Permeation of hydrogen through MPG-8 graphite

A. Spitsyn [a,*], A. Pisarev [b], A. Skovoroda [a], V. Gureev [a], Yu. Martynenko [a]

[a] *RRC 'Kurchatov Institute', Ac. Kurchatov sq., 1/1, Moscow RU-123182, Russia*
[b] *Moscow Engineering and Physics Institute, Moscow, Russia*

Abstract

Hydrogen gas driven permeation through fine-grain graphite MPG-8 has been investigated in the range of thickness from 0.55 to 4.38 mm and pressures from 10^{-2} to 1 Pa. The permeation rate is proportional to the gas pressure and inversely proportional to the thickness. It has been concluded that GDP through fine-grain graphite is due to gas flow through the internal porosity network in the molecular regime. The specific bulk conductivity of the graphite is measured to be of about $(5–7.3) \times 10^{15}$ molecules $s^{-1} m^{-1} Pa^{-1}$. Surface treatment influences the permeation through membranes thinner than 1 mm. Surface polishing, washing in the ultrasonic bath, hydrogen and argon plasma irradiation, methane plasma treatment, argon ion irradiation, and annealing at 1000 K have 0–10% influence on the permeation rate.
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1. Introduction

Carbon based materials will be used to protect some of the plasma-facing components in ITER [1]. The key problem of graphite in ITER is tritium inventory. One of the mechanisms of deep tritium permeation in graphite is migration through open porosity. One can expect that plasma–surface interaction, particularly erosion, heating, and deposition of films of various nature can reduce permeation of gas trough the network of pores.

Interaction of hydrogen isotopes with graphites and carbon based materials has been actively investigated last decades. At the same time, only few publications were devoted to hydrogen permeation through isotropic graphites [2–4] and not much is known about influence of the surface treatment.

This work is devoted to experimental investigations of the gas driven permeation (GDP) through graphite membranes with surfaces treated in various ways. The Russian fine-grain graphite MPG-8 (the density 1.85 g/cm^3, granule size 2–8 μm) was used. Surface was subjected to cutting, polishing, hydrogen and argon plasma irradiation, carbon sputter deposition, C:H deposition in methane plasma, and annealing.

2. Experimental

The experimental setup developed for investigation of plasma driven permeation and described in

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* Corresponding author. Fax: +7 495 9430073.
E-mail address: spitsyn@nfi.kiae.ru (A. Spitsyn).

[5] was used in this work for investigation of gas driven permeation. The residual pressure was 10^{-4} Pa. The permeation driving hydrogen gas pressure on the inlet side was from 10^{-2} to 1 Pa.

The sample and the sample holder are shown in Fig. 1. The geometry of the sample gave the opportunity to seal the samples of the thickness down to 0.5 mm. The sealing ring was made of rubber. Therefore, experiments were restricted by room temperature. The effective area of the membrane $A = 0.9 \times 10^{-3}$ m^2 was calculated taking the edge effects into account by using the formula $A = \pi \cdot (r + d/2)^2$, where r is the radius and d is the thickness of the thin part of the sample.

Vacuum leaks between the porous sample and the sealing ring could be a problem. As the area of the contact between the sealing ring and the sample was relatively small, influence of possible leak was supposed to be small too. The samples were sealed several times with subsequent permeation tests, and the results obtained were reproducible. Also, the inlet and the outlet sides of the membrane were mutually changed with no difference in the permeation rate.

An electrode for glow discharge formation was installed on the front side of the membrane as it is shown in Fig. 1 to investigate influence of the surface modification produced by plasma. The electrode was made either from molybdenum or from graphite MPG-8. The molybdenum electrode was kept under +450 V, so gas ions irradiated the surface of the graphite sample. Argon, hydrogen, and methane were used for the discharge. The graphite electrode was kept under a negative potential, so the products of erosion of the graphite electrode re-deposited onto the membrane. Irradiation

in methane plasma as well as co-deposition of carbon and hydrogen led to formation of hydrocarbon films on the sample surface. The graphite sample was at ground potential. The pressure in the discharge varied from 1 to 100 Pa to maintain the ion flux on the sample at 5 A/m^2.

The permeation flux was measured by using a calibrated orifice with the conductivity for hydrogen $s = 2.1$ l/s installed between the outlet chamber and the vacuum pump.

3. Experimental results and discussion

3.1. Specific gas conductivity

To investigate the features of hydrogen permeation through graphite, experiments were performed with membranes of various thickness (0.8–4.38 mm) loaded by various pressures (10^{-2}–1 Pa).

An example of the dependence of the permeation flux on the gas pressure is given in Fig. 2. For comparison, the permeation rate of Ar gas is also shown. There are two important observations from this figure: (i) permeation rate is proportional to the gas pressure and (ii) the permeation rate is inversely proportional to the square root of the molecular weight. The square root ratio of the molecular weights of Ar and H$_2$ is 4.47 that completely corresponds to experimental data.

Permeation in these experiments can not be described by diffusion. Diffusion limited permeation is characterized by the square root dependence of the permeation rate on the pressure. Besides, permeation of Ar through graphite matrix is rather
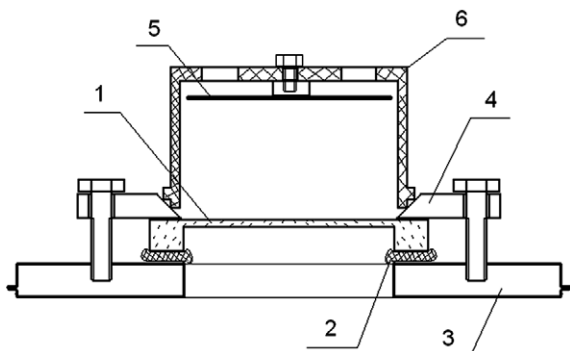

Fig. 1. Sample holder with a glow discharge unit on the inlet side: 1 – MPG-8 sample, 2 – sealing ring, 3 – flange, 4 – flange, 5 – electrode, 6 – teflon cup.
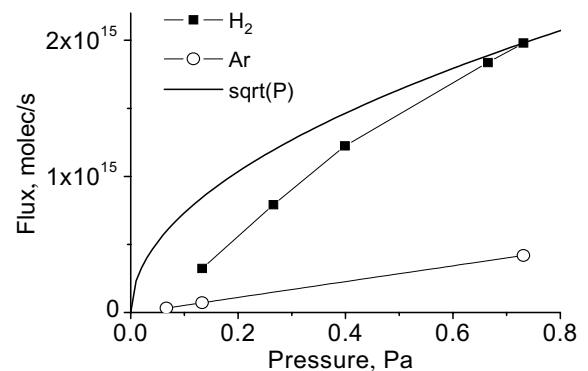

Fig. 2. Permeation flux through a graphite sample (1.26 mm thick, 30.5 mm in diameter) as a function of gas pressure. Solid line – square root pressure dependence normalized to H$_2$ signal that demonstrate permeation flux far is not proportional to square root molecular pressure.

questionable. Besides, estimations of the time-lag using diffusivities available from literature gave too large values.

The dependences of the permeation on the gas pressure and the molecular weight do not contradict to the conclusion that permeation of hydrogen through the porous MPG-8 samples can be formally described just as the gas flow in the molecular mode through curvilinear channels formed by the interconnected porosity in the sample bulk. In this case the permeation rate must be inversely proportional to the thickness.

Fig. 3 shows an example of the dependence of the permeation rate on the inverse thickness. To reduce possible sample-to-sample and sealing-to-sealing uncertainties, the experiment was performed with the same sample and without its re-sealing. This was made as follows. Initially, the sample was 4.38 mm thick, and then step-by-step the thickness was reduced by mechanical cutting of the inlet side. The sample was finally thinned to 0.8 mm. In this way, permeation measurements were performed with the thickness of 4.38, 3.3, 2.3, 1.5, and 0.8 mm. Some experiments were repeated twice: initially with as-cut and then with polished inlet surface. The outlet surface was mechanically polished and was not modified from experiment to experiment. One can conclude from Fig. 3 that the permeation rate is approximately inversely proportional to the thickness of the membrane.

From the observations of the pressure and thickness dependences one can write the permeation flux through a thick graphite membrane as $j = \Delta P \sigma A / d$, where σ is the specific gas conductivity of the membrane and ΔP is the pressure difference. This for-

mula looks similar to the formula for the electrical current through a resistance. The pressure difference is equivalent to the potential difference, while the σ is equivalent to the specific electrical conductivity.

The σ here is the characteristics of the bulk of the material. For a thin membrane, surface effects can influence hydrogen permeation. Indeed, one can see from Fig. 3 that polishing of the cut surface leads to decrease of permeation in the range of low thickness, though there is no difference in the range of high thickness. The surface effect in this particular case is connected with a very thin (<0.1 μm according to SEM) powder that is produced during polishing, blocks the near-surface channels, and prevents permeation through the membrane. The effect is observed if the membrane is thinner than $d = 1.5$ mm in Fig. 3.

Fig. 4 gives the values of the σ as a function of the inverse thickness. The values of the order of 5×10^{15} molecules s^{-1} m^{-1} Pa^{-1} measured for large thickness can be considered as a true bulk values. The values at low d are less due to blocking of the surface porosity by thin powder.

3.2. Influence of mechanical surface treatment

A series of experiments with thin samples ($d < 1$ mm) having the surfaces treated in various ways were performed.

Fig. 5 compares σ of a thin sample sequentially treated mechanically. The experiment was performed in a similar way as in measurements of the thickness dependence. Its surface was gently cut (a few μm) and polished without paste several times. The sample was initially 0.8 mm thick. Then, the sample holder with the sample was extracted, a thin
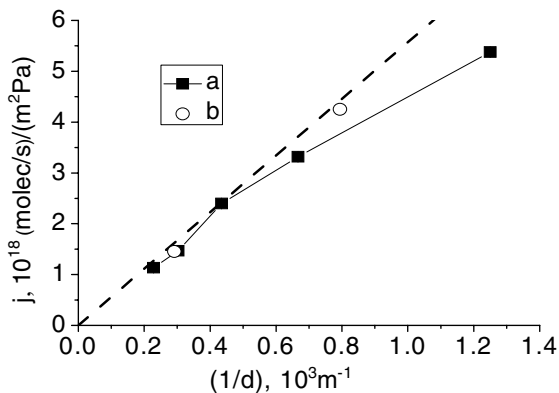

Fig. 3. Permeation flux normalized to the gas pressure and the sample area as a function of the inverse thickness: (a) only the outlet side is polished and (b) both sides are non-polished.
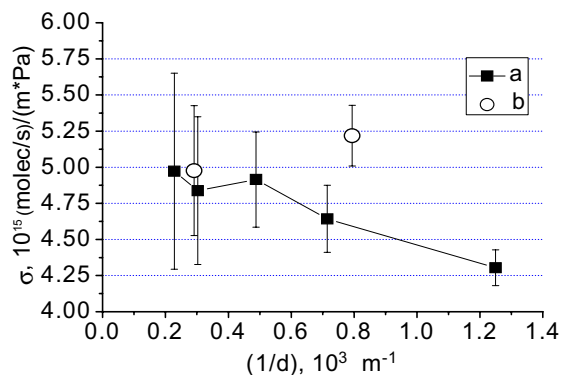

Fig. 4. The specific conductivity of MPG-8 samples calculated from data of Fig. 3.
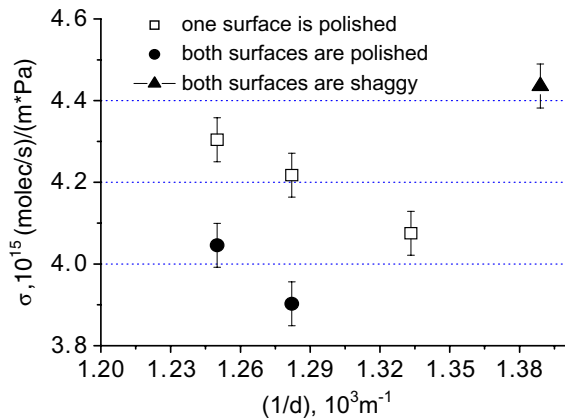
Fig. 5. The specific conductivity of a thin MPG-8 sample after repetitive cutting and polishing as a function of its thickness.

Table 1
Specific conductivity of several samples of MPG-8 graphite, molecules s^{-1} m^{-1} Pa^{-1}

Initial thickness (mm)	Before polishing	After polishing
0.78	$(4.20 \pm 0.05) \times 10^{15}$	$(3.90 \pm 0.05) \times 10^{15}$
0.7	$(4.30 \pm 0.05) \times 10^{15}$	$(3.60 \pm 0.05) \times 10^{15}$
0.8	$(4.30 \pm 0.05) \times 10^{15}$	$(4.00 \pm 0.05) \times 10^{15}$
4.38	$(5 \pm 0.3) \times 10^{15}$	$(4.8 \pm 0.3) \times 10^{15}$

Table 2
Specific conductivity of a 0.55 mm thick sample of MPG-8 graphite at different surface treatments

Surface conditions	σ (molecules s^{-1} m^{-1} Pa^{-1})
Cutting surface	5.7×10^{15}
Washing in the ultrasonic bath	5.7×10^{15}
Polishing surface	4.7×10^{15}
Washing in the ultrasonic bath	5×10^{15}
Irradiated by H^+ (5×10^{23} m^{-2})	5.6×10^{15}
Irradiated by H^+ (1.2×10^{24} m^{-2})	5.6×10^{15}
Irradiated by CH_4 plasma (2×10^{22} m^{-2})	5.3×10^{15}
Irradiated by CH_4 plasma (1×10^{23} m^{-2})	5.3×10^{15}

layer of the order of a few microns was mechanically removed from the inlet side, and permeation measurements were repeated. Then, the sample holder with the sample was extracted again, polished, and the permeation measurements were performed again. In this way, a series of measurements with the same sample (the thickness was changed only slightly) was performed. One can see from Fig. 5 that the permeation in experiments with both the inlet and outlet sides polished is about 5% less than in experiments with only the outlet side polished. The result for the sample with none of the sides polished gives even larger value of permeation (15% above the later value).

The surface of the polished sample observed in SEM was very flat – the pores were filled with fine powder. This can explain the decrease of the conductivity after polishing. It is important that this decrease is very small. That is, the very thin powder produced by mechanical polishing is rather transparent for hydrogen gas and is unable to block permeation from gas to the porosity in the graphite bulk.

The experiments of the kind were also performed with several samples of similar thickness to estimate the sample-to-sample uncertainty (Table 1). One can see that the results are well reproducible. For comparison, the data for a much thicker sample (4.38 mm) are given. The σ value of thin samples is smaller than that of the thicker sample. The value of the σ of the order of 5×10^{15} molecules s^{-1} m^{-1} Pa^{-1} obtained for the 4.38 mm sample with one side polished equals the value of σ obtained for the 0.8 mm thick sample with neither sides polished (Fig. 4). This is due to smaller influence of

the surface effects on the permeation through thick samples.

Washing of the sample in alcohol in an ultrasonic bath for 30 min gave no changes for the as-cut sample and led to a very small increase of the conductivity for the polished sample, see Table 2.

3.3. Influence of plasma impact

The experiments with a 0.55 mm thick sample were performed to analyze possible influence of plasma treatment on hydrogen GDP. The sample surfaces were initially cut mechanically. Then, the inlet surface was treated step-by-step in the following way: mechanical polishing without paste, washing in spirit in an ultrasonic bath, irradiation by Ar^+ ions in the glow discharge at 450 eV and 5 A/m^2, irradiation by H^+ ions in the glow discharge at 450 eV and 5 A/m^2, and deposition of C:H films in the methane glow discharge. The outlet surface was mechanically polished. The results of the experiments performed step-by-step at various conditions are summarized in Table 2.

Irradiation of the polished surface by Ar^+ ions in the glow discharge leads to initial increase of σ and then to its stabilization on a steady state level. That is, irradiation of the polished surface by argon ions

leads to restoration of the conductivity. Irradiation by hydrogen plasma gives the same effect as argon ion irradiation. The feature of hydrogen plasma impact is that essentially smaller fluence is necessary in this case.

Sample treatment in methane plasma lead to formation of a C:H film on the membrane outlet side. Nevertheless, this gave only a very small decrease of the GDP rate, which was within the experimental uncertainty.

Two explanations of small influence of the C:H film can be proposed. Film deposited at low temperatures are usually characterized as soft films, and one can suppose they are porous. Besides, sputter deposition on porous surfaces, like that of graphite, often produces non-continuous films, which can be expected to be transparent for gas. The result is not contradict with [6] where was shown that an a-C:H layer is permeable for H_2 molecules.

GDP permeation was measured also after high fluence irradiation by low energy Ar ions in the arc discharge (energy of ions 50 eV, ion flux 5×10^5 A/m^2, and the average fluence of 1.8×10^{25} m^{-2}). The thickness of the graphite sample was 2.48 mm. The conductivity after irradiation increased only slightly.

So, surface treatment of samples led either to a very small increase of the permeation rate or to no effect at all. This agrees with the conclusion made in [4] that amorphous hydrocarbon film does not influence permeation properties of graphite. Annealing of the sample to 1000 K has no effect too. This contradicts the result of [2] where 50% increase in the hydrogen permeation rate was observed after annealing to 1023 K. The possible reason of the discrepancy may be connected either with difference in the graphites used or with possible problems in the sample sealing after high temperature annealing in [2].

3.4. Sample-to-sample variations

Though fine-grain graphites are considered to be isotropic materials, SEM images give slightly different porosity of the surfaces cut in different directions. The pressure in the graphite production was applied in one direction, and this could be the reason of a difference in the porosity structure in the direction parallel to the pressure applied and in the perpendicular directions.

All the samples were cut in the same direction but from different parts of the graphite block. The

Table 3
Specific conductivity of a 2.48 mm thick sample of MPG-8 graphite after Ar$^+$ irradiation (arc discharge, 50 eV, 5×10^5 A/m^2)

	σ (molecules s^{-1} m^{-1} Pa^{-1})
Virgin graphite	7.3×10^{15}
Irradiated by Ar$^+$	7.1×10^{15}

results for the samples cut from the same parts of the block were well reproducible. At the same time the results for the samples taken from different parts were slightly different. For example, the data given in Tables 1 and 3 differ. The specific bulk conductivity for samples in Table 1 are 5×10^{15} molecules s^{-1} m^{-1} Pa^{-1}, while the specific bulk conductivity for sample typical for Table 3 are 7.3×10^{15} molecules s^{-1} m^{-1} Pa^{-1}.

4. Conclusion

Gas driven permeation rate of hydrogen through membranes made of fine-grain graphite MPG-8 was found to be proportional to the pressure difference and inversely proportional to the membrane thickness. In comparison with argon GDP, the permeation rate of hydrogen was the square root ratio of the molecular weight higher. Permeation was supposed to take place due to hydrogen gas flow in the molecular regime through the interconnected porosity. The specific gas conductivity σ of graphite for hydrogen gas was introduced, so that the permeation rate is the product of σ, the membrane surface area, and the gas pressure difference divided by the membrane thickness. For thick samples, σ was measured to be $(5–7.3) \times 10^{15}$ molecules s^{-1} m^{-1} Pa^{-1}. For samples thinner than 1.5 mm, σ is less, possibly due to surface effects.

Influence of surface treatment of the GDP was investigated for thin samples of the thickness down to 0.5 mm. It was shown that dry surface polishing without paste leads to 5–15% reduction of σ, possibly due to blocking of the porosity by fine powder. The small level of reduction means that this fine powder is well transparent for gas. Washing of graphite samples in the ultrasonic bath in alcohol lead to only a small restoration of the conductivity. Possibly, cleaning employed in those experiments was ineffective, and SEM supports this conclusion.

Argon and hydrogen plasma irradiation of MPG-8 surface restores the conductivity after polishing.

Treatment in methane plasma as well as sputter deposition of carbon have no influence on σ. The

structure of deposited C:H films is possibly not dense and not continuous.

Annealing at 1000 K was of no effect.

Acknowledgements

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