Interaction of Beryllium Oxide with Hydrogen Plasma

C. Tomastik, W.S.M. Werner, H. Störi

Institut für Allgemeine Physik, Vienna University of Technology
Wiedner Hauptstraße 8-10, A-1040 Wien, Austria

e-mail contact of main author: tomastik@iap.tuwien.ac.at

Abstract. Beryllium is considered a candidate material for the first wall of nuclear fusion plasma devices, e.g. ITER. For this application, the interaction of beryllium oxide with a D/T plasma is important with respect to beryllium as oxygen getter. Since it is not yet fully clear if and how much oxide will develop during operation, we investigated the interaction of beryllium samples with hydrogen plasma. Oxide layer thicknesses were measured by sputter depth profiling, using a high resolution Auger electron microscope. Exposure of beryllium samples with native oxide layers and pre-oxidized samples to hydrogen plasma resulted in an oxide layer of similar thickness, suggesting the development of an equilibrium state during exposure. In order to determine the relation between equilibrium oxide layer thickness and oxygen concentration in the plasma, the samples were exposed to hydrogen plasma with various additions of water vapour. The water vapour concentration was monitored with a quadrupol mass spectrometer. The experiments so far suggest that higher water vapour concentration results in a higher oxide layer thickness, as would be expected, and that oxide layer formation takes place down to a water vapour concentration of at least $3 \cdot 10^{-6}$. An operation of beryllium liners as a non-evaporable getter (NEG) is therefore not to be expected. Getter activity linked to the transport of beryllium from the liner to some deposition areas is however possible.

1. Introduction

Beryllium is considered as a first wall material for magnetic confinement fusion devices [1]. It is hoped that, in addition to the advantage of its low atomic number, beryllium will also act as a getter for oxygen. By diffusion into the bulk of the beryllium metal substantial amounts of oxygen would be absorbed over time. This would act as a long acting sink of oxygen, permanently reducing the level of impurities in the plasma. Another type of getter action would be due to the sputter-induced transport of beryllium. Oxygen would be gettered and subsequently buried in places, where Beryllium is only deposited, but not sputtered. The aim of the present study is to investigate the behaviour of beryllium surface oxide layers under hydrogen plasma conditions in order to predict the influence of beryllium liners on the plasma operation.

2. Previous Experiments

2.1. Oxidation

These experiments were performed in order to determine the oxidation kinetics of beryllium in air. Samples were heated in air for different periods of time at different temperatures. After every heating cycle the sample was transferred into our Auger electron microscope and depth profiles were recorded in different places on the sample surface. At 390°C, a protective oxide layer of up to 20 nm thickness was formed. At the higher heating temperatures investigated the oxide growth is accelerated as expected. At 500°C and at 600°C, the parabolic oxide growth seems to be limited to a thickness of approximately 60 nm. The activation energy for oxidation evaluated from these experiments is 1,16 eV [2].
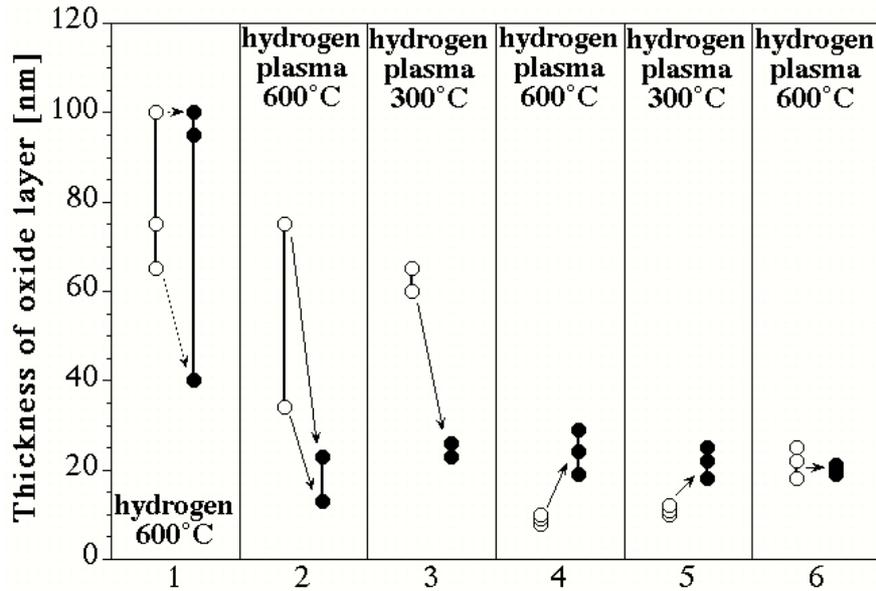
*FIG. 1. Change of oxide thickness due to hydrogen treatment (six examples).
The open symbols denote thicknesses before hydrogen treatment and the full
symbols show the situation after treatment.*

2.2. Interaction with Hydrogen

Samples that were pre-oxidised to provide different oxide layer thicknesses were exposed to hydrogen atmosphere at 500°C and hydrogen plasma (pure hydrogen in both cases) at temperatures from 300°C to 600°C, for 5 to 6 hours each. The subsequently obtained depth profiles of the sample surface show that hydrogen atmosphere does not have any distinctive effect on the oxide layer thickness. In hydrogen plasma, however, thick oxide layers are reduced to approximately 25 nm, whereas thinner oxide layers are further oxidised to the same thickness (see FIG. 1.). This suggests the development of an equilibrium state in the plasma which yields an equilibrium oxide layer at the end of the exposure experiment with a thickness depending on the plasma conditions, especially on the concentration of oxygen-containing impurities [2].

3. Experimental

3.1. Samples

As it is unlikely that rolled beryllium sheet would be used as a first wall, work concentrated on sintered and sprayed samples. Our set of samples comprised three sintered and three plasma-sprayed samples. The size of each sample was approximately 5 · 5 · 2 mm. Each experiment was performed with at least one sintered and one plasma sprayed sample, in order to detect any differences in behaviour. As no difference was detected at any temperature, the results presented apply to both types of materials. In order to be analysed (see below) the sample surface had to be polished. For this purpose a glove box with integrated grinding machine and filtered air circulation system was set up.

3.2. Heating and Plasma Treatment

Heating experiments were performed in a tubular furnace where temperatures up to 1100°C can be reached. The furnace is equipped with a supply of hydrogen and nitrogen and a vacuum pumping system. This permits heating of Be-samples in non-oxidizing atmosphere. Nitrogen is used to flush the system (including the pump exhaust) free of oxygen prior to admission of hydrogen to prevent the formation of explosive mixtures.
Additionally, external electrodes have been attached along a length of 20 cm to the middle section of the furnace tube. These permit the excitation of an r.f. plasma inside the tube, provided the pressure in the tube is in the mbar range. The plasma volume is roughly 100 cm^3 and r.f. powers up to 1100 W are available. Usually, we used a power of 100 W. Further plasma diagnostics were not available. The temperature in this case was kept below 400°C to avoid contamination of the furnace without use of additinal sample containers.

3.3. Water Vapour Supply

The gas supply system of our furnace has been equipped with a facility to add minute amounts of water vapour to the gas. This consists of a chamber where part of the hydrogen is conducted through distilled water and thus saturated with water vapour. The chamber is cooled to 13°C, giving a water vapour pressure of 15 mbar. With a hydrogen pressure of 1500 mbar at this point, this results in a water vapour concentration of 1% (10^{-2}). This is also the upper limit for the water vapour concentration for our experiments. The mixture is then dynamically diluted in a second mixing stage with pure hydrogen (99,999 %) using mass flow controllers. A Balzers QMG 420 quadrupole mass spectrometer is used to monitor the water vapour concentration in the furnace. During experiments with pure hydrogen plasma the water vapour concentration remained below $3 \cdot 10^{-6}$, which sets the lower limit for our experiments.

3.4. Analysis

For the analysis of the samples a field emission Scanning Auger Microscope, model VG Microlab 310F, was used. The base pressure was $2,5 \cdot 10^{-10}$ mbar. According to residual gas analysis, interference of residual oxygen during the analysis 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 some systematical error in the elemental concentrations. 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, our depth measurements have been compared to values from similar experiments[3], resulting in an estimated error of 20 % for the depth scale [2]. The oxidised and the metallic beryllium can be distinguished due to a shift of the Auger peak energy [4-6].

4. Results and Discussion

The formation of an oxide layer of uniform thickness during hydrogen plasma treatment, independent from the initial oxide thickness, might be expected considering the empirical concept of "plasma-chemical quasi equilibrium" introduced by Rutscher and Wagner [7]. According to these concepts, various plasma-induced processes lead to a steady state, which behaves superficially equivalent to a thermodynamic equilibrium, leading in this case to an eqilibrium oxide thickness. Such an equilibrium would be reached regardless of the plasma conditions, i.e. concentration of residual impurities, varying only in the thickness of the oxide

layer. A similar concept can be found in [8]. However, this study only distinguishes between the two cases of existence of an oxide layer and clean beryllium surface, depending on plasma conditions.

Our recent experiments aim at obtaining the dependence of the equilibrium oxide thickness developed during hydrogen plasma treatment on the concentration of water vapour in the hydrogen. Several plasma exposure experiments at three different concentrations of water vapour have been performed, at a temperature of 390°C and for 6 h each. Experiments with pure hydrogen are listed at a water vapour concentration of $3 \cdot 10^{-6}$, according to our mass spectrometry measurements. Further experiments have been performed at concentrations of 10^{-4} and 10^{-2}. Prior to the experiments, the samples had only their native oxide layer, without any pre-oxidation. After each experiment, the oxide layer thickness was measured in at least four spots on the sample surface.

FIG. 2 shows the results for the experiments performed so far. The thickness values and scatter of values are comparable for the two lower water vapour concentrations, whereas higher thickness values appear at a concentration of 10^{-2}, increasing the scatter considerably. This scatter, from about 15 nm to more than 80 nm thickness, is very likely due to spalling of oxide flakes of higher thickness, leaving patches of surface with thin oxide layers, as was demonstrated earlier [2]. A relation between equilibrium oxide thickness and concentration of water vapour is discernible, but the data are still insufficient for a thorough analysis to that effect.

5. Conclusion

In our opinion, the native oxide layers of the beryllium liners will develop an equilibrium with the oxygen content of the plasma during operation. Therefore oxygen will not be removed permanently from the plasma phase by the gettering action of the bulk of the liners. Most likely, oxygen will only be removed by irreversible transport of beryllium from the liners to other parts of the vessel.
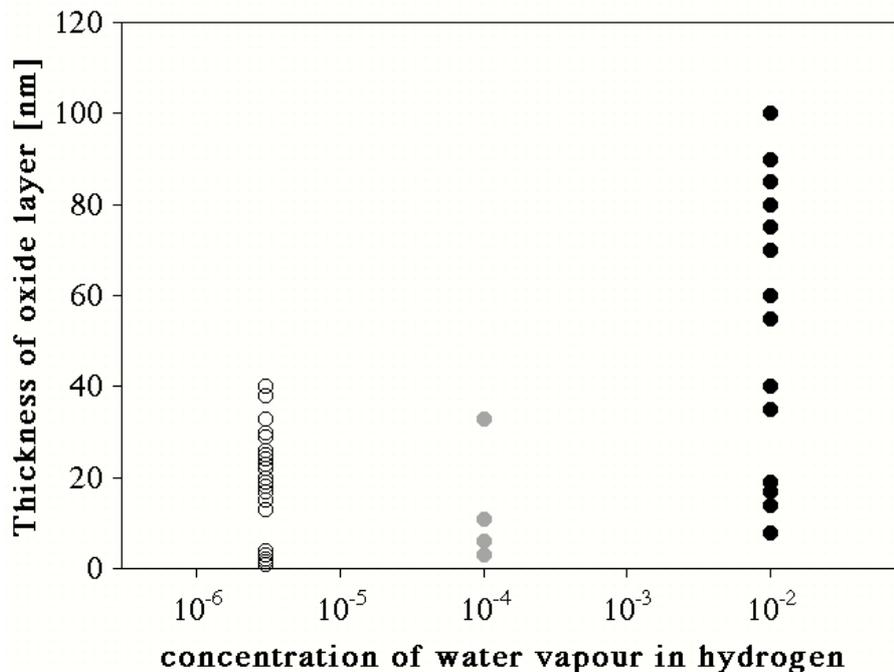
FIG. 2. Measured oxide thicknesses of beryllium samples exposed to hydrogen plasma with various added concentrations of water vapour

6. References

[1]   DIETZ, K.J., and the JET team, "Effect of beryllium on plasma performance in JET", Plasma Physics and Controlled Fusion **32** (1990) 837

[2]   TOMASTIK, C., WERNER, W.S.M., STÖRI, H., "Oxidation of Beryllium - a Scanning Auger Investigation", Nucl. Fusion **45** (2005) 1061

[3]   ROTH, J., WAMPLER, W.R., JACOB, W., J. Nucl. Mat. **250** (1997) 23

[4]   SULEMAN, M., PATTINSON, E.B., "Interpretation of the Auger Spectrum of Clean and Oxidized Be", J. Phys. F **3** (1973) 497

[5]   LEJEUNE, E.J., DIXON, R.D., "Interpretation of the Auger Electron Spectrum from Oxidized Beryllium", J. Appl. Phys. **43** (1972) 1998

[6]   FORTNER, R.J., MUSKET, R.G., "Chemical Effects in the Auger Electron Spectra of Beryllium", Surface Science **28** (1971) 339

[7]   Rutscher, A., Wagner, H.E., Plasma-Sources, -Science and -Technology **2(4)** (1993) 279

[8]   Bastasz, R., Thin Solid Films **121** (1984) 127