Interaction of Beryllium Oxide with Hydrogen Plasma

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Abstract. Beryllium is considered a candidate material for the first wall of nuclear fusion plasma devices. 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 oxide layers 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 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 fraction in hydrogen of at least $3 \times 10^{-6}$. Water vapour fractions above $10^{-2}$ seem to lead to erosion of the samples. An operation of beryllium liners as a non-evaporable getter 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. 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. Experimental

2.1. 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 $5 \times 5 \times 2$ 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 in any of the experiments, 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.
2.2. 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 approximately 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.

2.3. Water Vapour Supply

To provide oxygen in small concentrations in the plasma, 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 fraction of 1% (10$^{-2}$). This is the upper limit for the water vapour fraction 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 3·10$^{-6}$, which sets the lower limit for our experiments.

2.4. Analysis

For the analysis of the samples a field emission Scanning Auger Microscope, model VG Microlab 310F, was used. The base pressure was 2.5·10$^{-10}$ 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$_2$O$_5$) films. As the ratio of sputter yields between BeO and Ta$_2$O$_5$ is not known, our depth measurements have been compared to values from similar experiments [1], 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 [3-5].

3. Preliminary Experiments on Interaction with Hydrogen Plasma

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 15 - 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
FIG. 1. Experimental data for the change of oxide thickness due to hydrogen plasma treatment. 
a) reduction of thick oxide layers; b) further oxidation of thin oxide layers; c) thickness unchanged. 
The blue area indicates the measured thickness range for the equilibrium oxide layer. 
♦ ... thickness before treatment, ◆ ... thickness after treatment

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].

4. Recent Results and Discussion

Our recent experiments aim at obtaining the dependence of the equilibrium oxide thickness 
developed during hydrogen plasma treatment on the concentration of oxygen-containing 
impurities in the hydrogen. For this purpose, minute amounts of water vapour were added to 
the hydrogen. Several plasma exposure experiments have been performed at water vapour 
fractions of $10^{-4}$, $10^{-3}$ and $10^{-2}$ in hydrogen, at a temperature of 390°C and for 6 h each. 
Analogous experiments without addition of water vapour are listed at a water vapour fraction 
of $3 \times 10^{-6}$, according to our mass spectrometry measurements. 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 $10^{-3}$, increasing the scatter considerably. 
This scatter, from about 15 nm to more than 200 nm thickness, is 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.

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
FIG. 2. Measured oxide thickness of beryllium samples exposed to hydrogen plasma with various added concentrations of water vapour

concept of “plasma-chemical quasi equilibrium” introduced by Rutscher and Wagner [6]. 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 equilibrium oxide layer. 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 [7]. However, this study only distinguishes between the two cases of existence of an oxide layer and clean beryllium surface, depending on plasma conditions.

After each plasma treatment secondary electron images of the sample surface were taken. FIG. 3 and 4 show examples in different resolutions for dry hydrogen and a water vapour addition of 1%, respectively. The former surfaces, corresponding to an oxide thickness of 5 - 10 nm, are quite smooth, whereas the latter show clear signs of structural damage (oxide thickness approximately 80 nm). This suggests that an equilibrium oxide layer develops only if the oxygen concentration remains below a certain level that has yet to be determined, while higher oxygen concentrations lead to erosion. The extent of these destructive processes will have to be examined with experiments taking time dependence into account.

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. 3. Secondary electron image of beryllium sample surfaces after exposure to hydrogen plasma.
a) dry hydrogen; b) hydrogen with 1% water vapour added
Image size 120 x 90 µm

FIG. 4. Secondary electron image of beryllium sample surfaces after exposure to hydrogen plasma.
a) dry hydrogen; b) hydrogen with 1% water vapour added
Image size 24 x 18 µm

6. References