Plasma-wall interactions with nitrogen seeding in all-metal fusion devices: formation of nitrides and ammonia

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Nitrogen is routinely used to control the power load to the divertor targets of tokamak fusion reactors. However, its chemical reactivity can have implications on design and operation of a fusion device. In this contribution experimental results from recent years on three topics are briefly presented. These are the formation of nitrides, the sputtering of beryllium in the presence of nitrogen and the production of ammonia. Laboratory experiments have shown that surface nitrides are formed both on beryllium and tungsten upon exposure to energetic nitrogen ions. Erosion rates of Be by energetic N ions are in good quantitative agreement with modeling. Erosion upon exposure of Be to a mixed N/D plasma is reduced with respect to a pure D plasma. Finally, the appearance of ammonia has been observed in mixed N/D plasmas as well as in the exhaust gas of AUG and JET. The production rate in AUG reached 5% of the injected N atoms in a series of three subsequent N_2-seeded discharges.

Keywords: plasma-wall interaction, nitrogen seeding, erosion, nitride, ammonia, gas balance

1. Introduction

Excessive local heat loads onto the divertor target plates can cause surface melting in tokamaks with metallic plasma-facing materials such as AUG and JET. In order to attenuate the local heat loads extrinsic radiating species are injected in the divertor region. Besides noble gases, nitrogen is very successfully used for this purpose because of its favorable radiative characteristics at the relevant electron temperatures around 30 eV (see e.g. [1] [2] [3]).

However, although molecular N_2 is chemically inert, its radicals and ions do react easily with many elements. As a consequence the interaction of a N containing plasma with the first wall of a fusion reactor can have various implications, ranging from the modification of material properties over increased erosion and hydrogen isotope retention to the production of ammonia. Potential safety and operational issues for ITER need to be identified and studied to evaluate the applicability of N_2 as seeding gas in future nuclear fusion devices.

2. Implantation of nitrogen into plasma-facing materials and retention in nitrides

Upon injection of N_2 into the 'scrape-off layer' of fusion plasmas the molecules are dissociated and/or ionized. Energetic N ions are implanted into the plasma-facing surfaces. As a consequence chemical compounds can form. In fact both plasma-facing materials foreseen in ITER, beryllium and tungsten, are known to form stable nitrides [4] [5]. It is important to clarify whether the formation of nitrides appreciably affects material properties of the first wall and to what extent they constitute a sink and subsequently also a possible source

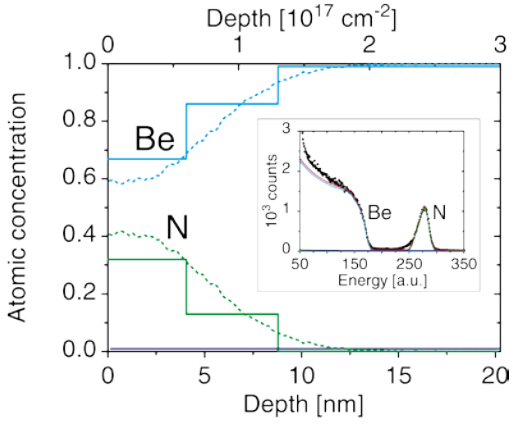

Fig. 1 Depth distribution of N and Be close to the surface of the N-implanted Be sample. The full lines are the result from adaptation of SIMNRA simulations to the RBS measurement. The dotted lines are the depth profiles resulting from a dynamic SDTrim.SP calculation. The insert shows the experimental and simulated RBS spectra.

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for N.

To study the interaction of energetic N ions with Be surfaces laboratory experiments have been performed in an ultra-high vacuum apparatus [6]. In a fusion reactor like ITER the Be surfaces in the main chamber are exposed to a continuous flux of D ions on the order of 10^{17} atoms/cm^2/s [7]. The induced sputtering keeps the surfaces free of impurities, in particular of oxygen. In a controlled laboratory experiment a base pressure of $1x10^{-10}$ mbar is necessary to sufficiently suppress oxidation (after cleaning by argon sputtering and annealing) for the duration of an experiment and allow investigations on a clean metallic Be surface. Such a surface has been exposed at room temperature to a mono-energetic beam of N_2^+ ions at various energies and fluences. Fig. 1 shows results from Rutherford backscattering analysis (RBS) performed after implantation of N at 2.5 keV/atom under an incidence angle of 45° to a fluence of roughly $1x10^{18}$ N/cm^2 [6]. RBS analysis was performed with ^{4}He at 800 keV under a scattering angle of 105° and a surface-detector angle of 7.5° to increase the depth resolution. The nonetheless strongly peaked N signal (see raw data in the insert of Fig. 1) indicates a very shallow layer with considerable N content. The N and Be depth profiles in the sample have been reconstructed from the RBS spectrum using the SIMNRA code [8]. They are in good agreement with a dynamic simulation of the N implantation with SDTrim.SP [9] [10]. In this simulation the maximum N concentration was limited to 40%, which corresponds to the N atomic fraction in the stoichiometric nitride Be_3N_2. This approach relies on the assumption that any N in excess of the thermodynamically stable stoichiometry would not remain bound inside the material but instead diffuses to the surface and desorbs in the form of N_2.

The measured depth profiles remain unchanged upon annealing to 1000 K. The nitride formation is therefore a strong sink for N impinging on metallic Be surfaces in a fusion experiment. Thermal release or diffusion of N into greater depths does not occur. The surface nitride can however be removed by erosion caused by other impinging species (see section 3).

Also on W the implantation of energetic N leads to the formation of surface nitrides [5] [11]. Laboratory experiments have shown that the implantation of N into W at ambient temperature is well described by SDTrimSP. In agreement with the known phase of WN the N concentration for these simulations was limited to 50 %. A diffusive loss of N from W only sets in at about 850 K. However, the N saturation areal density under ion bombardment already decreases above 500 K. In a reactor this could lead to an increased loss of N from W plasma facing components with increasing surface temperatures in long plasma discharges or under thermal excursions.

The results for both Be and W alleviate concerns about modified material properties such as a reduction in conductivity or melting point, since the thickness of the N-enriched surface layer is limited to the ion implantation depth which is on the order of some nm.

However, recent experiments on W raise the concern that the presence of a surface nitride layer might increase hydrogen retention by acting as a diffusion barrier for implanted hydrogen isotopes [12] [13].

3. Erosion of beryllium by energetic nitrogen ions and mixed deuterium-nitrogen plasmas

The ultimate aim of injecting a seed impurity into the fusion plasma is to reduce the heat load and the sputtering rate at the divertor targets. This is achieved above a certain level of locally radiating impurities [14]. However, energetic impurity atoms originating from charge exchange reactions could cause excessive erosion at the main chamber walls: The sputtering threshold for impurities is generally lower than that for hydrogen isotopes due to their higher mass and nuclear charge and the corresponding collision kinematics.

To quantify the sputtering of main chamber Be plasma-facing surfaces by energetic N ions a series of in-situ laboratory experiments has been performed. The sputtering yield was measured by the quartz microbalance (QMB) technique [15]. Quartz crystals were coated with Be layers of 500 nm thickness by means of thermionic vacuum arc deposition [16] and mounted on a QMB setup (see Fig. 2). These surfaces were bombarded with mono-energetic N ions under perpendicular incidence at a flux of about $2x10^{13}$ N/cm^2/s and at a base pressure < 10^{-10} mbar. The sample temperature upon exposure to the ion beam was 465 K. At this temperature the resonance frequency of the crystal is to first order independent of temperature changes thus providing the lowest temperature-induced fluctuations. At the same time this temperature is in the range expected at the Be surfaces in ITER [17]. The changes in the resonance frequency observed in real-time upon exposure of the samples to N ions is converted into a mass change. An extensive report on these experiments (including subsequent exposure to D ions and oxidation behavior) is to be published in a forthcoming paper.

Fig. 2 displays the mass change upon exposure to N ions at 2.5 keV/atom observed in these experiments as a function of fluence. At low fluences a net mass increases is observed due to dominant N implantation. (The QMB

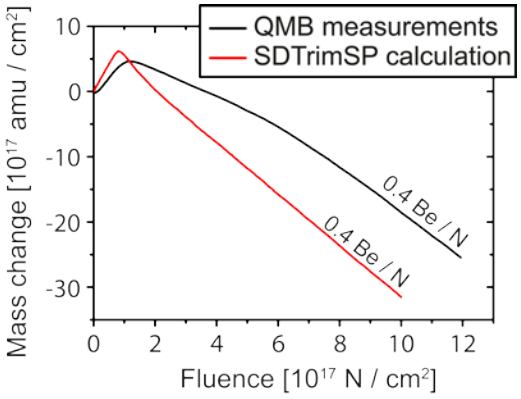

Fig. 2 Mass change of the Be-covered quartz crystal as a function of N fluence: Comparison of the QMB measurements to dynamic calculations with SDTrim.SP. The inserts show an exploded view of the QMB setup and a photograph of four Be-coated quartz crystals with gold rims.

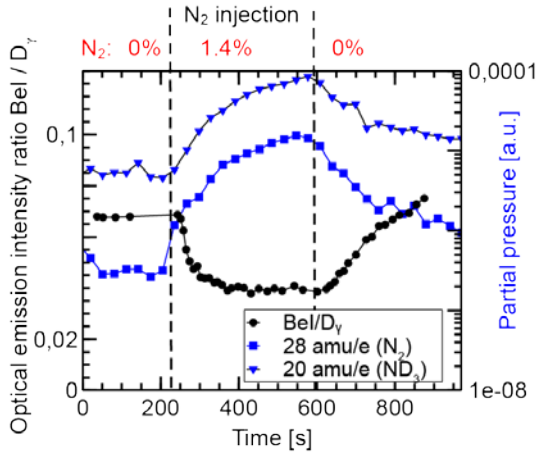

Fig. 3 Signals from optical emission spectroscopy and mass spectrometry upon exposure of Be to pure D and mixed N/D plasmas in PISCES-B.

method always only measures the *net* mass change.) Saturation with N within the ion range causes a transition to dominant surface erosion. Steady state conditions are reached after a cumulative fluence of roughly $8x10^{17}$ N/cm^2. This number must be compared to main chamber wall fluxes in ITER on the order of 10^{17} atoms/cm^2/s, a fraction of which would be N atoms. It can be concluded that steady state conditions at the ITER Be surfaces would be established within several seconds. The measured steady state sputtering yield approaches 0.4 Be atoms per impinging N atom. This result is compared in Fig. 2 to a dynamic calculation of the N bombardment with SDTrim.SP. The two curves are in reasonable quantitative agreement, confirming the above interpretation. The somewhat slower evolution with fluence observed in the experiment could be due to remaining oxidation or surface morphology modifications caused by the ion beam exposure and accompanying nitride formation [18]. The steady state sputtering yield in the calculations corresponds to the measurements. Any chemical erosion (like chemically enhanced sputtering) is not included in the simulations. Consequently, it can be concluded from the agreement between simulation and experiment that the erosion rate of Be by energetic N ions is determined by physical sputtering and chemical processes do not lead to a measurable increase in the sputtering yield at the applied energy and flux.

The effective sputtering yield of Be in N_2 seeded plasmas depends on the energies and relative fluxes of the impinging D and N particles. To investigate the effect of simultaneous D and N impact Be surfaces were exposed in the linear plasma device PISCES-B [19]. Plasmas were either generated in pure D_2 or in N_2/D_2 mixtures. Fig. 3 shows the time evolution of the optical emission intensity of BeI normalized to the D_γ signal (black dotted line). This ratio is a measure of the Be sputtering yield. The yield drops within seconds after the onset of N_2 injection. This is attributed to the formation of a thin nitride layer at the surface. After several seconds' exposure a dynamic equilibrium of constant formation and erosion is reached. Upon subsequent exposure to pure D plasma the nitride layer is removed and the sputter yield recovers to its original level within several minutes.

4. Ammonia production

In the presence of N and hydrogen ions and radicals ammonia can be formed. Metal surfaces have been shown to be suitable for the plasma-activated catalytic production of ammonia [20, 21]. Very recently the ammonia production upon interaction of mixed N/D plasmas with stainless steel, W and aluminum surfaces has been investigated and an increased formation rate with increasing surface temperature up to 620 K has been observed [22]. The production of considerable quantities of ammonia in a fusion reactor would increase the in-vessel inventory of tritium. Furthermore, ammonia can stick to surfaces in the pump duct and impact the design of the tritium plant of ITER and of a future power plant. Quantification of the rate of ammonia production is therefore of considerable importance.

Formation of ammonia has also been observed in the afore-mentioned laboratory experiment [19]. Fig. 3 shows the mass spectrometry (MS) time traces at mass-to-charge ratios of 28 (N_2) and 20 (ND_3). The measured build-up of the N_2 and ammonia partial pressures upon N_2 injection is slow compared to the reduction in sputtering yield. This is explained by additional chemical pumping of the berylliated walls of PISCES-B.

MS has also been applied at AUG and JET to quantify the ammonia production in N_2-seeded discharges. The interpretation of such measurements is challenging due to the additional presence of water and methane and due to isotope exchange reactions with H in the pump ducts that lead to the spectrometers. A decomposition procedure on the basis of effective cracking patterns is necessary to extract the pumped amounts of each molecular species from the recorded mass spectra. The effective cracking patterns are calculated under the assumption that each species can be assigned a well-defined isotopic ratio H/(H+D), which is established by interaction of the molecules with the surfaces in the torus vessel and the pump ducts. Fig. 4 shows the resulting N balance and ammonia production in three consecutive N_2-seeded discharges in AUG [23]. In the first discharge 30% of the injected N_2 molecules are missing in the balance, i.e. they are not pumped by the cryo- and turbo molecular pumps. Instead they are

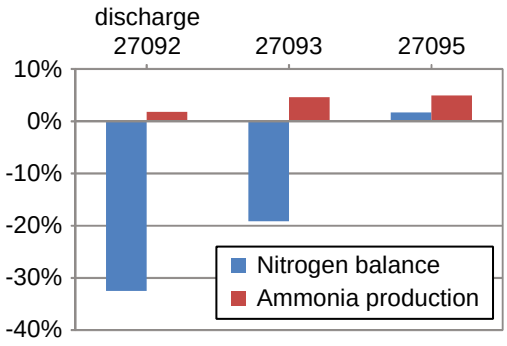

Fig. 4 Nitrogen gas balance (left blue columns) and ammonia production (right red columns) for three consecutive N_2-seeded AUG discharges.

lost to the wall by implantation or converted to ammonia. After three similar discharges the amount of pumped N_2 equals roughly the amount of injected N_2, thus closing the balance. The ammonia production resulting from the decomposition procedure reaches 5% (ammonia molecules / N atom injected) in the third discharge.

Such an analysis has recently also been applied to mass spectra recorded in N_2-seeded and non-seeded discharges at JET. The preliminary results confirm the production of ammonia in measurable amounts also in JET.

5. Summary and conclusions

The injection of N_2 into fusion plasmas for the aim of radiative cooling can entail implications owing to the chemical reactivity of N. The most important concerns are connected to modifications of material properties of plasma-facing surfaces and their hydrogen retention characteristics, enhanced erosion of plasma-facing surfaces and production of ammonia.

Laboratory investigations have shown that surface nitrides are formed upon bombardment of Be or W with energetic N. The thickness of the resulting N-rich surface layer is in the range of the ion implantation depth. N is released from W at temperatures above 500 - 850 K while Be_3N_2 is stable beyond 1000 K. Upon exposure of Be to a mixed N/D plasma the Be sputtering yield is reduced with respect to a pure D plasma. These findings alleviate concerns about (bulk) material modifications. However, hydrogen retention could be increased because the nitride layer acts as a diffusion barrier for out-diffusing hydrogen atoms.

N_2 injection into the scrape-off layer of tokamak plasmas reduces the erosion of W at the strike point by the effect of radiative cooling and particle detachment. On the other hand the presence of a heavier impurity such as N could increase the Be erosion rate in the main chamber. In the performed QMB experiments the erosion is limited to physical sputtering with no additional chemical component. The effective sputtering yield will also depend on the flux ratio and energy distribution of the impinging N and D atoms. In PISCES-B accumulation of N in a shallow surface region has been shown to reduce the Be sputtering yield due to surface dilution and/or an increased sputtering threshold for D, which is the dominant impinging species.

A gas balance of N_2–seeded discharges in AUG indicates that saturation of the accessible surface areas with N is reached within three typical N_2-seeded discharges. Decomposition of MS signals in the mass-to-charge range between 12 and 20 amu/e allows disentangling the contributions from water, methane and ammonia. In the third consecutive N_2-seeded discharge the ammonia production reaches 5% of the injected N atoms. Recent preliminary analyses of RGA data from JET also clearly indicate ammonia formation. This can have implications on the gas plant of ITER if N_2 is to be routinely used as an extrinsic radiator for divertor cooling.

Acknowledgments

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