Nuclear Materials and Energy 45 (2025) 102028

Contents lists available at ScienceDirect

Nuclear Materials and Energy

journal homepage: www.elsevier.com/locate/nme

Boron layer preparation, characterization and hydrogen isotope permeability for fusion application

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ARTICLE INFO

Keywords:
Boronization
Boron layers
Magnetron sputter deposition
Hydrogen isotope permeability
Material characterization

ABSTRACT

Due to the re-baseline of the fusion device ITER and the strategical decision to change from Be to W as first wall material, a boronization procedure has to be implemented into the wall conditioning phase. Since the functionality of boron layers in carbon free fusion devices is not understand in detail so far, this study aims to be a starting point of the investigation of boron layers for fusion applications.

In the first step, pure boron coatings are prepared in a magnetron sputter deposition device on W and steel substrates. The homogeneity, crystal phase and composition is studied and it is proved that an amorphous, stable boron layer is obtained with this deposition procedure. No impurities, e.g. O, N, C, are detected and a deposition rate of 20 nm/h is reached. The coatings are temperature stable up to 1000 °C. No oxidation of the boron layer is detected when exposed to air, but a uptake of humidity is possible. Therefore, the samples should be stored in vacuum after deposition.

The hydrogen isotope permeability is studied and a low layer permeability, which is four orders of magnitude lower as steel is found.

In the future, the investigation will be broadened to mixed boron layers, e.g. B:D and B:W, which are more alike as boron layers in fusion devices, and these mixed layers will be compared to the pure boron layers as a next step.

1. Introduction

The worldwide largest fusion device ITER, which is currently under construction in France, changed for strategical reasons from Be to W as first wall material [1]. The final decision for this approach was made in summer 2024, which effect the plans for material studies in the whole community. One aspect that was not considered for ITER until this decision is the implementation of a boronization system into the device. This boronization system is required, because oxygen and other impurities in the vessel are not sufficiently gettered by a W wall as it would be the case with Be as first wall material. This could lead to an insufficient start-up phase and problems during plasma operation. It was shown in many fusion devices that thin boron layers which are applied during the regular wall conditioning phase can solve the problem and a more efficient plasma operation can be obtained [2].

Even though the boronization process was and is used in many fusion devices worldwide and well established for several decades, only few studies were dedicated to the investigation of the functionality of these boron layers [3,4] and the detailed knowledge of the functionality of boron coatings is missing. Furthermore, since graphite tiles were used a lot in the past fusion devices and C and B are forming stable compounds, which probably change the functionality of B coatings, the findings in former fusion devices cannot be taken into account for the estimation of the effect of boronization in carbon free fusion devices as ITER [5].

Therefore, pure boron layers fabricated by magnetron sputter deposition on W and steel samples are characterized by different methods. This study is important for creating a data base and characterization methods for boron coatings are established and enhanced on these standardized samples. Next to the fabrication and characterization of the boron layers, the hydrogen isotope permeability in boron layers is investigated. This study is important in order to compare it with mixed B layers, such as B:W and B:D, and can be seen as an starting point for further studies on this material system.

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https://doi.org/10.1016/j.nme.2025.102028
Received 23 September 2025; Received in revised form 13 November 2025; Accepted 14 November 2025
Available online 15 November 2025

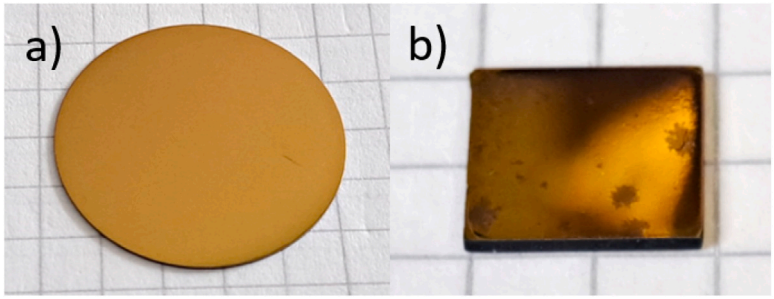

Fig. 1. Photographs of the B coated samples: (a) on a 316L substrates after deposition, (b) on a W substrates after storing in air for several weeks. The dots indicate the areas where a detachment of the layer took place.

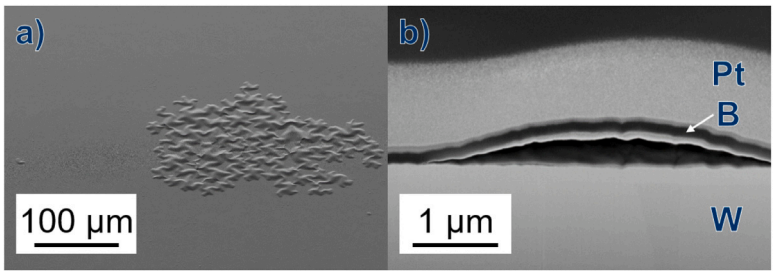

Fig. 2. (a) a SEM on the surface of a partially detached area. The wavy structure (blister) is the area, where the visible change of color can be identify by eye. (b) A SEM on the cross section on one of the blister in the detached area. In black the intact B layer is visible. The bright area in the lower part of the picture is the W substrate. The two grey layers on top of the B layer are Pt layers, which has to be applied for cutting.

2. Sample fabrication

Two types of sample substrates are used in this study: 316L(N)-ITER Grade steel (named 316L) and W-ITER Grade (named W). The substrates are cut in the desired geometry, dependent on the need for the applied characterization method: the geometry of the 316L substrates are disks with a diameter of 25 mm and a thickness of 0.5 mm for permeation studies, whereas the W substrates are cut in 1×1 cm^2 plates with a thickness of 1 mm. All samples are mirror polished with our standard polishing procedure for 316L and W and annealed in a vacuum oven at 550 °C (316L) or 1000 °C (W) for 2 h before deposition. The annealing is done in order to remove the intrinsic hydrogen content and minimize the surface oxidation, which can lead to a peeling of the coating.

For the layer deposition, our in-house Magnetron sputter device (PREVAC) is used. After inserting the substrates, the chamber is pumped to a base pressure of 10^{-7} mbar. A pure boron target (Kurt J Lesker Company GmbH) and an applied power of 140 W in RF-mode are used. The Ar sputter gas is inserted during deposition close to the magnetron and the deposition time is 5.5 h. The sample stage is rotating during deposition in order to guarantee a homogenous layer deposition. Several substrates can be coated during one deposition process and the layers from one deposition process are identical in thickness and composition. The chamber pressure during deposition is around $6{\cdot}10^{-3}$ mbar. For the permeation study, 316L substrates are coated on both sides. The W substrates are coated on one side only.

3. Characterization

3.1. Optical appearance and temperature stability

After deposition, the layers appear golden, see a photograph in Fig. 1a. No peeling of the layers from the substrates is observed when storing the samples in a desiccator in vacuum.

If the samples are not stored in vacuum after deposition, following observations are made: depending on the substrate material and surface conditions, the B layer detaches from the substrate and this detachment is visible by eye due to a change of color from gold to pink dots, see Fig. 1b. This change of color is not due to an oxidation of the B layer, but to a detachment of the layer, see the scanning electron microscopy (SEM) figures in Fig. 2 and the details of the microscopy device in the next section. By X-ray photoelectron spectroscopy (XPS), see below, it is confirmed that the composition of the layer is not changed and no B oxides are observed. The time span between deposition and detachment depends on the substrate material and the surface conditions between days (non annealed W), weeks (annealed W) and months (annealed 316L steel) in air. The explanation of this behavior is under investigation and the assumption is that the humidity in the air leads to an expansion of the layer or a part of the layer and depending on the adhesion to the substrate, the detachment occur sooner or later. Even though, we do not understand the mechanism in detail, all substrates are annealed in a vacuum oven before deposition and stored in a vacuum desiccator after deposition. With this procedure, the detachment of the B layer is successfully avoided and only samples with intact and attached layers are used in the permeation measurement.

The temperature stability of the layer is investigated in a vacuum oven with a base pressure in the 10^{-7} mbar range. B coated W, with a partially detached layer (left) and B coated 316L (right) substrates are placed in the oven and heated in steps of 100 °C. In Fig. 3 the photographs are shown for selected temperatures. The selection is done according to a change of sample appearance between the lower and higher temperature. The observations are that the B layer on a W substrate is unchanged up to 1000 °C, only the detached areas are slightly increased. In opposite to this, the B layer on a 316L substrate seems to be altered at 700 °C already and is completely removed at 800 °C. This behavior can be explained by the change of the substrate microstructure and phase transition in the steel at around 750 °C and therefore a weakening of the adhesion to the layer takes place.

3.2. Microstructure, layer thickness and composition

The surface of the coatings is analyzed by SEM with a Crossbeam 540 device (Zeiss) after layer deposition. On the cross sections, which

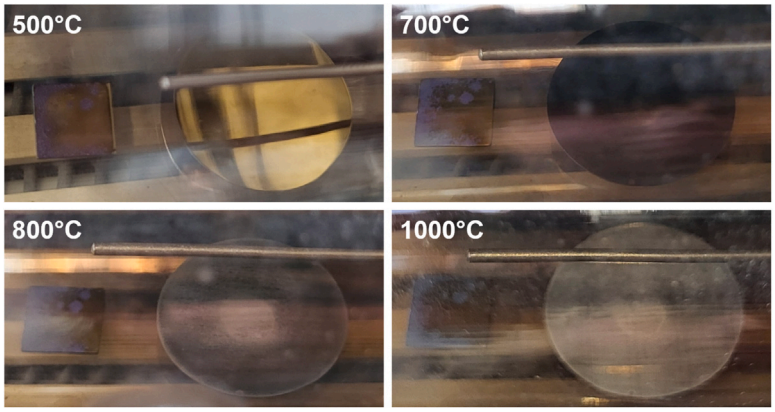

Fig. 3. B coated W substrate (left sample in each photo) and 316L substrate (right sample in each photo) at different annealing temperatures. The annealing oven temperatures are indicated in the figures correspondingly.

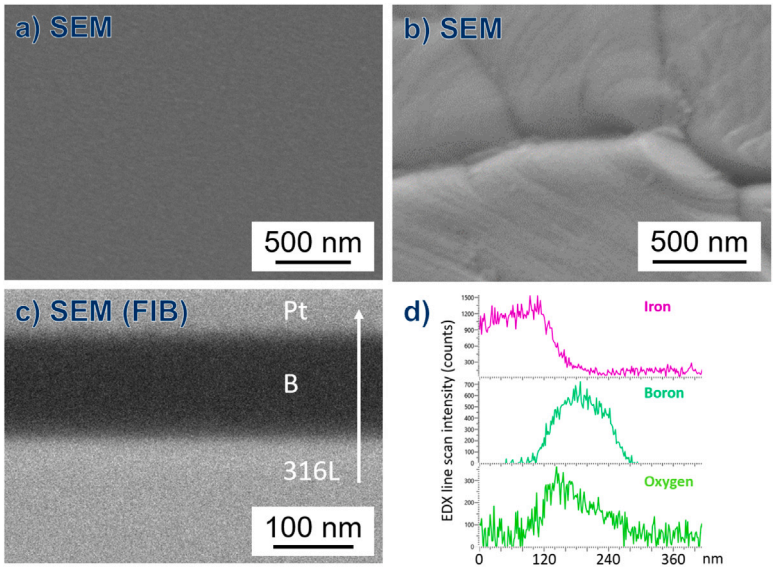

Fig. 4. (a) a SEM on the surface of a B coated 316L substrate. (b) a SEM on the surface of a B coated W substrate. (c) A SEM on the cross section on a B coated 316L substrate. In black the B layer is visible. The bright area in the lower part of the picture is the 316L substrate. The grey layer on top of the B layer is a Pt layer, which has to be applied for cutting. The white line indicate the EDX linescan. (d) EDX linescan on the SEM in (c) for iron (top), boron (middle) and oxygen (bottom).

are prepared by a focused ion beam (FIB), the layer thickness and homogeneity were studied in the same device, see Fig. 4. Please note that the gray layer on the top of the SEM figures on the cross sections corresponds to a Pt coating, which have to be applied for cutting. The B layer is visible in black. No grains or pores are visible in the layer. The amorphous phase of the B layer is verified by X-ray diffraction, not shown. The layer thickness is 110 nm for a coating obtained with our standard deposition time of 5.5 h. In Fig. 4b a B layer on a W substrate is shown as an example. Due to the small thickness of the layer, the microstructure of the W substrate is visible through the coating. In Fig. 4d an EDX linescan on the cross section of a B coated 316L substrate is shown. Due to the large penetration depth of the electrons compared to the layer thickness, the composition analysis especially for oxygen is inaccurate and give just a rough estimation of the oxygen content. The oxygen content is further studied in detail by XPS and no B oxides are observed, see below.

3.3. X-ray photoelectron spectroscopy

In order to identify a possible oxidation of the boron layer, XPS studies are made in our in-house device in ultra high vacuum. An Al anode is used as X-ray source and the device is equipped with a hemispherical electrostatic analyzer with a multi-channel detector (PHI) [6]. Before measurement, the surface area is cleaned by an Ar ion beam in order to remove oxygen, water and other impurities from the surface. In Fig. 5 the boron peak is shown for B layers on 316L and W substrates. The measurement on the B on W substrate is done on two different areas: on the 'golden' area, in which the layer is attached to the W substrate and on the detached, 'pink' area. The B peak maximum is around 188 eV, which is in agreement with the binding energy of elemental boron, and only a very small shift is observed for the different samples. There are no B oxides, e.g. B_2O_3, visible, since the binding energy is around 193 eV and therefore clearly distinguishable from the elemental B peak [7].

3.4. Ion beam analysis

The B atom concentration is measured by a 2950 keV proton beam of 10 nA current (10 μC total dose) and a 300 μm Si-PIN detector on several B layers. The signal is analyzed by SimNRA7.03 using the 11B(p,p0)11B elastic backscattering reaction. All measured samples show a similar B concentration of around $900{\cdot}10^{15}$ $\frac{\text{B atoms}}{\text{cm}^2}$. With the

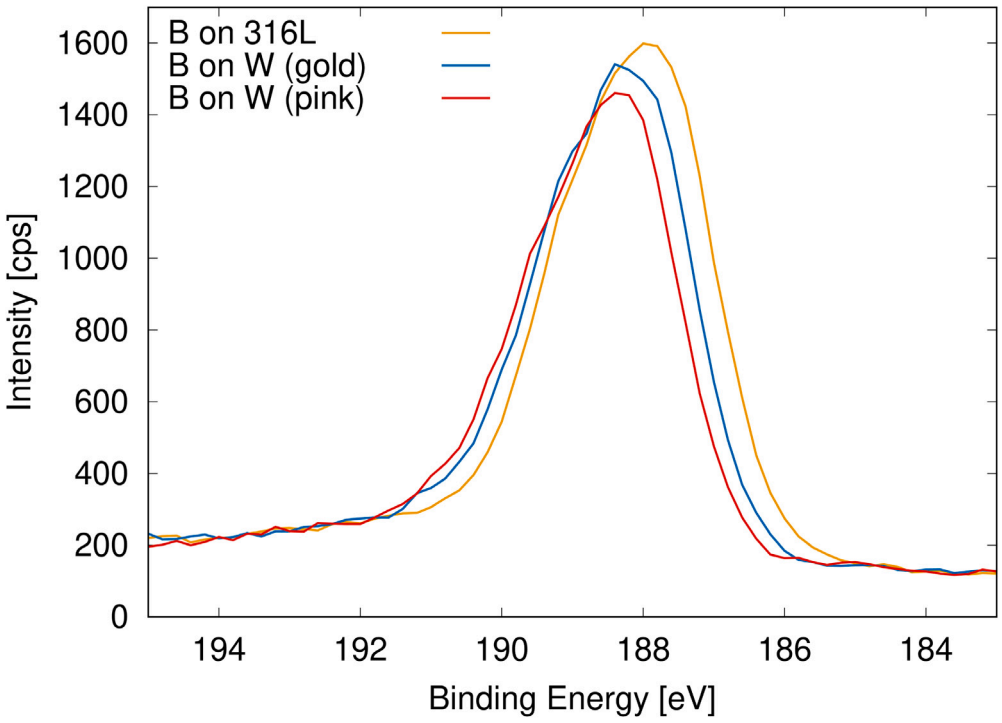

Fig. 5. XPS spetra on different samples: B layer on a 316L substrate (yellow curve), B layer on a W subtrate, where the layer is attached to the substrate and appear golden (blue curve) and on the pink area, where the layer is detached from the substrate (red curve).

thickness of 110 nm obtained from FIB/SEM, a density of 1.5 $\frac{g}{cm^3}$ is calculated. This density is significant lower as the literature value [8] of about 2.3 $\frac{g}{cm^3}$ and has to be considered for plasma erosion [9] or retention measurements. No measurable impurity concentration of C, O, and N was detected. This is another verification that no significant oxidation occur in these pure B layers.

3.5. Hydrogen isotope permeability

The deuterium permeation through a boron layer is studied in a gas-driven permeation setup [10]. The selection of the steel substrate is made in order to significantly change the permeability of the layer system by a thin coating. Measuring the permeability of a B layer on a W substrate would lead to very difficult and inaccurate extraction of the layer permeability, since W has a several orders of magnitude lower hydrogen isotope permeability compared to steel [11] in the measured temperature range. After inserting the disk shaped sample into the sample holder, the sample holder is installed into the device. Both vacuum volumes, which are separated by the sample, are pumped to a base pressure in the 10^{-9} mbar range. For the measurement, the sample is heated with the following temperature steps: 300 °C, 400 °C, 500 °C, and 550 °C. After stabilizing the desired sample temperature, deuterium gas with varying pressure with steps in the range of 25 mbar to 800 mbar is inserted in the high pressure volume. In the low pressure volume, the deuterium flux is measured by a quadrupole mass spectrometer and as an example, the raw data for a 500 °C measurement is shown in Fig. 6. After a stabilization of the permeation flux, the pressure is increased to the next pressure step. The signal of the mass spectrometer is calibrated by four deuterium calibration leaks with different calibrated deuterium fluxes (LACO Technologies). These calibration leaks are covering four orders of magnitude in particle flux in the typical permeation flux region.

In Fig. 7 the stabilized permeation flux for all measured temperature and pressure steps is shown. At 300 °C, the permeation flux signal at the pressure steps in the range between 25 mbar and 100 mbar is too low for a reliable separation between permeation flux and background. Therefore, these points are not taken into account. In order to observe possible changes of the sample during the permeation measurement, the measurements are repeated after reaching 550 °C (up- and down-measurements). Since the up- and down measurements corresponds to each other, an unchanged sample state can be assumed.

From the dependence of the permeation flux (J_P) on the applied deuterium pressure (p), the process limiting regime can be determined [10]. If J_P is proportional to the square root of the applied pressure, diffusion is limiting the process. From the data in Fig. 7 a dependence of $p^{0.6}$ is obtained. Therefore, we assume a diffusion limited regime and the permeability constant P_0 and the activation energy E_P can be obtained:

$$J_P = \frac{P_0\sqrt{p}}{d} e^{\frac{-E_P}{RT}} \tag{1}$$

wherein d is the thickness of the sample, R is the ideal gas constant and T the sample temperature. The permeability $P = P_0 e^{\frac{-E_P}{RT}}$ with $P_0 = 1.9(5) \cdot 10^{-6}$ $\frac{\text{mol}}{\text{sm}\sqrt{\text{mbar}}}$ and $E_P = 72(3)$ $\frac{\text{kJ}}{\text{mol}}$ is valid in the measured temperature and pressure range only and compared to the permeability of an uncoated 316L substrate [10] in Fig. 8.

From the obtained permeability of the B coated substrate P_{tot} and the permeability of the 316L substrate P_{sub}, the layer permeability of the boron layer P_{lay} is calculated using the equation:

$$P_{lay} = \frac{d_{lay}}{\frac{d_{tot}}{P_{tot}} - \frac{d_{sub}}{P_{sub}}} \tag{2}$$

wherein d_{tot}, d_{sub}, and d_{lay} are the thicknesses of the layered substrate, the substrate and the layer, respectively [12]. The values of $P_{0,lay} = 4 \cdot 10^{-9}$ $\frac{\text{mol}}{\text{sm}\sqrt{\text{mbar}}}$ and $E_{P,lay} = 78$ $\frac{\text{kJ}}{\text{mol}}$ are obtained by this assumption. Since this layer permeability is not dependent on the substrate and layer thickness, a comparison to other materials is possible and the layer permeability is shown in Fig. 8 as well.

4. Discussion

After deposition, no delamination of the layer is observed, if the substrate surfaces are polished and annealed before deposition and the

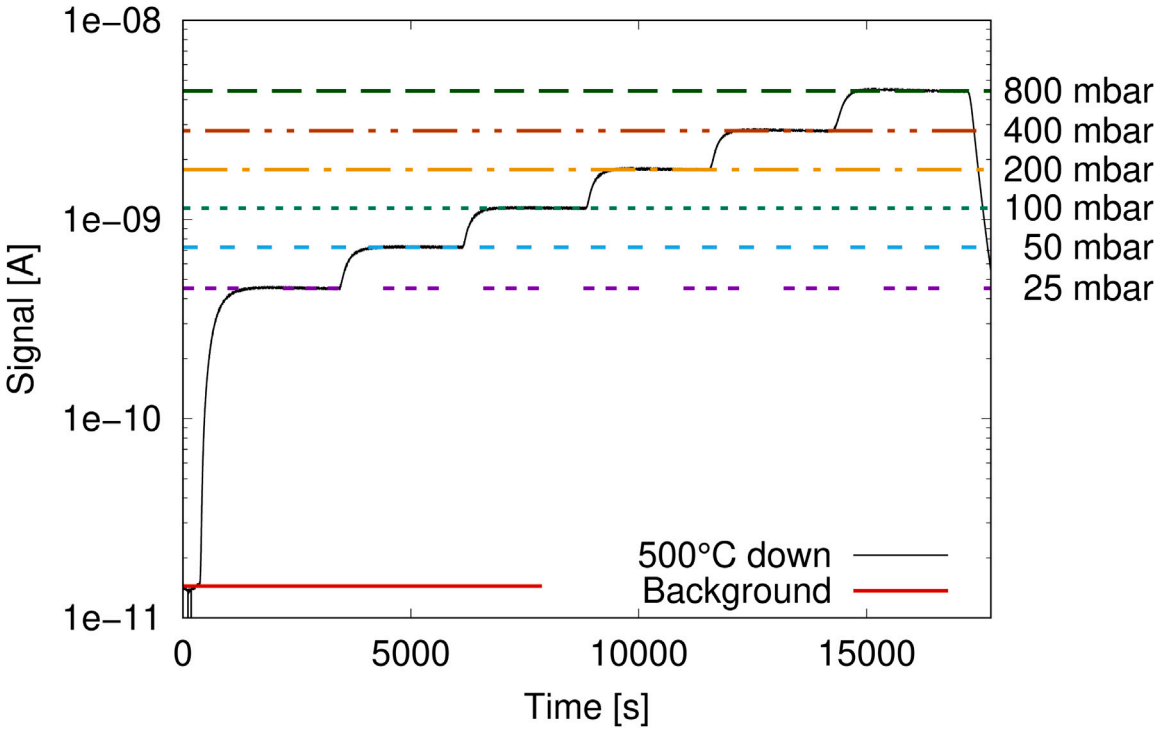

Fig. 6. The mass 4 signal of the permeation measurement at 500 °C down (black curve) versus time. The solid red line represents a fit to the background level of the signal, before the deuterium gas is inserted into the high pressure volume. The dotted lines represent the fits to the curve in the stabilized flux region after inserting a specific D_2 pressure in the high pressure volume and the corresponding D_2 pressures are indicated on the right hand of the figure.

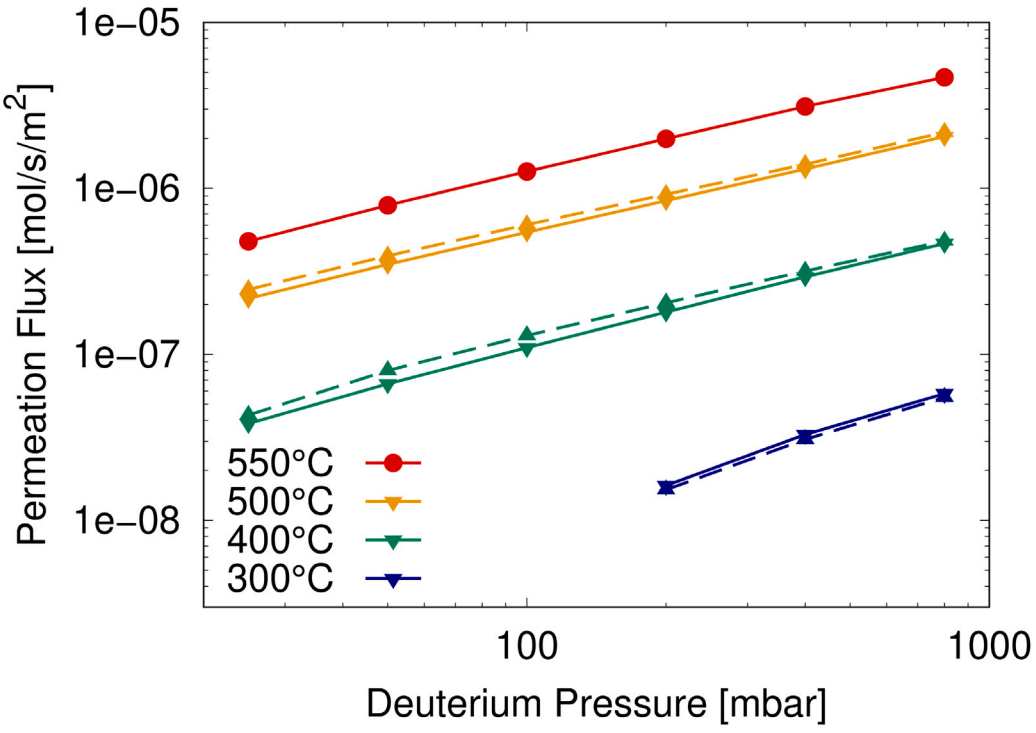

Fig. 7. The stabilized permeation flux versus the applied deuterium pressure. The colors indicate the corresponding sample temperature. The lines are for eye guidance, only. The dotted lines indicates the up-measurements, whereas the solid lines represent the down-measurements.

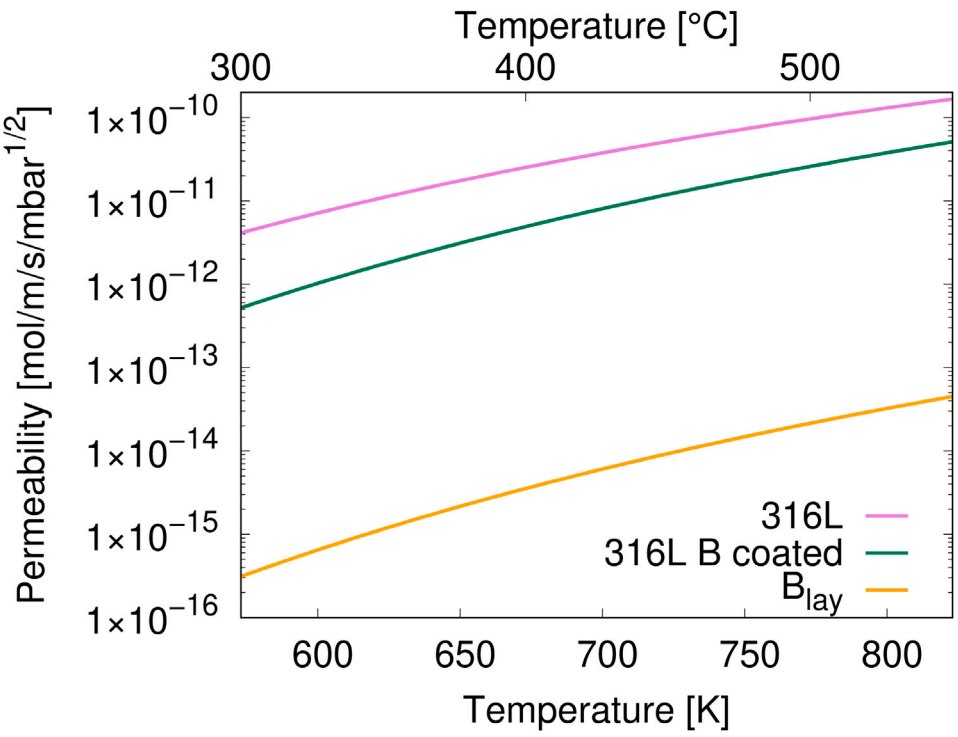

Fig. 8. The deuterium Permeability versus the sample temperature in the measured temperature range. The permeability of the coated 316L substrate is shown in green. In comparison, the permeability of a uncoated 316L substrate [10] is shown in pink. The layer permeability of the B layer is shown in orange.

samples are kept under vacuum after deposition. If the coated sample is not stored in vacuum, layer detachment can be observed after days, weeks or month, depending on the substrate and the surface conditions of the substrate. The detachment is visible by eye and not due to a B oxide formation in the layer, as confirmed by XPS. The reliability of the deposition parameters is confirmed. From the temperature stability test it is observed that the B layer on W does not change visibly up to a temperature of 1000 °C, whereas the B layer is completely removed from a 316L substrate at 800 °C, already.

From the FIB/SEM measurements it is concluded that the B layers are homogeneous and smooth. The thickness of the layers are around 110 nm with a deposition time of 5.5 h, from which a deposition rate of around 20 nm/h is obtained. EDX measurements suggested that no significant amount of oxygen is presented in the boron layer, but on the interface to the 316L substrate an increase of oxygen is detected. Due to the small thickness of the B coating, the EDX results are inaccurate. By XPS, no boron oxides are observed. No other impurity elements are observed by EDX, XPS and IBA.

The IBA measurements show that the density of these layer is around 1.5 g/cm^3. This is significant lower than the literature value of B of 2.3 g/cm^3. This has to be consider in further experiments, e.g. erosion or retention measurements.

By applying a 220 nm thick B coating on a 316L substrate, the permeability is reduced by one order of magnitude compared to an uncoated 316L substrate. No change of the layer is observed during the permeation measurement. The permeation flux is mainly diffusion limited. After deduction of the substrate permeability, a B layer permeability of $P_{0,lay} = 4 \cdot 10^{-9} \frac{\text{mol}}{\text{sm}\sqrt{\text{mbar}}}$ and $E_{P,lay} = 78 \frac{\text{kJ}}{\text{mol}}$ is obtained. The B layer permeability is around four orders of magnitude lower compared to the steel substrate and in the range of tritium permeation layers [12], e.g. Y_2O_3. Nevertheless, the deuterium retention is not studied in detail so far and the low hydrogen permeability might be influenced by deuterium retention in this layer.

5. Summary and outlook

We developed deposition process parameter in order to fabricate amorphous B layers in our magnetron system. These layers are characterized in terms of composition, layer behavior and deuterium permeability. It is confirmed that the process parameters can be used reliably to produce homogeneous and smooth B coatings with a deposition rate of 20 nm/h. If the substrate surface is clean before deposition and the deposited samples are stored in vacuum after deposition, the layers are stable and do not peel from the substrate.

The temperature stability is investigated and the B layers are stable until 1000 °C. A removal of the layer from the substrate is only observed, if the substrate material change in this temperature range, e.g. due to a phase transition.

The layers are pure boron and no impurities, e.g. boron oxides, are observed by EDX, XPS and IBA. The change of color observed on samples stored in air after a time duration of weeks to months, are due to a detachment of the boron layer from the substrate, but not due to a formation of boron oxides, as confirmed by XPS. The assumption is that a layer expansion takes place due to an uptake of the air humidity. The density of the boron layers is around 1.5 g/cm^3.

A low hydrogen isotope permeability of the boron layers is obtained by gas-driven permeation measurements. The B layer permeability is four orders of magnitude lower as uncoated 316L steel and diffusion limited.

The erosion of these B layers by deuterium plasma is studied and the results can be found in Sackers et al. [9]. The hydrogen retention in pure boron layers loaded by a deuterium ion beam and the oxidation behavior will be investigated in the future. Furthermore, this study will be broadened and compared to mixed boron layers, e.g. B:D and B:W layers, since the boron layers in real fusion devices will always be mixed with oxygen, tungsten and other impurities. With the comparison of the hydrogen retention, permeability and erosion of pure B layers with mixed B layers, the influence of the B density in these

layers and the effect of impurities on these properties will be obtained. These mixed layers will be fabricated by magnetron sputter deposition (D, H, W) and in our linear plasma device PSI-2 as well as standardized samples.

CRediT authorship contribution statement

A. Houben: Writing – original draft, Visualization, Supervision, Investigation, Conceptualization. **E. Warkentin:** Visualization, Investigation, Formal analysis. **M. Rasiński:** Investigation, Formal analysis. **T. Dittmar:** Writing – review & editing. **H.R. Koslowski:** Writing – review & editing. **S. Möller:** Investigation. **B. Unterberg:** Writing – review & editing. **Ch. Linsmeier:** Writing – review & editing, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thank B. Göths for substrate preparation and F. Weitz for annealing and taking photographs of the samples.

This work has been carried out within the framework of the EUROfusion Consortium, funded by the European Union via the Euratom Research and Training Programme (Grant Agreement No 101052200 — EUROfusion). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Commission. Neither the European Union nor the European Commission can be held responsible for them.

Data availability

Data will be made available on request.

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