaluation of the experimental data has to be performed carefully. In both chapter 2 and 3 of this work the quantification of thickness and composition from XPS spectra has been improved by considering the intrinsic plasmon excitation contributions to XPS spectra. These intrinsic intensity contributions normally are neglected and thus somewhat falsify the results for both quantities mentioned. In chapter 2 a new method, based on the reconstruction of an experimentally measured spectrum of pure Mg, has been used for determination of the intrinsic plasmon intensity contribution, whereas in chapter 3 a series of differently oxidised Mg samples have been used to evaluate an existing method and an alternative approach is introduced.

In chapter 4 the quantitative XPS information gained in chapters 2 and 3 has been used to present thickness and composition data of the initial magnesium oxidation stage. Thereby other techniques, like high resolution elastic recoil detection analysis (HERDA) and ellipsometry have been used as well, yielding additional (quantitative) information concerning oxygen concentration, growth kinetics and electronic properties (band gap). The results are compared and combined with available information from literature. A theoretical model due to Fromhold and Cook has been applied to quantitatively describe the oxidation kinetics.

Chapter 5 contains a short summary (in german language) of the complete work presented in the former chapters.