Oxidation of Beryllium – a Scanning Auger Investigation

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Abstract. Beryllium is considered a candidate material for the first wall of nuclear fusion plasma experiments, e.g. ITER. For this application, the interaction of beryllium with oxygen is important for several reasons. One aspect is the reaction of hot beryllium with air in case of a catastrophic leak, the other is the action of beryllium as a getter, binding oxygen impurities and thus helping to keep the level of contamination in the plasma low. We therefore investigated the interaction of beryllium with air at elevated temperatures up to 600°C on a microscopic level, using a high resolution Auger electron microscope. At 390°C, a thin protective oxide film is formed, while at 500°C oxidation starts to enter into the grain boundaries, leading to the loosening of small particles of beryllium already at 600°C. This temperatures are considerably lower than the previously reported onset of catastrophic oxidation at 750°C. This could be due to our more sensitive methods of analysis or due to the higher impurity content of the plasma-sprayed and sintered samples we have used. The expected diffusion of oxygen from the surface into the bulk has not been observed up to 390°C, the highest temperature to be safely applied in UHV inside the Auger microscope. Thus, an operation of beryllium liners as a non-evaporable getter (NEG) is not to be expected in this temperature range. Getter activity linked to the transport of beryllium from the liner to some deposition areas is however possible. Carbon impurities included in the beryllium samples diffused to an atomically clean surface produced by sputtering already at room temperature. This points to a possible problem of carbon contamination of the plasma, when carbon containing beryllium material is used as a first wall.

1. Introduction

Beryllium is seriously considered as a first wall material for magnetic confinement fusion devices [1]. It is hoped that beryllium will also act as a getter for oxygen. The diffusion of oxygen into the bulk would permit to getter substantial amounts. Older publications seemed to point to that direction. Another type of getter action would be due to the sputter-induced transport of beryllium. The aim of the present study is therefore to test this assumption and revisit the interaction of oxygen and beryllium in more general terms.

The oxidation of beryllium has previously been investigated by a few authors. A number of papers on the subject appeared in the Journal of Nuclear Materials in the years 1961 to 1964 [2-7]. This work was done by optical microscopy, transmission electron microscopy of carbon replicas and thermogravimetry. The articles point to the formation of a protective oxide at lower temperatures, and catastrophic oxidation at higher temperatures.

In 1984 Fowler and Blakely [8-10] reported on the initial oxidation of a beryllium (0001) single crystal surface, studied by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED). Two low-pressure oxidation modes are found, which are distinct from the two modes observed at atmospheric pressures. The first is the chemisorption of oxygen on a clean beryllium surface, the second the logarithmic growth of very thin oxide films, limited by electron tunnelling.

More recent publications are related to the use of beryllium as a first wall material or in tritium breeding blankets [11-13]. Main focus of these articles is interaction of hot beryllium with air or water vapour in case of a catastrophic leak.

Literature up to 1968 is summarised in a paper by Adams and Hurd [14]. Oxidation kinetics is found to vary strongly between different batches of beryllium, suggesting that impurities or structural differences have an important influence on oxidation behaviour.

2. Experimental

2.1. Samples

The beryllium samples were previously used for outgassing experiments. We had three sintered and three plasma-sprayed samples, measuring 5 x 5 x 2 mm each. The experiments were performed using one sample of each type, but no difference was detected. For the safe handling and manipulation of beryllium samples, a glove box with integrated grinding machine and filtered air circulation system was set up. The grinding machine is supplied with a closed water circulation system.

2.2. Analysis of Samples

For the analysis of the samples a field emission Scanning Auger Microscope (SAM), model VG Microlab 310F, was used. The base pressure was $1{,}5\times10^{-10}$ mbar. According to residual gas analysis, interference of residual oxygen with diffusion experiments can be ruled out. The thickness of oxide films was determined by sputter depth profiling using 3 keV Argon ions. Sensitivity factors have been used for data reduction, introducing errors in the concentrations shown in depth profiles. The depth scale is referenced to electrochemically produced tantalum oxide (Ta_2O_5) films. As the ratio of sputter yields between BeO and Ta_2O_5 is not known, no attempt has been made to correct for the different sputter yields. Depths given are “equivalent depths”. The oxidised and the metallic beryllium can be distinguished due to a shift of the Auger peak energy [15-17].

2.3. Heating of Samples

Samples were heated *in situ* in the SAM up to 390°C, limiting the vapour pressure of beryllium to 10^{-12} mbar. The error in temperature was ±10°. Heating experiments *ex situ* up to 600°C were performed in a tubular furnace. The error in temperature was ±3°C. When heating beyond 390°C, fused silica test tubes were used in order to avoid contamination.

3. Experiments and Results

3.2. Diffusion of Oxygen

Two polished samples with native oxide layers were heated at 390°C *in situ* for several hours each. Subsequently several Auger depth profiles on different places on the surface were taken. Only native oxide layers with a thickness of a few nanometers were observed. In an attempt to increase the oxygen inventory available, samples have been heated *ex situ* in air at 390°C and subsequently *in situ* for several hours. No effect of the heating in UHV could be observed.

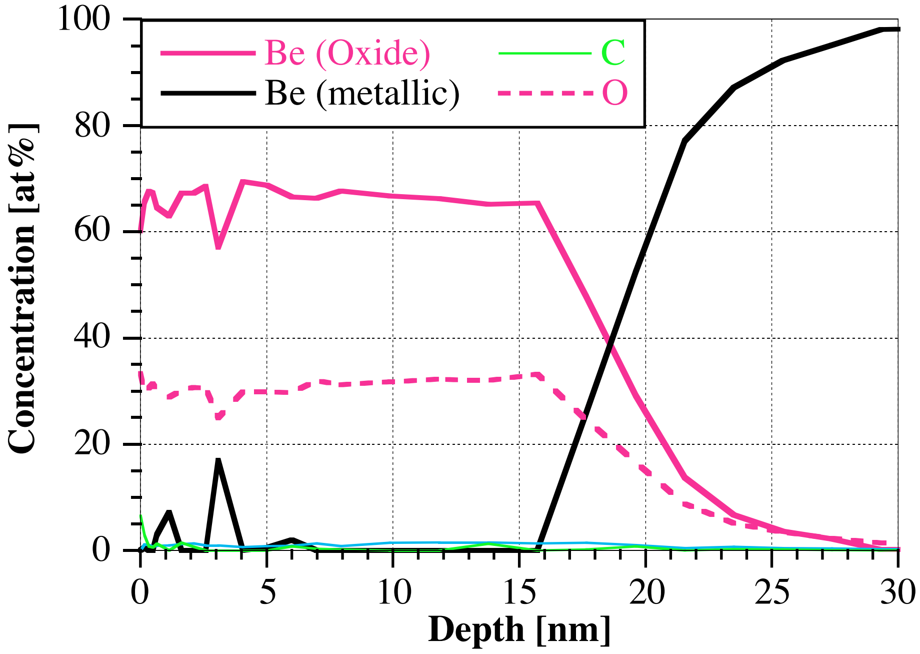

FIG. 1. Depth profile after heating for 43 hours at 390°C in air.

3.3. Oxidation

In order to determine the oxidation kinetics of beryllium in air, a sample was repeatedly polished and heated in air for different periods of time. After every heating cycle depth profiles were recorded in different places. In the first series the heating time was up to 43 hours at 390°C. During the heating period, the oxide thickness grew from 1 nm to roughly 20 nm. The lower value corresponds to the natural oxide layer at room temperature. The oxide layer formed on the freshly polished surface shows a fairly low level of carbon contamination.

FIG. 1 shows a depth profile after a heating period of 43 hours. The two peaks of metallic beryllium in the first part of the profile are most likely due to an error in the data reduction software. From the deviation of the oxygen and beryllium concentrations from 50% each a deviation from the nominal composition cannot be deduced due to uncertainties of the sensitivity factor method applied. The small oxygen concentration at the end of the profile is most likely an artefact due to a not perfectly flat surface.

FIG. 2 shows the growth of the oxide thickness at 390°C with time. Points show experimental data, the line is a square root fit. Within the limits of experimental error the thickness grows with the square root of time. This is to be expected for diffusion limited oxide growth. Possibly, we could claim that the points at 43 hours are consistently below the fit, hinting towards a saturation of the oxide growth.

After finishing the depth profiles, secondary electron images have been taken in order to find any oxides grown into the bulk or oxides formed in grain boundaries. We found only oxide particles in scratches, produced most likely by the polishing process.

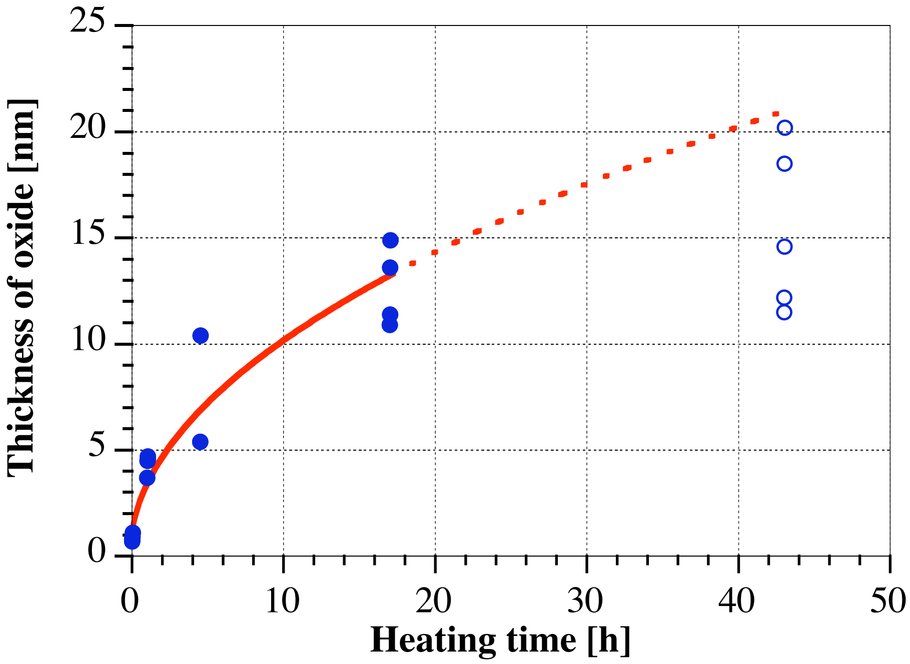

FIG. 2. Growth of the oxide thickness vs. time at 390°C. The curve has been fitted to the full symbols. The thickness of the natural oxide layer (at time zero) is approximately 1 nm.

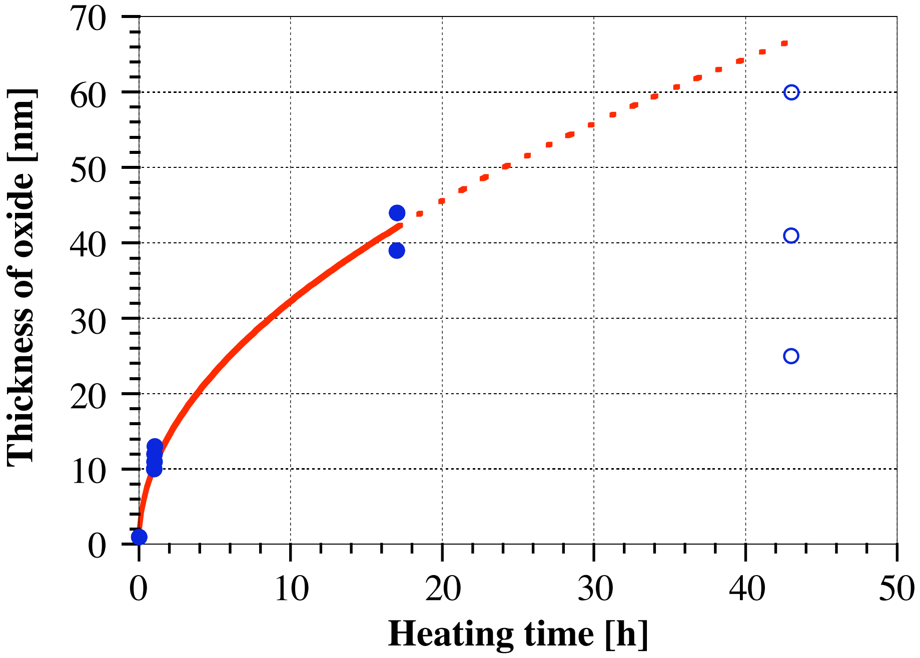

FIG. 3. Growth of the oxide thickness vs. time at 500°C. The curve has been fitted to the full symbols.

At the higher heating temperatures investigated (500°C and 600°C) the oxide growth is accelerated as expected. The saturation and the scatter of oxide thicknesses obtained are however more pronounced, as *FIG. 3 and 4* clearly demonstrate. At 500°C *(FIG. 3)* and at 600°C *(FIG. 4)*, the parabolic oxide growth seems to be limited to a thickness of approximately 40 nm. If the diffusion coefficients at the three temperatures (390°C, 500°C and 600°C) are evaluated, an Arrhenius type behaviour with an activation energy for the diffusion of around 1,16 eV is observed *(FIG. 5)*.

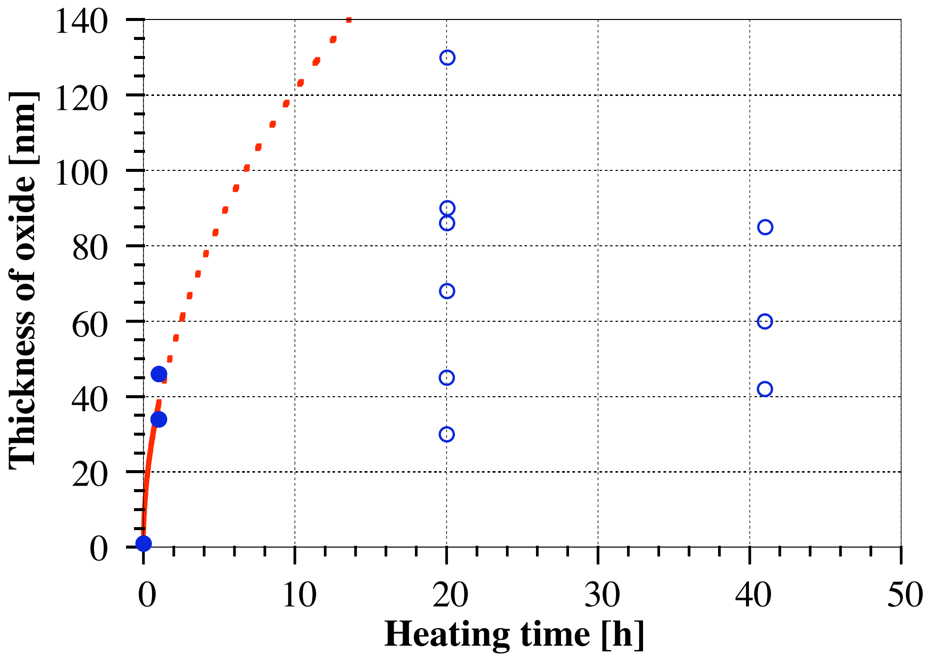

FIG. 4. Growth of the oxide thickness vs. time at 500°C. The curve has been fitted to the full symbols.

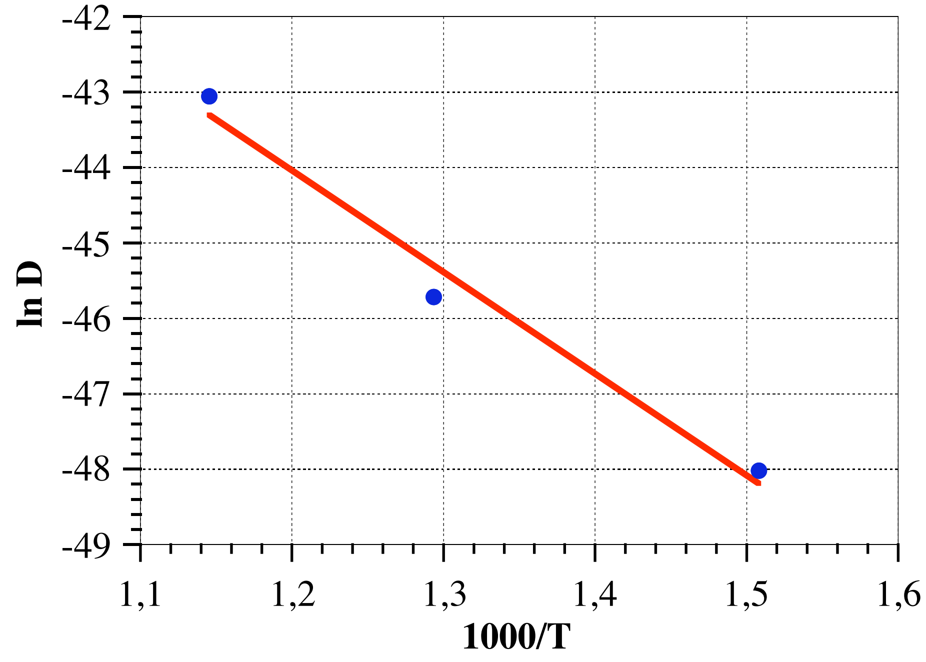

FIG. 5. Arrhenius-plot of the diffusion coefficients obtained from parabolic growth curves (FIG. 2, 3 and 4). The activation energy evaluated from this plot is 1,16 eV. This value is independent of errors in the absolute depth scale of the oxide thicknesses.

Electron micrographs were taken from samples heated to temperatures of 500°C and 600°C after finishing the sputter depth profile. In contrast to the 390°C samples, these micrographs show that the oxide grows into the bulk, most likely along grain boundaries *(FIG. 6)*. In some places, the grain boundaries seem to be cracked open by the oxide. After extensive heating (20 h) at 600°C the oxide has loosened micrometer sized beryllium particles from the surface *(FIG. 7)*. The oxide appears brighter than beryllium metal due to its higher secondary electron yield [18]. The identification of beryllium metal and beryllium oxide has been confirmed by scanning Auger maps and Auger spectra.

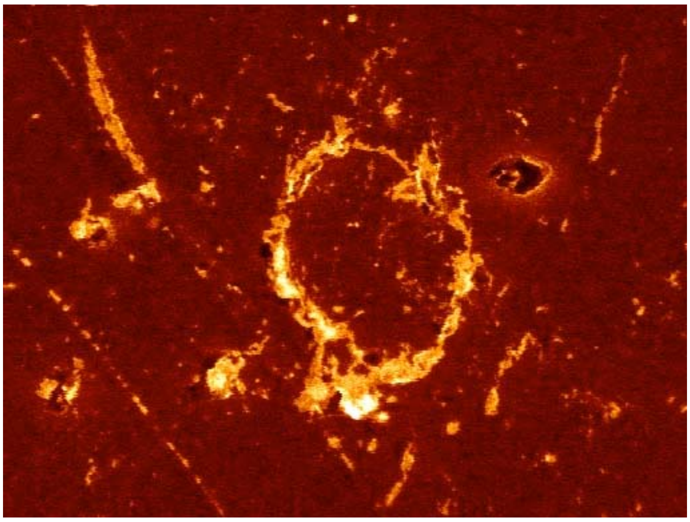

FIG. 6. Scanning electron micrograph of a sample surface, heated for 1 hour at 600°C in air. The oxide layer has been removed by sputtering. The oxide in the grain boundaries is clearly visible. The oxide appears brighter due to its higher secondary electron yield. Image size is 24 x 18 µm.

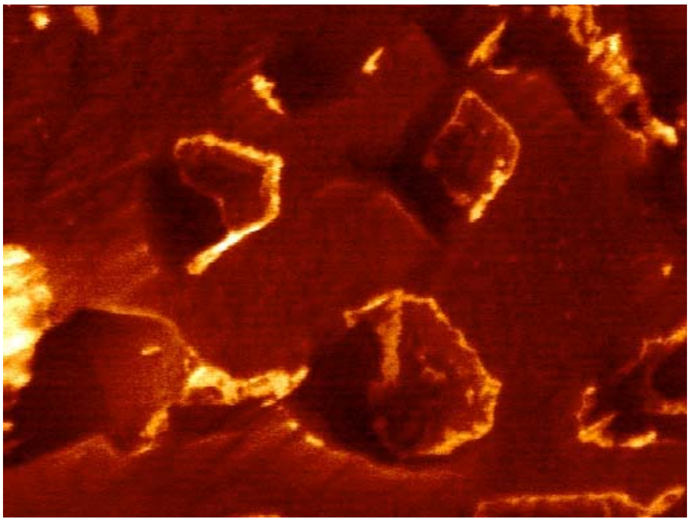

FIG.7. Scanning electron micrograph of a sample surface, heated for 20 hours at 600°C in air. Pits from missing grains are clearly visible. The oxide appears brighter due to its higher secondary electron yield. Image size is 8 x 6 µm.

4. Results and Discussion

Beryllium forms a continuous, thin-oxide layer at temperatures up to 390°C. Diffusion of oxygen into the grain boundaries has not been observed at such temperatures.

In contrast, diffusion into grain boundaries has been observed at temperatures of 500°C and 600°C. This leads eventually to the loosening of individual grains and the formation of beryllium dust. We expect therefore that prolonged oxidation will ultimately result in a loss of structural strength of beryllium. This temperature is considerably lower than the transition to catastrophic oxidation, observed around 750°C by other authors [2]. This discrepancy could be due to different reasons. First, the sprayed and sintered materials investigated are possibly more prone to catastrophic oxidation due to their structure and impurity content. Second, our scanning Auger investigations are more sensitive to the onset of internal oxidation than the classical methods applied in earlier work.

The range of activation energies for the oxidation (i.e. the metal transport through the oxide layer) reported earlier (0,4…2,8 eV) is compatible with our activation energy of 1,16 eV. The large range of activation energies points to a combination of several diffusion mechanisms or to the role of structure and impurity content [14] of the samples.

According to our depth scale, referenced to Ta_2O_5, the native oxide thickness is 1 nm, while it is 10 nm according to Adams and Hurd [14], suggesting a depth error of a factor of 10 for our measurements. The value of Adams and Hurd is however based on an even older publication, and it is not clear whether this value is actually based on a measurement or it is simply an estimate. Weight gain measurements published by Aylmore et al. [6] point to the formation of a protective oxide at 500…600°C in oxygen at a weight gain of 30 $\mu g/cm^2$. The thickness in this case can be calculated to be 150 nm. We observe 30…40 nm on our depth scale, pointing to a more plausible depth error of a factor of 3 to 4. The error could be even less if grain boundary oxidation occurred also in the experiments of Aylmore et al., contributing to weight gain, but not to oxide thickness.

From preliminary experiments we have no indication of oxygen moving from a surface oxide layer into the bulk during heating in UHV up to 390°C. We intend to clarify this point further by heating to higher temperatures in hydrogen atmosphere. If the experiments planned confirm the preliminary findings, beryllium liners will not be able to act as a getter removing oxygen from the gas phase. Beryllium can however act as a getter if it is transported from the surface of the liner to some deposition areas by sputtering.

5. References

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