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Development of tritium permeation barriers for future fusion devices

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Comparison of the hydrogen permeation through fusion relevant steels and the influence of oxidated and rough surfaces

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Abstract

The development and application of tritium permeation barriers (TPB) are crucial for a safe and economical fusion reactor operation. In order to specify the requirement and important characteristics of TPB, the deuterium permeation flux through two different fusion relevant steels, namely Eurofer97 and 316L(N)-IG, were measured and compared. Furthermore, the influence of oxidized and rough surfaces on the deuterium permeation flux was investigated. With this study, the influence of technical or plasma roughened surfaces on the permeation behavior can be estimated.

Keywords:

- deuterium gas driven permeation
- tritium permeation barriers
- RAFM steel / Eurofer97
- 316L(N)-IG (ITER grade)
- surface oxidation
- surface roughness

I. INTRODUCTION

In order to reduce fuel loss and due to safety issues, tritium accumulation into reactor walls and permeation through walls have to be prevented. Therefore, the development of tritium permeation barriers (TPB) is crucial for a safe reactor operation¹⁻³.

Deuterium permeation studies were performed on steels, which are intended to be used as wall and structural materials in ITER and future fusion devices, namely 316L(N)-IG (ITERgrade) and Eurofer97. By comparing the deuterium permeation flux through these different samples, the requirement and important characteristics of TPB can be specified. In order to answer the question, if the results measured on polished samples can be applied on technical surfaces, the influence of oxidized and rough surfaces was measured. For separating the influence of oxidation and roughness on the permeation flux, an oxidized Eurofer97 sample and a rough 316L sample were measured. These data can be used to estimate a potential influence of surface roughness caused by plasma exposure, as well.

II. MATERIAL AND METHODS

Four steel samples were prepared and measured. All samples have a disk shape with a diameter of 25 mm, a thickness of 0.3 mm and have the same surface state on both sides. For the polished Eurofer97 (Eu97) and 316L(N)-IG (316L) samples, the substrates were grinded and mirror finish polished. The last polishing step was with a 1 μ m diamond suspension and a cleaning with an oxide polishing suspension was applied afterwards. The oxidized Eurofer97 (oxi Eu97) sample was mirror finished polished and afterwards oxidized at 600°C in a thermobalance with an atmosphere of 20% O₂ and 80% Ar for several hours. The rough 316L(N)-IG (rou 316L) sample was grinded by the standard procedure, but the process was stopped after using the sandpaper P1200 (average particle diameter 15.3 μ m).

All samples were analyzed by scanning electron microscopy (SEM) with a Zeiss Crossbeam 540. A cross section can be created by a focused ion beam (FIB) enabling a side view of the sample surface. All figures shown were recorded in SE mode. If needed, energy dispersive X-ray spectroscopy (EDX) measurement were used for element analysis. The EDX measurement setup (Oxford X-Max 80) is attached to the SEM(FIB) device.

The deuterium gas permeation setup consists of two volumes, the high and low pressure

volume (HPV/LPV). The volumes are separated by the sample, which can be heated by a tube furnace. The base pressure of both volumes is in the 10^{-9} mbar range. In the HPV deuterium gas can be inserted and in the LPV the permeation flux is detected by a quadrupole mass spectrometer. Details of the setup can be found in Engels *et al.*⁴. The signal of the mass spectrometer was calibrated to a deuterium flux by 4 calibration leakages (LACO Technologies). The same measurement cycles were performed on all samples. Each cycle consist of 7 temperature steps (300°C, 400°C, 500°C, 550°C, 500°C, 400°C, 300°C). After stabilizing the sample at a specific temperature, the deuterium pressure was increased in 6 steps between 25 mbar and 800 mbar. The oxi Eu97 sample was measured at 600°C instead of 550°C.

In order to measure the deuterium permeation lag-time and thus evaluate the diffusion constant and the diffusion activation energy, a valve with a diaphragm was inserted in the setup located in front of the sample in the HPV. Due to this special valve, the deuterium pressure can be rapidly increased up to 800 mbar in the HPV. The lag-times of 316L and the rou 316L samples were measured in additional measurements at 400°C and 500°C at 4 pressure steps (25 mbar, 100 mbar, 400 mbar, 800 mbar).

III. DATA ANALYSIS

The permeation flux J_P through the sample is dependent on the solubility and the diffusion coefficient of deuterium in the sample and of surface processes, like dissociation of the deuterium molecule, absorption and desorption. In the diffusion-limited case, in which surface processes are quick and therefore negligible regarding limiting the permeation process, the permeation flux can be expressed by^{5,6}

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

wherein d is the thickness of the sample, R is the ideal gas constant and T the temperature. The permeability P_0 is defined by $P_0 = D_0 K_0$ with the diffusion constant D_0 and the solubility constant K_0 . The permeation activation energy E_P is defined by $E_P = E_D + \Delta H$ with the diffusion activation energy E_D and the standard enthalpy of dissolution ΔH . By measuring the samples pressure and temperature dependent, the permeability and the permeation activation energy can be obtained with an Arrhenius plot, see as an example figure 3. If the data do not fulfill the Arrhenius equation, a second temperature (points can not be fitted with a line) or pressure dependence (lines of different pressures are not parallel to each other) of the permeation process is indicated. Furthermore, from the pressure dependence the limiting regime can be derived. In the diffusion-limited case, the permeation flux is proportional to the square root of the pressure, see equation 1. If the surface processes are limiting the permeation flux, the flux is proportional to the pressure^{5,6}. By the slope of the pressure dependence one obtain information about the limiting regime.

For the analysis of the lag-time, the increase of the permeation flux versus time is integrated, see figure 4b. The lag-time (L) is obtained from the abscissa value at y = 0 from a line fitted to the linear part of the graph⁷. The diffusion coefficient D of deuterium through the sample is calculated by $D = \frac{d^2}{6L}$. By measuring the lag-time at different temperatures and pressures, the diffusion constant D_0 and the diffusion activation energy E_D can be obtained by a Arrhenius plot $D = D_0 e^{\frac{-E_D}{RT}}$. Taking the values for P_0 and E_P into account, the solubility constant and the heat of dissolution can be calculated.

IV. RESULTS

As descripted above, all samples were analyzed by SEM(FIB). No smear layer can be detected on both polished samples (Eu97 and 316L) with SEM in the cross section (FIB), see figure 1. Due to the oxidizing procedure of the oxi Eu97 sample, an about 30 nm thick continuous Cr-oxide layer was produced at the surface and on top of this Cr-oxide layer Fe-oxide particles with a size of about 80 nm are found in SEM(FIB) images, see figure 1d. The oxides were analyzed by EDX, not shown. The grinding procedure of the rou 316L sample leads to a scratch depth in the range of 500 nm, see figure 1e. On top of this surface profile an about 500 nm thick smear layer is observed in the same SEM(FIB) image. The smear layer is produced by stress introduced on the surface due to the grinding procedure and consist of the same material as the bulk sample and no oxygen was observed by EDX, not shown. The grain size is much smaller and the microstructure is different in the smear layer compared to the bulk of the sample.

The permeation flux versus the applied deuterium pressure is shown in figure 2. The slope of the permeation flux versus temperature is indicated in table I. For all samples, the Arrhenius equation is fulfilled and the lines for different pressures are parallel to each other.

Sample	p^x	P_0	E_P	D_0	E_D	K_0	ΔH
		$\left[\frac{10^{-7}mol}{ms\sqrt{mbar}}\right]$	$\left[\frac{kJ}{mol}\right]$	$\left[\frac{10^{-7}m^2}{s}\right]$	$\left[\frac{kJ}{mol}\right]$	$\left[\frac{mol}{m^3\sqrt{mbar}}\right]$	$\left[\frac{kJ}{mol}\right]$
Eu97	0.5	5.7(4)	41.6(5)	-	-	-	-
316L	0.5	8(1)	58(1)	6(1)	51(1)	1(2)	7(2)
oxi Eu97	0.55	5(2)	46(1)	-	-	-	-
rou $316L$	0.6	7(1)	63(1)	1(1)	47(1)	7(2)	16(2)

TABLE I. The results obtained from temperature and pressure dependent permeation measurements (x, P_0, E_P) and time-lag measurements (D_0, E_D) . K_0 and ΔH can be calculated with the other values according to the formulas given in part III.

As an example, the Arrhenius plot for the sample Eu97 is shown in figure 3. The obtained values for P_0 and E_P can be found in table I, as well.

The deuterium lag-time was measured for the 316L and rou 316L sample. The data for the 316L sample are shown in figure 4 as an example. The obtained values for D_0 , E_D , K_0 and ΔH can be found in table I.

V. DISCUSSION

The deuterium permeation through the two polished samples (Eu97 and 316L) is limited by diffusion $(J_P \sim p^{0.5})$, so they are both in the diffusion-limited regime. The pressure dependence of the permeation flux through the oxi Eu97 and the rou 316L sample has a slight deviance from the square root pressure dependence. One can assume that in this samples the surface processes have a small influence on the permeation process. Nevertheless, the major limiting process for the permeation flux is the diffusion in all samples.

The permeation flux of Eu97 and 316L is in good agreement with the published data in Causey *et al.*⁵ for RAFM steels (Eu97) and austenitic stainless steel (316L). The permeation flux through the Eu97 sample is about one order of magnitude higher than through the 316L sample. This can be explained by the huge difference in microstructure, see figures 1a and 1b. The grain size is different by two orders of magnitude. Furthermore, as a rule of thumb, there is a slower deuterium diffusion through fcc (316L) metals, than through bcc (Eu97)

metals⁸. We did not measured the same lattice structure with different microstructure, which is not relevant in steels, but we assume, that the main deuterium diffusion is through the grain boundaries and not through the lattice. Due to this reason, the difference in microstructure is assumed to be the main reason for the lower deuterium permeation flux through 316L compared to Eu97.

By oxidizing the surface of the Eu97 sample, the permeation flux is lowered. The Cr/Feoxide layer reduces the permeation flux by less than an order of magnitude. The permeation constant remains at the same value and the permeation activation energy is slightly increased, if one compare the samples Eu97 and oxi Eu97. A natural oxide layer on steel samples has a permeation reduction factor (J_P of the substrate divided by J_P of the oxidized or coated substrate) of less than an order of magnitude and is therefore not sufficient as permeation barrier.

The roughening of the 316L substrate surface lowers the permeation flux as well. Due to the fact, that the permeation through the 316L samples is diffusion-limited, the effect of the surface roughening is expected to be small⁹. The slight decrease of the permeation flux through the rou 316L sample compared to the 316L sample might be caused by the smear layer on top of the roughness profile. The permeation constant is similar in both 316L samples, whereas the permeation activation energy is increased by roughening the surface. Comparing the diffusion of 316L and rou 316L, the diffusion constant and the diffusion activation energy are lower in rou 316L. This leads to a lower diffusion coefficient of rou 316L in the measured temperature regime. Since it is not expected that the diffusion coefficient of the bulk of the sample is changed, the diffusion process in the smear layer is slower compared to the diffusion in the bulk of the sample. Furthermore, the solubility of the rou 316L sample is higher compared to the 316L sample. This leads to the conclusion, that more deuterium will be stored in the smear layer compared to the bulk part of the sample. The different diffusion coefficient and solubility of the smear layer as in the bulk can be explained by the different grain size and microstructure, see figure 1. There might be more traps and different grain boundaries in the smear layer, which have an influence on the permeation flux¹⁰. To conclude, we assume, that due to the smear layer, the permeation flux is slightly reduced in the rou 316L sample, the diffusion coefficient is lower and the solubility is higher at the measured temperature range. But these data have a large error bar and due to the reason that the sample is not in the diffusion-limited regime, one has to be careful with the interpretation and further measurements have to be done in order to clarify this behavior.

In order to give an assumption for the permeation behavior for technical surfaces, one has to consider both effects of oxidation and roughening of the surface on the permeation flux. In both cases a small reduction of the permeation flux is observed. Therefore, we conclude, that the permeation flux is reduced by maximum one order magnitude due to technical surfaces compared to polished surfaces. The reduction of the permeation flux due to surface roughening by plasma exposure is less than one order of magnitude. In future fusion devices (e.g. DEMO) the deuterium permeation will not be sufficiently reduced by a technical surface and a TPB has to be applied, which reduces the permeation flux by at least two orders of magnitude.

VI. CONCLUSIONS

In both polished steels samples, Eu97 and 316L, the deuterium permeation flux is limited by diffusion. The permeation flux through the 316L sample is about one order of magnitude smaller than through the Eu97 sample and the permeation activation energy is higher. Oxidation or roughening of the surface leads to a small reduction of the permeation flux. It is supposed that in the case of roughening, the reduction is due to the lower diffusion coefficient and the higher solubility in the smear layer compared to the bulk. We conclude, that a technical surface will reduce the deuterium permeation flux by not more than one order of magnitude. In future fusion devices a TPB is required for sufficient reduction.

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Captions:

Figure 1: a) SEM on a cross section prepared by FIB of the sample Eu97. The bright area at the top is a platinum layer, which was deposited in order to perform the FIB cut. b) SEM on a cross section of the sample 316L. The bright area at the top is a platinum layer. c) Top view SEM on the oxi Eu97 sample. d) SEM on a cross section of the sample oxi Eu97. The dark area on top of the Eu97 surface is a Cr-oxide, the grains are Fe-oxide, analyzed by EDX. The bright area at the top of the figure is a platinum layer. e) Top view SEM on the rou 316L sample. f) SEM on a cross section of the sample rou 316L. The smear layer of about 500 nm is visible. The bright area at the top is a platinum layer.

Figure 2: The deuterium permeation flux versus the applied deuterium pressure through sample a) Eu97, b) 316L, c) oxi Eu97, and d) rou 316L. The colors represent the sample temperature. Note, that in case of the oxi Eu97 sample, the measurement was performed at 600°C instead of 550°C

Figure 3: Arrhenius plot for the sample Eu97 with $J_0 = 1 \frac{mol}{m^2 s}$. The lines represent the fitted lines to the data in order to obtain E_P and P_0 , see table I. The color points represent the measurement points at different applied deuterium pressure.

Figure 4: a) Time-lag measurement (Mass spectrometer signal versus time) on the sample 316L at 400°C and 400 mbar. b) Integrated Intensity signal versus time from the data shown in a). The black line indicate the line fit through the linear part of the curve. The lag-time is defined as the abscissa value at y = 0, in this case 350 s.

Table I: The results obtained from temperature and pressure dependent permeation measurements (x, P_0, E_P) and time-lag measurements (D_0, E_D) . K_0 and ΔH can be calculated with the other values according to the formulas given in part III.



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