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Analysis of low Pressure Hydrogen Separation from Fusion Exhaust Gases by the Means of Superpermeability

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The effect of superpermeability is capable of separating hydrogen and its isotopes out of gas mixtures at low pressures even against a pressure gradient. This process allows strongly enhanced permeation. It relies on metal membranes that are exposed to atomic hydrogen. If the surface inhibits the chemisorption on its surface, the atomic hydrogen can still enter the bulk, but hydrogen recombination on the surface is suppressed. This is an ideal concept for the implementation of Direct Internal Recycling (DIR) in future fusion machines. DIR is one of the measures aiming to drastically decrease the tritium inventory of a Demonstration fusion power plant which will be necessary due to tritium availability and regulatory issues. In this publication the influence parameters on superpermeation are outlined and their influence is discussed in detail. Additionally permeation measurements are shown and interpreted which were performed in the HERMES facility at KIT. During the measurements a change of the surface properties was found. These stability issues are discussed.

Keywords: Superpermeability, Fuel Cycle, Vacuum technology, Membrane technology, Plasma-Surface Interaction

1. Introduction

Besides the scarce resources of tritium, the maximum inventory allowed by a nuclear regulator demands an intelligent design for any setup with tritium. Especially the development of the fusion fuel cycle of a fusion power plant such as DEMO has to take this as a guideline. This is the motivation for the development of Direct Internal Recycling (DIR). This concept tries to decrease the inventory by separating most of the hydrogen from the exhaust gases close to the torus and feed it back to the fueling system [1]. This approach can be boosted by introducing several tritium loops as shown in Figure 1 [2]. They are based on the idea to have small residence time but high tritium content close to the torus. For total separation of the gases systems with longer residence time are allowed because their tritium inventory will be small. The most crucial subsystem of this concept has to separate most of the hydrogen isotopes very close to the torus as this will drastically decrease the amount that needs to be handled by all other systems. It should be able to work continuously and separate hydrogen at low pressures.

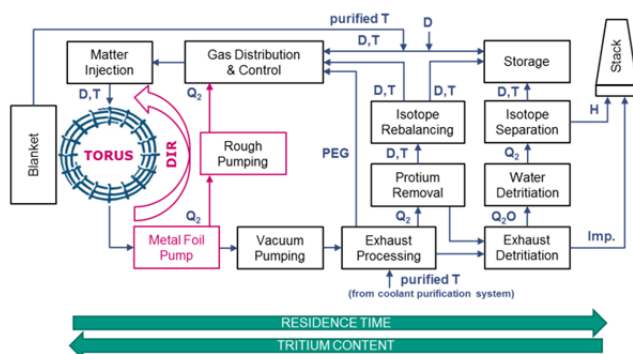


Fig. 1. Flow diagram of the envisioned tritium fuel cycle for the EU DEMO, after [2].

2. Superpermeation

The effect of superpermeation fulfills all criteria demanded for an inner DIR loop and is thus investigated further. It was observed the first time in 1938 [3], but only from 1975 [4] it was investigated in detail, especially by I.A. Livshits and his coworkers. Significant contributions to the underlying processes were also done in Jülich under F. Waelbroeck [5]. The term “superpermeability” was coined by I.A. Livshits for systems with a high likelihood ($\alpha = 0.1 \dots 1$) for any incident particle to permeate a membrane [6]. It is based on the combination of a metal membrane with high diffusivity with a permeation barrier on the upstream side that is subjected to an atomic hydrogen flux. Livshits definition does only work at low pressures, but we use it for any system that meets the requirement of a drastically enhanced permeation due to a surface barrier and incident atomic hydrogen, even at higher pressures.

2.1 Process of molecular hydrogen permeation

The process of permeation of molecular hydrogen occurs in various steps. The hydrogen molecules adsorb on the upstream surface of a membrane by dissociative chemisorption, breaking the molecule. Then the atoms get absorbed into the metal lattice, where they can diffuse through the membrane. On the downstream side they desorb by reemerging to the surface where they can recombine with another atom to be able to leave into the gas phase. These processes are essentially the same for hydrogen molecules and atoms with exception of the adsorption step. The activation energy for the chemisorption presents an energy barrier for molecules, but atomic hydrogen does not need to dissociate anymore and can thus be absorbed easily.

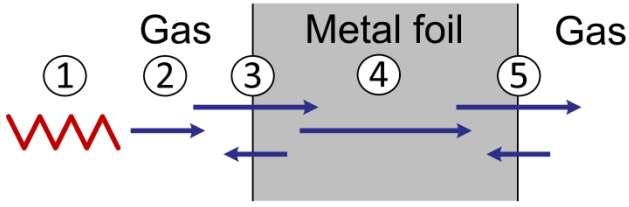


Fig. 2. Relevant locations of process steps for superpermeation.

2.2 Process of superpermeation

In Figure 2 the areas of interest of the various processes for superpermeation are shown and numbered. First atomic hydrogen has to be produced ①. It will be transported to the metal foil ②, where ad- and absorption as well as desorption on the upstream surface ③ occurs. It can then move through the metal bulk ④. The hydrogen on the back surface ⑤ can leave into the gas phase by desorption, but of course re-adsorption is also possible.

2.3 Influence parameters

The production of atomic hydrogen ①, is often done by an incandescent metal wire. Although this is easily achievable, this method has a number of drawbacks. Besides the high temperature that causes limited lifetime and sputtering of the wire this method becomes increasingly ineffective at pressures above 10^{-5} Pa [7]. As alternatives various plasma configurations are in discussion such as the ECR plasma used in the experiment of this paper.

The transport between the hydrogen source and the metal foil ② is extremely dependent on operating pressure and the geometric arrangement of the setup.

Normally hydrogen membranes are operated in the diffusion-limited regime as this gives an upper limit to the hydrogen flux that can permeate a membrane. But as superpermeation relies on a surface barrier ③, it is a special case of surface-limited permeation. The rate determining step for surface limited permeation is normally the dissociative chemisorption of the hydrogen molecules that can be described by equation (1).

$$J_m = \frac{p}{\sqrt{2kTm}} \alpha_m 2 \quad (1)$$

The atomic hydrogen flux into the membrane J_m is given by an impingement rate that is given by the gas kinetic theory times a probability factor α_m for the likelihood of adsorption times two for the number of atoms per molecule. For superpermeation the flux of hydrogen to the surface is the sum of the molecular and atomic hydrogen. The probability factor for adsorption α_a of atomic hydrogen is in the order of unity and thus the adsorbed flux J_a is determined by the incoming atom flux J_{aS} . The factor of two is not needed in this case.

$$J_a = J_{aS} \alpha_a \quad (2)$$

Equation (2) shows this relationship, which totally governs the permeation for superpermeability as it is much bigger than J_m .

Although the process is governed by the surface this does not mean the diffusivity is irrelevant for this process ④. Just contrary, the diffusion needs to be so rapid that it is not the rate determining step. As the diffusivity D always rises with temperature as can be seen in eq. (3), because the diffusion activation energy is always positive E_D , this gives a minimum operation temperature for a superpermeable membrane.

$$D = D_0 \exp \left\{ \frac{-E_D}{kT} \right\} \quad (3)$$

The processes on the downstream side ⑤ are basically the reverse as in ③ without the presence of atomic hydrogen. The surface on the up- and downstream side does not need to be in the same condition. In fact an “asymmetric” membrane can be used to enhance the desorption.

Figure 3 shows this process in an idealized way. The energy barrier on the upstream side is that high because of a non-metal film on the surface. In vacuum a hydrogen molecule has to overcome its binding energy in order to split up. This energy barrier is considerably lowered in the presence of metals, as their valence electrons can assist this process. This catalytic behavior can be shielded by non-metal films such as oxygen. The figure shows a material with a negative heat of solution (E_{sol}) such as vanadium which is also used in the experiment of this paper.

If one relies on “natural” surface layers such as oxides, it is unlikely that there is only a surface layer on the upstream side. In case of surface layers on both sides, the membrane will gather a high internal concentration of hydrogen that will leave the membrane on both sides equally ($x = 0.5$).

The amount of hydrogen within the metal foil depends on its dimensions and the solubility of hydrogen in it. The solubility S can be described by an Arrhenius Ansatz like in Eq.(3):

$$S = S_0 \exp \left\{ \frac{-E_{sol}}{kT} \right\} \quad (3)$$

In contrast to the diffusivity, the activating energy of the process E_{sol} can be both positive and negative. A temperature change will increase the solubility for metals with an endothermic solution process such as iron and decrease for metals with an exothermic solution process such as vanadium.

There are even more factors that are temperature dependent. The stability of a surface layer can change with temperature. This is valid both for the non-metal layers as used by Livshits as well as the approach by the group of Waelbroeck that employed metal membranes covered with a second metal [8]. In the latter case an increased temperature can limit the lifetime of such a membrane as diffusion will mix the layers. Other relevant points are changes in the crystal structure and the formation of hydrides with the used metal(s). Figure 4 shows the phase diagrams of vanadium with the three hydrogen isotopes. For temperature above 200°C only one phase appears. This avoids a lot of stress on the

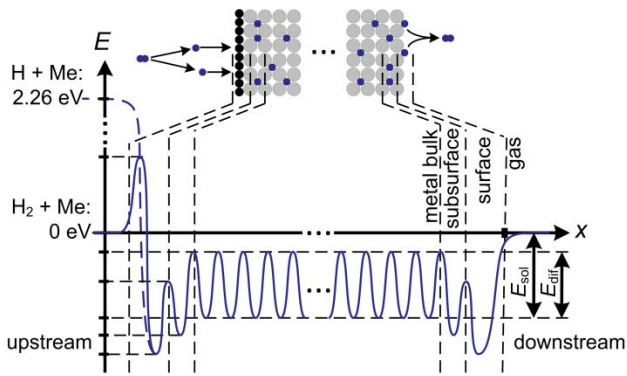


Fig. 3. Idealized potential energy diagram for hydrogen passing a superpermeable metal foil.

membrane, although the metal lattice still gets widened by the hydrogen.

4. Experiment

4.1 HERMES setup

At KIT the Hydrogen Experiment for Research on MEtal foils and Superpermeability (HERMES) has been setup. It consists of two vacuum chambers that are separated by a metal foil. One chamber is equipped with an ECR (2.45 GHz, GenII by tectra) plasma source. Both chambers are separately pumped and the pressure is determined by various gauges. A layout of HERMES can be seen in Figure 5.

4.2 Measurement procedure

Measurements are normally done by establishing constant conditions in the upstream chamber and at the metal foil. The downstream chamber is meanwhile evacuated to pressures in the 10^{-5} Pa region. The measurement is started by closing a gate valve between the turbo molecular pump and the downstream chamber. The pressure rise in this chamber holds the information about the permeated hydrogen flux. A gas-driven permeation without the plasma source is conducted before each superpermeation measurement in order to prove the integrity of the metal foil and get qualitative information on the surface condition of the foil.

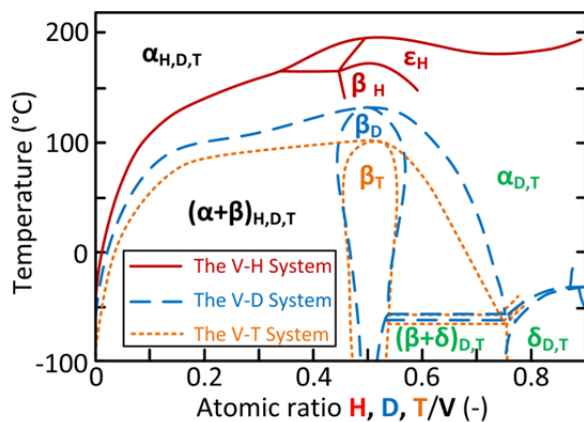


Fig. 4. Hydrogen-Vanadium phase diagram for all three hydrogen isotopes, protium (H), deuterium (D) and tritium (T), data from [9] and [19].

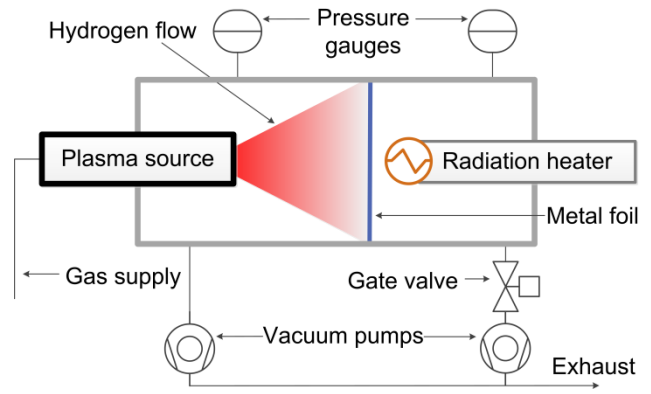


Fig. 5. The HERMES Setup at KIT.

4.3 Compression experiment

For this experiment an industrial grade vanadium foil with a thickness of $100 \mu\text{m}$ was used. During the experiment the foil had a temperature of about 290°C with slight variations during the experiment. The plasma source was running during the whole experiment. The upstream pressure was constant at 2 Pa , as can be seen in Figure 7. As soon as the measurement starts, a pressure rise in the downstream chamber can be observed. The pressure rise is nearly linear during the course of the nine hours of the experiment and reaches a pressure of 140 Pa . This gives a compression factor of 70. The pumping speed is roughly constant. A slight sawtooth variation can be seen. The origin of these variations is not yet explained.

4.2 Change of surface layers

Figure 6 shows five consecutive gas driven permeation experiments with the same vanadium foil as in the previous experiment. Once again the pressure rises are shown but now they are in the mPa region. The upstream pressure was again 2 Pa during the experiment. After an initial quick rise, which could be caused by the closing gate valve, a nearly linear pressure rise is established in each of the measurements. At 1 mPa a step in the pressure rise can be observed which is probably a feature of the used pressure sensor.

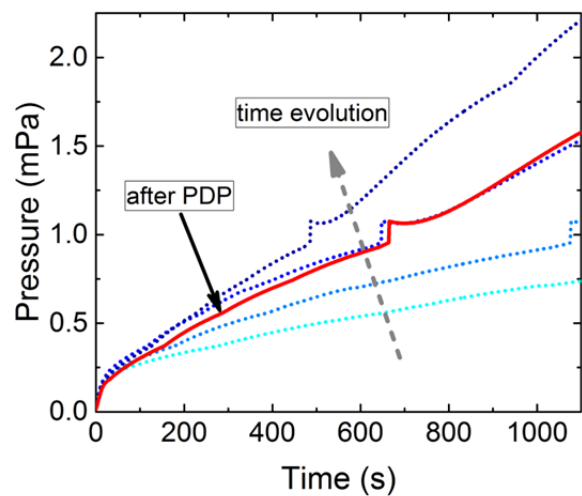


Fig. 6. Measurements of gas driven permeation in HERMES

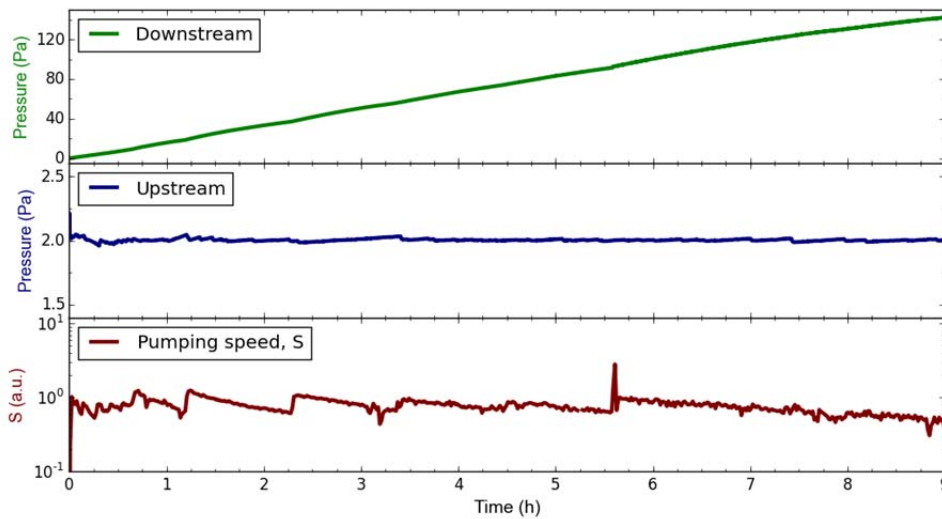


Fig. 7. Superpermeation test in HERMES of a vanadium membrane with natural oxygen surface layers.

The four dotted lines give the pressure rise of four consecutive gas driven permeation experiments. The experiment with the weakest pressure rise was performed first. Each of the following had a steeper rise. After the four measurements a plasma experiment was performed. It is not shown here. Afterwards a fifth gas driven experiment was done, its pressure rise is shown with the solid line. We assume degradation of the surface energy barrier during the first experiments. The slight “recovery” of it could be caused by the temperature rise of the foil that occurs when the plasma source is switched on.

5. Conclusion and Outlook

The effect of superpermeation was used to demonstrate its capability as a hydrogen selective vacuum pump. Hydrogen was compressed by a factor of 70. A change of the metal surface was observed and presented. The relevant influence factors for superpermeation were discussed in detail. This gives the basis for both experimental and theoretical studies that will be conducted at KIT. It was proven, that Direct Internal Recycling (DIR) can be based on a unit relying on superpermeation.

Acknowledgments

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References

- [1] C. Day, T. Giegerich, The Direct Internal Recycling concept to simplify the fuel cycle of a fusion power plant, *Fusion Engineering and Design*. 88 (2013) 616–620.
- [2] C. Day, B. Butler, T. Giegerich, P.T. Lang, R. Lawless, B. Meszaros, Consequences of the technology survey and

- gap analysis on the EU DEMO R&D programme in tritium, matter injection and vacuum, *Fusion Engineering and Design*. 109-111 (2016) 299-308.
- [3] A. Güntherschulze, H. Betz, H. Kleinwächter, (in German) Die Diffusion von Wasserstoff und Deuterium durch Eisen, *Z. Physik*. 111 (1939) 657–679.
- [4] A.I. Livshits, Interaction of membranes with nonequilibrium gases, *Sov. Phys. Tech. Phys.* 20 (1976) 1207–1212, Translation of: *Zh. Tekh. Fiz.* 45 (1975) 1915–1922.
- [5] F. Waelbroeck, P. Wienhold, J. Winter, E. Rota, T. Banno, Influence of Bulk and Surface Phenomena on the Hydrogen Permeation through Metals, *Berichte der Kernforschungsanlage Jülich – Nr. 1966*, Jülich, 1984.
- [6] A.I. Livshits, Superpermeability in the atomic hydrogen-nickel system, *Sov. Tech. Phys. Lett.* 3 (1977) 236–237, Translation of: *Pis'ma Zh. Tekh. Fiz.* 3 (1977) 576-580.
- [7] A. Livshits, N. Ohyabu, M. Notkin, V. Alimov, H. Suzuki, A. Samartsev, M. Solovyev, I. Grigoriadi, A. Glebovsky, A. Busnyuk, A. Doroshin and K. Komatsu, Application of superpermeable membranes in fusion: the flux density problem and experimental progress, *J.Nucl.Mater.* 241–243 (1997) 1203.
- [8] W.T. Shmayda, F. Waelbroeck, P. Wienhold, J. Winter (Kernforschungsanlage Jülich GmbH, Germany) Schutzrecht DE 3434150 A1, 1984
- [9] R. Lässer, *Tritium and Helium-3 in Metals*, Springer, Berlin, 1989.
- [10] R. Lässer et al., *Tritium in Metallen: Präparationstechnik (Tritiumlabor); Eigenschaften von Tritium in Vanadium, Niob, Tantal und Palladium*, *Berichte der Kernforschungsanlage Jülich – Nr. 1800*, Jülich, 1982.