Available online at www.sciencedirect.com
SCIENCE @ DIRECT®
Journal of Nuclear Materials 328 (2004) 103–106
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Deuterium permeation through Eurofer and α-alumina coated Eurofer

D. Levchuk [*], F. Koch, H. Maier, H. Bolt

Max-Planck-Institut fuer Plasmaphysik, EURATOM Association, Boltzmannstr. 2, 85748 Garching, Germany

Received 29 January 2004; accepted 18 March 2004

Abstract

Experiments on deuterium permeation through Eurofer have been performed in the temperature range 573–873 K at driving pressures 10^3–10^5 Pa. The permeability is found to be coincident with literature data on Eurofer measured at a fixed pressure and on F82H steel as well. A crystalline alumina coating of 1 μm in thickness produced on the surface by means of filtered arc discharge has led to a marked decrease of the permeation flux compared to bare material in the temperature range 973–1073 K. Surface effects appear to play a noticeable role in this decrease. In spite of this, a reduction factor of 10^3, perfect layer stability to thermal cycling, and a relatively low deposition temperature make α-alumina a very promising material for fusion applications.

1. Introduction

Eurofer is a ferritic martensitic steel developed for use in the first wall of the fusion reactor DEMO. Being placed behind a plasma facing material (PFM), say tungsten, it must provide some specific mechanical properties and have low radiation induced activation as well. Eurofer is in composition rather close to another low activation steel F82H. In spite of almost a decade since the material has been introduced, a lack of data on hydrogen transport in Eurofer is observed. This fact can partially be explained by its conformity to F82H, which has been investigated (e.g. [1,2]), and it could be concluded that these steels have very similar transport parameters such as diffusivity, permeability, etc.

Nevertheless, only a few papers exist [3,4], where hydrogen isotopes permeation through Eurofer is reported, and values of permeability diverge up to a factor two. Thus, this material still requires some experimental investigation.

Another important point is that a hydrogen barrier is planned to be placed between PFM and Eurofer that will suppress tritium accumulation in and penetration through the first wall. One of the promising materials for this purpose is aluminum oxide. Alumina has been tested widely for many years [4–10], mostly in combination with MANET as a substrate, and has revealed a large spread in the permeation reduction factor (PRF) values with respect to hydrogen. An important reason to aim for a very thin (microns) alumina coating is to strongly reduce the neutron induced activation from Al which is significant for thick barrier layers.

The goal of our work was to investigate the deuterium permeation through Eurofer, then produce a stable alumina coating on a Eurofer substrate keeping the structure of the substrate unchanged, and finally test the coated sample on the permeability and compare it to the permeability of the uncoated one. This will allow an assessment of the permeation reduction capability of the alumina coating.

---

[*] Corresponding author. Tel.: +49-089 3299 1254; fax: +49-089 3299 1212.
E-mail address: denis.levchuk@ipp.mpg.de (D. Levchuk).

0022-3115/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2004.03.008

2. Experimental

2.1. Experimental set-up

The sketch of the facility, typical for permeation experiments, is given in Fig. 1. A membrane sealed with two gold O-rings divides the device in two parts: the high-pressure volume (HPV) and the low-pressure volume (LPV). The membrane can be heated by means of the electric furnace Carbolite HST 12 up to 1100 K.

Deuterium is introduced into the HPV using the mass-flow controller MKS 1179A through a liquid nitrogen trap to reduce water contamination in the incoming gas. Besides, rapid hydrogen introduction is possible with an electromagnetic valve. This is useful for measurements on highly permeable materials when the lag time is small and comparable with the time of pressure rise in the HPV. The pressure is controlled with two baratrons: one for the range of 10^{-2}–10^{2} Pa and another one for 10–10^{5} Pa.

Registration of the permeated gas is carried out either by a quadrupole mass spectrometer (QMS, Balzers QMA 125) or by a baratron (MKS Baratron 120). The first one is used for low signals, while the baratron is applied for high signals and for QMS calibration. Measurements of weak signals are also available with the baratron as the leak rate for the LPV is known and is relatively low and stable. Both the devices allow measurements in two regimes: (1) when the LPV is continuously pumped (dynamic regime), and (2) when the LPV is not pumped (static regime). In the dynamic regime, that has been applied in our experiments, the QMS working range lies within 10^{-7}–10^{-2} mol/m^{2}s for D_2. Base pressures in the LPV and the HPV are 10^{-7} and 10^{-6} Pa, respectively.

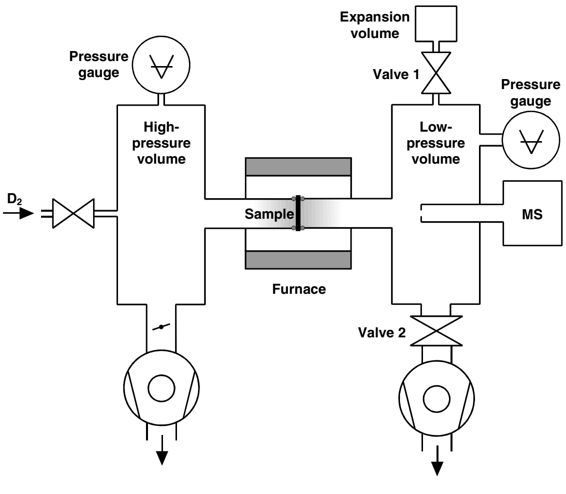

Fig. 1. Permeation facility.

2.2. Sample preparation

Two disk-shaped Eurofer samples, both 0.5 mm in thickness and 20 mm in diameter, were cut from a slab of material followed by mechanical polishing down to 0.46 and 0.27 mm. The first sample was then used as it was; the second one was one-side covered with an alumina layer of about 1 μm in thickness employing a filtered arc deposition device. Deposition was performed by running an arc discharge on an aluminum cathode, filtering plasma from metal droplets and introducing oxygen into the main chamber. The coating was deposited on the sample at 973 K applying −200 V bias voltage to build up the dense crystalline α-alumina phase. The quality of the coating was then examined with SEM and EDX techniques. The structure of the coating and its dependence on the deposition parameters are discussed in detail in [11]. An advantage of the technique used was the relatively low temperature of the substrate needed to produce α-alumina: without bias it normally required temperatures of 1300 K and above, which could easily destroy the microstructure and mechanical properties of martensitic steel.

The thickness of the deposited layer was controlled with a Tencor Instruments alpha-step 200 profilometer (as the edge of the sample was shielded during deposition by the sample holder, profilometry was a useful tool for that purpose) and was found to be similar to the value estimated from the weight increase.

Since the deposition time was about 30 min and the sample was continuously exposed to oxygen, the back side was determined to be strongly oxidized. To remove this oxide layer, an argon glow discharge was applied to that side after the alumina coating had been formed. It has been proved experimentally that argon processing had no influence on permeability properties.

2.3. Experimental procedure

Deuterium gas was introduced stepwise in portions; the next portion was added when a steady-state level of permeation rate had been achieved. After each experimental run at a fixed temperature, the sample was heated up to 773 K (for the uncoated sample) or up to 1023 K (for the coated sample) for about 1.5 h to release hydrogen accumulated in the bulk. The measurements for each sample were performed until data reproducibility was reached for all temperatures applied to the sample.

The coated sample was installed with the coating directed towards the HPV. It was assumed that in this configuration a possible surface contamination with impurities had a lower influence than the opposite sample positioning: elevated temperatures could lead to a strong oxidation of the Eurofer surface due to oxygen traces in the incoming gas while for alumina this was not of concern. No surface oxidation on the low-pressure region surface was observed for both the samples after the experiments.

3. Results and discussion

3.1. Bare sample

The bare substrate has been subjected to deuterium gas pressure ranging from 10^3 to 10^5 Pa at temperatures from 573 to 873 K. Four sets of data points representing the permeation flux J dependence on the driving pressure p at different temperatures are given in Fig. 2. At high temperatures the data are well fitted with straight lines (solid lines) resulting in a value n of about 0.6, where n is the power in the approach $J \sim p^n$. That means the permeation regime appears to be close to diffusion limited (described with $n = 0.5$), i.e. permeability is governed mainly by hydrogen transport through the bulk, whereas surface effects like adsorption and/or recombination can be neglected. At the lower temperatures 573 and 673 K, the pressure dependence of J is somewhat steeper in the low-pressure range of the data, which is indicated by the dashed lines in Fig. 2. This fact is obviously explained by a more pronounced surface influence on the permeability compared to data taken at higher temperatures and pressures.

3.2. Coated sample

While the pressure range was the same as for the bare sample, the temperatures applied to the coated ones were higher (up to 1073 K) because of insufficient QMS sensitivity for detecting permeated deuterium with acceptable precision in the latter case. Such an increase in temperature provoked a noticeable rise of the partial pressure of hydrogen coming from the walls and consequently caused a rise of the HD signal, which would be taken into account for counting the net permeation flux and was not of concern in case of the bare sample. The HD signal was found to be close or even slightly dominated over D_2 only at the lowest driving pressures, and the QMS sensitivity was supposed to be equal both for HD and D_2 molecules during estimation of the net flux. This probably led to a moderate overestimation in J but one could neglect the effect at higher pressures.

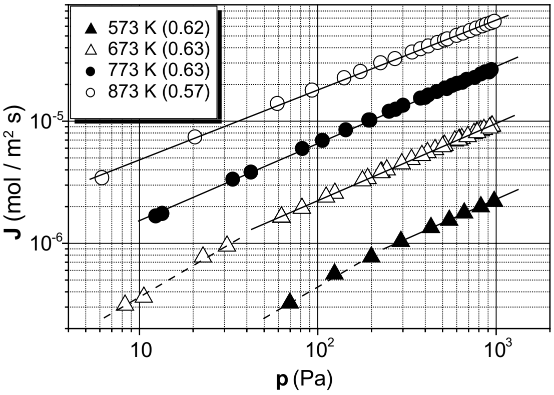

Fig. 2. Deuterium permeation flux through Eurofer as a function of driving pressure given at different temperatures. Numbers in parenthesis are the pressure exponents n corresponded to the high-pressure range.

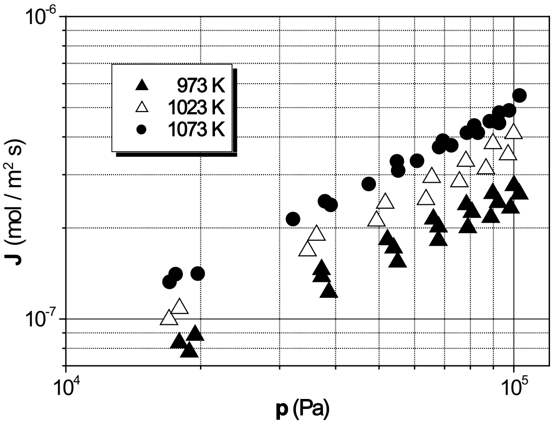

Fig. 3. Deuterium permeation flux through Eurofer sample coated with 1 μm α-alumina as a function of driving pressure given at different temperatures.

Much attention has been paid to data reproducibility. To our experience, amorphous and a mixture of amorphous and crystalline alumina have tendencies to change their permeation properties subjected to thermal cycling loads. As it has been found [12], the permeation signal changes from cycle to cycle, which results in almost one order of magnitude gradual increase in permeated flux with respect to its initial value. These changes are not caused by surface cleaning but are explained by structural changes in the layers due to thermal cycling.

Fig. 3 demonstrates selective data sets found for the coated Eurofer sample at 973, 1023 and 1073 K while 5 to 8 runs have been performed at each temperature. Being fitted with $n \approx 0.7$, the values taken at these particular temperatures reveal spreads in the permeation flux between runs rather than within separate points. In other words, data points lie well on one straight line in each run at a given temperature but do not deviate stochastically around this line.

3.3. Comparison

In Fig. 4, the comparison of our data on the deuterium permeability through Eurofer with those found in

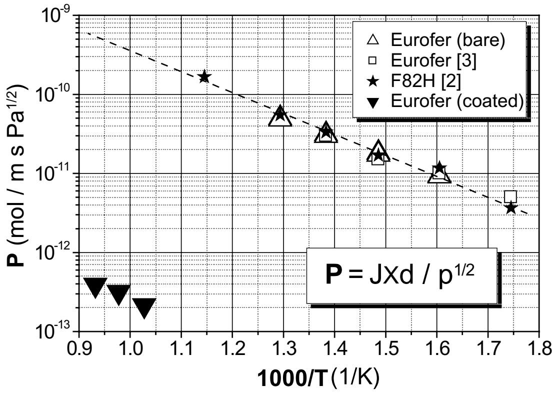

Fig. 4. Comparison of deuterium permeabilities through the uncoated and the coated Eurofer samples. Data on bare Eurofer [3] as well as F82H [2] are also given.

literature [3] as well as with those of F82H steel [2], both 1 mm in thickness, shows very good coincidence in terms of the $P(1/T)$ dependence, where T is the temperature and P, named permeability, is determined as

$$P = Jd/p^{0.5}.$$

Here, d is the thickness of a sample. Since our data do not correspond to $n = 0.5$, the permeability appears to be a function of the pressure, therefore the values of J have been taken from the high pressure data both for the uncoated and coated samples where the surface influence is less marked. As it has been mentioned before, the hydrogen transport rate through these steels looks to be similar which is shown in Fig. 4. However, confronted with these numbers, a higher deuterium permeability through F82H is reported in [1], while about two times lower values are given for Eurofer in [4]. The latter fact can be tentatively explained by different facilities and experimental conditions used in the investigations.

The ratio of the permeability through the uncoated sample to the coated one (see Fig. 4) results in promising 10^3 and even higher values of PRF for the layer of only 1 μm in thickness. We have earlier investigated amorphous and γ-alumina coatings deposited on Pd–Ag substrates and a reduction factor of 10–40 only has been evaluated [12].

Roughly estimated from three temperature points, the activation energy for the permeability is just over 50 kJ/mol. Both numbers – activation energy and PRF – are in good agreement with the highest values presented in the literature. However, surface effects still play a role in hydrogen transport suppression.

4. Conclusion

Permeation experiments have been done on bare Eurofer and Eurofer coated with crystalline alumina. The uncoated sample reveals a permeability coincident to some data presented in the literature both for Eurofer and F82H. The coated sample has been produced using a PVD technique, and the coating just 1 μm in thickness is found to cause a decrease in the permeation flux of more than three orders of magnitude. Besides, the deposited layer has demonstrated a very good structural stability with respect to thermal cycles up to a temperature as high as 1073 K, which even overestimates the envisaged operating temperature of such coatings in a fusion device. Finally, no degradation of the barrier performance has been observed, so α-alumina is a real candidate for use as a hydrogen barrier.

References

[1] E. Serra, A. Perujo, G. Benamati, J. Nucl. Mater. 245 (1997) 108.
[2] A. Pisarev, V. Shestakov, S. Kulsartov, A. Vaitonene, Phys. Scr. T94 (2001) 121.
[3] A. Aiello, I. Ricapito, G. Benamati, R. Valentini, Fusion Sci. Technol. 41 (2002) 872.
[4] A. Aiello, I. Ricapito, G. Benamati, A. Ciampichetti, Fusion Eng. Des. 69 (2003) 245.
[5] K. Verghese, L.R. Zumwalt, C.P. Feng, T.S. Elleman, J. Nucl. Mater. 85&86 (1979) 1161.
[6] K.S. Forcey, D.K. Ross, J. Nucl. Mater. 182 (1991) 36.
[7] G.W. Hollenberg, E.P. Simonen, G. Kalinin, A. Terlain, Fusion Eng. Des. 28 (1995) 190.
[8] A. Perujo, K.S. Forcey, Fusion Eng. Des. 28 (1995) 252.
[9] A. Perujo, E. Serra, H. Kolbe, T. Sample, J. Nucl. Mater. 233–237 (1996) 1102.
[10] E. Serra, P.J. Kelly, D.K. Ross, R.D. Arnell, J. Nucl. Mater. 257 (1998) 194.
[11] R. Brill, F. Koch, J. Mazurelle, D. Levchuk, M. Balden, Y. Yamada-Takamura, H. Maier, H. Bolt, Surf. Coat. Technol. 174–175 (2003) 606.
[12] D. Levchuk, F. Koch, H. Maier, H. Bolt, Phys. Scr., in press.