ELSEVIER

Journal of Nuclear Materials 266–269 (1999) 417–422

journal of nuclear materials

Oxygen incorporation into beryllium under D-ion bombardment in O_2 atmosphere

V.Kh. Alimov *, R.Kh. Zalavutdinov, A.P. Zakharov

Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky prospect 31, 117915 Moscow, Russian Federation

Abstract

Oxygen incorporation into beryllium under the irradiation with 3 keV D-ions in ^{18}O enriched (80%) oxygen atmosphere (at the pressure range from 10^{-5} to 10^{-3} Pa) at 300 and 700 K has been investigated by means of SIMS depth profiling. Two stages of oxygen accumulation in dependence upon the D-ion fluence were observed. At the first stage ($<5 \times 10^{17}$ D/cm^2), the oxygen atoms are incorporated into BeO initially present on the metal surface and the metal layers adjacent to the oxide (up to a depth of about 20 and 40 nm at 300 and 700 K, respectively). At the second accumulation stage ($>1 \times 10^{18}$ D/cm^2), the development of an interconnected and open gas porosity, caused by D-ion implantation, leads to the interaction of oxygen with a newly created beryllium inner surface which results in a noticeable increase of the oxygen content in the ion stopping zone (at a depth up to 200 nm). The maximum amount of ^{18}O accumulated in the bulk depends on the oxygen pressure and reaches a value within the range from 1×10^{17} to 2×10^{17} O/cm^2 for 300 K and from 6×10^{16} to 2×10^{17} O/cm^2 for 700 K. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Beryllium; Depth profile; Deuterium irradiation; Oxygen gettering

1. Introduction

Present concepts for the ITER consider beryllium as a candidate plasma-facing material [1,2]. It is well known that beryllium reacts rapidly with oxygen or oxygen-bearing compounds to form beryllium oxide BeO, with a large exothermic enthalpy of formation (about −140 kcal/mol [3]). A saturated BeO layer has been observed to form on clean Be surface for oxygen exposure of only 10 Langmuirs (1 L is equivalent to 1.3×10^{-4} PaS [4]. For oxygen exposure of 4×10^5 L at room temperature the BeO thickness was found to be 1.3–1.4 nm [5]. Under conditions of thermal oxidation at O_2 pressures between 3×10^{-6} and 2×10^{-4} Pa and in the temperature range 300 to 770 K the time dependence of the thickness of the beryllium oxide film obeys the logarithmic law [5]. After air exposure at room temperature electropolished hot-pressed beryllium is normally covered with a non-porous protective oxide film of about 5–7 nm [6].

The increase of oxygen content in beryllium after D- or He-ion bombardment under relatively poor vacuum conditions has been reported by Langley [7]. Recently [6], we presented results on the oxygen sorption in beryllium irradiated with D- and He-ions and then exposed to air and oxygen at 300 K. A comparison of oxygen depth profiles with D/He-ion ranges made it possible to establish that the oxygen accumulation in the subsurface layer with the thickness equal to the ion mean range took place after the ion implantation with high fluences (at which the reemission of deuterium/helium appeared). It was suggested that a kind of open porosity developed in the ion stopping zone. Actually, a TEM study of the microstructure of Be irradiated with D- and He-ions in the temperature range 300–700 K revealed the development of interconnected bubbles at room temperature and labyrinth structure of flattened-out wide channels at temperatures ⩽ 500 K [8]. Obviously, this porosity was responsible for the penetration of oxygen-containing molecules into the near-surface layer of the ion implanted Be, that led to the increase of oxygen content after the ion irradiation.

The present work has been made in order to study the oxygen accumulation in beryllium under irradiation

---

* Corresponding author: Tel.: +7 095 330 2192; fax: 7 095 334 8531; e-mail: alimov@ipcras.msk.ru

PII: S 0 0 2 2 - 3 1 1 5 (9 8) 0 0 8 2 6 - 5

with D-ions at 300 and 700 K in oxygen atmosphere at pressures ranged 10^{-5} to 10^{-3} Pa.

The oxygen incorporation into solid targets due to ion implantation in the presence of O_2 molecules was studied for quite different systems: metal targets/metal ions [9–11], titanium target/argon ion [12], silicon target/nitrogen ions [13] and carbon-boron materials/deuterium ions [14]. It was shown that a large amount of oxygen could be accumulated in the target. A strong dependence on oxygen pressure was found and saturation values of the oxygen concentration were obtained for each pressure. No oxygen was detected beyond the ion stopping zone [9–11,14] at room temperature.

2. Experimental

Hot-pressed beryllium grade S-65B (Brush Wellman, USA), containing about 1 wt% of BeO, was used. Samples were polished mechanically and electropolished prior to the ion implantation.

The experiments were performed in a special two chamber UHV system with a typical base pressure $<10^{-7}$ Pa. The samples were irradiated in the first vacuum chamber with 6 keV D_2^+ ions at temperatures, T_{irr}, of 300 and 700 K in the presence of oxygen atmosphere. The mass-separated ion beam of 0.5 mm diameter was swept electrostatically in two mutually perpendicular directions over the area of 4.0×4.5 mm^2. The ion flux density was $(6.3 - 6.9) \times 10^{14}$ D-ions/cm^2 s. The positive bias of 15 V was applied to a target to suppress the secondary electron emission during the measurements of the ion current. The oxygen was pumped out immediately after switching off the ion beam.

The oxygen pressure in the implantation chamber was varied by backfilling with O_2 (enriched with ^{18}O) using a needle valve. The isotope composition was determined by quadrupole mass spectrometer. The relations between intensities of 32 ($^{16}O_2$), 34 ($^{16}O^{18}O$) and 36 ($^{18}O_2$) masses were 1 : 9.5 : 19.5, respectively. It follows that oxygen consisted of about 20% of ^{16}O-atoms and 80% of ^{18}O-atoms. The oxygen pressure was measured by a Bayard Alpert type gauge. The sensitivity factor was taken into account.

After implantation Be samples were transferred in vacuo into the second analytical chamber for SIMS measurements of ^{16}O and ^{18}O containing secondary ion yields ($^{16}O^-$, $^{18}O^-$, $Be^{16}O^-$, $Be^{18}O^-$) in the course of surface sputtering. All measurements were made at 300 K. To attain a uniform erosion rate, the beam of 4 keV Ar^+ ions was focused to about 100 μm and was scanned over an area of 0.4×0.5 mm^2 at 45° to the surface. Rim effects from the sputtered crater were avoided by reducing the area of the measurement up to 0.2×0.3 mm^2 (in the center of sputtered spot). The sputtering interval was 1–2 min, measurement time was 5–6 s. The sputtering rate was calculated as a ratio of the depth of a crater produced by sputtering at an edge of thin foil to the sputtering time. The height of the step was measured using optical microinterferometer within accuracy of 20% [15].

The measurements of oxygen sorption in D-ion irradiated Be were additionally performed for revealing of the open porosity development. Be samples irradiated with 3 keV D-ions at 300 and 700 K in vacuum in the first chamber were exposed in situ at the same temperature, $T_{irr/exp}$, to oxygen enriched with ^{18}O at pressure of 10^{-1} Pa for 30 min and then transferred in vacuo into another analytical chamber to make SIMS measurements of ^{16}O and ^{18}O depth distributions.

The ratio of the oxygen concentration to the SIMS count rate was determined by the comparison of the integral of the $^{16}O^- + {}^{18}O^-$ signal intensity (over the whole penetration depth) with the total amount of oxygen isotopes ($^{16}O + {}^{18}O$) in Be sample irradiated with D-ions in O_2 atmosphere. For the calibration the Be samples irradiated to fluences above 1×10^{19} D/cm^2 and then exposed to air were chosen. Since ^{16}O atoms are present in Be due to the manufacturing process, the intensity of $^{16}O^-$signal obtained after sputtering of about 400 nm was taken as the signal caused by the bulk oxygen and was subtracted from the measured $^{16}O^-$signal. The total content of oxygen isotopes in the near-surface layers of the Be sample was measured by electron probe microanalysis (EPMA) in a Cameca microanalyzer equipped with two wavelength dispersive spectrometers. The bulk oxygen amount was subtracted from the total measured oxygen amount. SiO_2 was used as a standard for the analysis of oxygen. For EPMA measurements the samples were transferred 'off-vacuum', and that is the reason why calibration of SIMS O^-signal was done after air exposure of the Be samples.

3. Results and discussion

One of the characteristics influenced on the oxygen-beryllium interaction during D-ion bombardment is the increase of the surface area which takes place due to the high interconnected porosity formation in the ion stopping zone of Be [6]. The coefficient of the surface area increase, $K_{surface}$, could be obtained from results of the experiments on the oxygen sorption in Be irradiated with D-ions and then exposed to O_2.

EPMA inspection of the original Be samples shows that the initial oxygen amount is $(5 \pm 0.3) \times 10^{16}$ O-atoms/cm^2 and the thickness of the surface oxide does not exceed 7 nm. The annealing of the samples at 700 K in oxygen atmosphere at pressure of 10^{-1} Pa for 30 min increases oxygen content to $(6 \pm 0.3) \times 10^{16}$ O-atoms/cm^2.

The oxygen-18 content and total content of oxygen isotopes (^{16}O and ^{18}O) in the near-surface layer of Be implanted with 3 keV D-ions at 300 and 700 K and then exposed to ^{18}O enriched oxygen at the same temperature, $T_{irr/exp}$, are plotted in Fig. 1 as a function of ion fluence. The depth profiles of oxygen-18 in these Be samples are shown in Fig. 2. The irradiation with low D-ion fluences (below 5×10^{17} D/cm^2) hardly influences the oxygen content. After the irradiation to these low fluences and following oxygen exposure the ^{18}O atoms do not interact with Be atoms due to the presence of Be^{16}O film on Be surface. The irradiation to fluences above 5×10^{17} D/cm^2 leads to the formation of interconnected gas porosity at a depth of deuterium accumulation [8] and to the increase of oxygen content under following oxygen exposure. When $T_{irr/exp}$ increases from 300 to 700 K, the onset fluence of the open porosity formation decreases from $(5–7) \times 10^{17}$ to $(3–5) \times 10^{17}$ D/cm^2 (Fig. 1). After the implantation to high fluences (at 1×10^{19} D/cm^2) and following oxygen exposure at $T_{irr/exp}$ of 300 and 700 K, the total content of oxygen isotopes increases by a factor of ~3 and ~2, respectively, as compared with the content after the low fluence implantation (Fig. 1(b)). Based on the latter fact, the coefficient $K_{surface}$, which is defined as the ratio of surface areas accessible for oxygen before and after D-ion irradiation, is estimated to be ~3 and ~2 for 300 and 700 K, respectively.

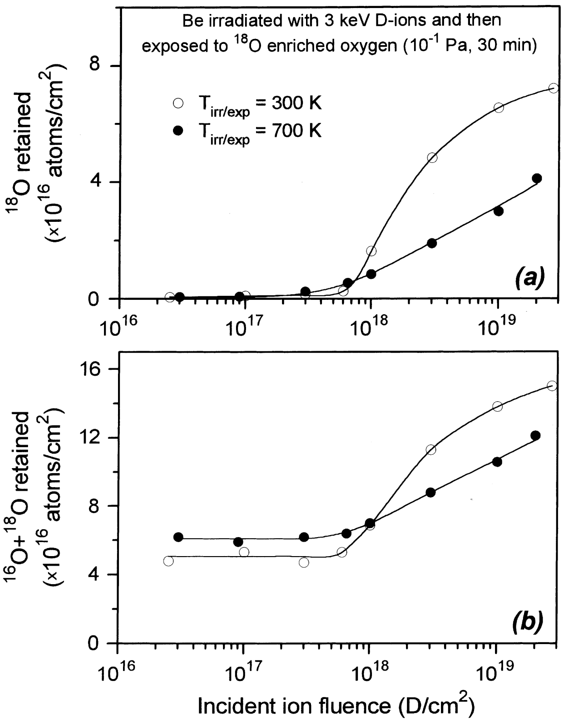

Fig. 1. ^{18}O content (a) and total content of oxygen isotopes ^{16}O and ^{18}O (b) in Be irradiated with D-ions at 300 and 700 K and then kept in ^{18}O enriched oxygen atmosphere at pressure of 10^{-1} Pa for 30 min without temperature changing, as a function of the ion fluence.

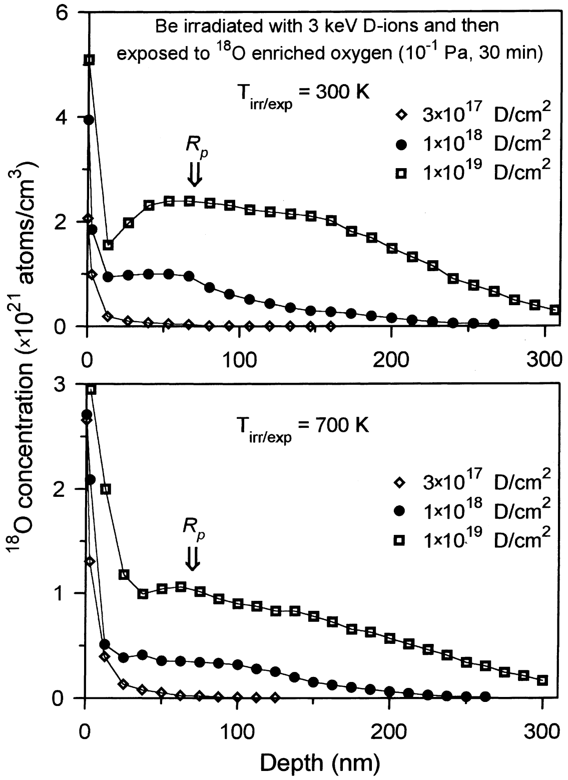

Fig. 2. Depth profiles of oxygen-18 in Be irradiated with D-ions at 300 and 700 K and then kept in ^{18}O enriched oxygen atmosphere at pressure of 10^{-1} Pa for 30 min without temperature changing. The arrows indicate the mean projected range, R_p, of the implanted D ions.

The depth profiles and the areal densities of incorporated ^{18}O for Be irradiated with D-ions in O_2 atmosphere at different oxygen pressures, P_{oxygen}, and irradiation temperatures, T_{irr}, are presented in Figs. 3–5, respectively. For low implant fluences (below 7×10^{17} D/cm^2) at 300 K the mean range of ^{18}O penetration is about 20 nm. With T_{irr} rising to 700 K, this range increases by 1.5–2 times. At fluences above 1×10^{18} D/cm^2 (when an open porosity is developed, see Fig. 1) the ^{18}O atoms penetrate into the bulk at the depth of D-ion stopping zone (Figs. 3 and 4). It should be noted that for Be the mean projected range of 3 keV D-ions was measured to be about 70 nm [6]. The maximum ^{18}O concentration in the bulk was found to depend on T_{irr} and P_{oxygen}. As the T_{irr} increases from 300 to 700 K, the maximum ^{18}O concentration decreases by about 3 times for the each oxygen pressure in the range 10^{-5} to 10^{-3} Pa. Both at 300 and 700 K, the ^{18}O concentration in the

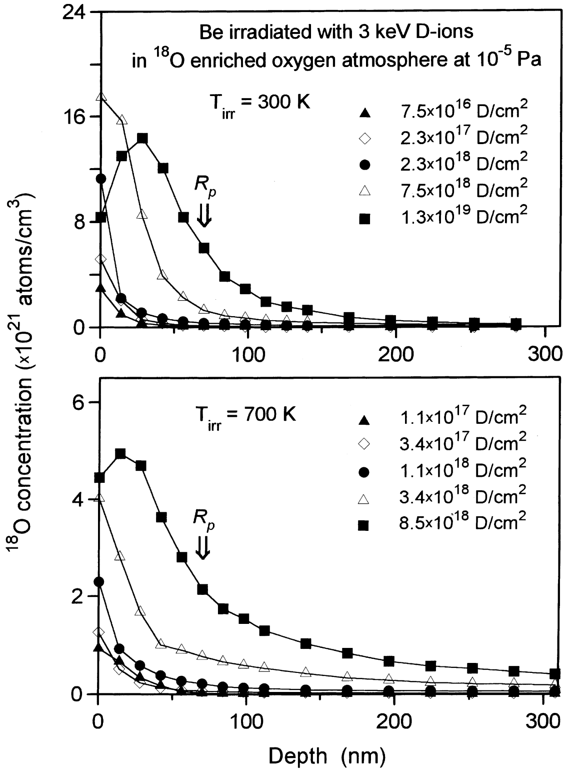

Fig. 3. Depth profiles of ^{18}O in Be irradiated with D-ions at 300 and 700 K in ^{18}O enriched oxygen atmosphere at pressure of 10^{-5} Pa. The arrows indicate the mean projected range, R_p, of the implanted D-ions.

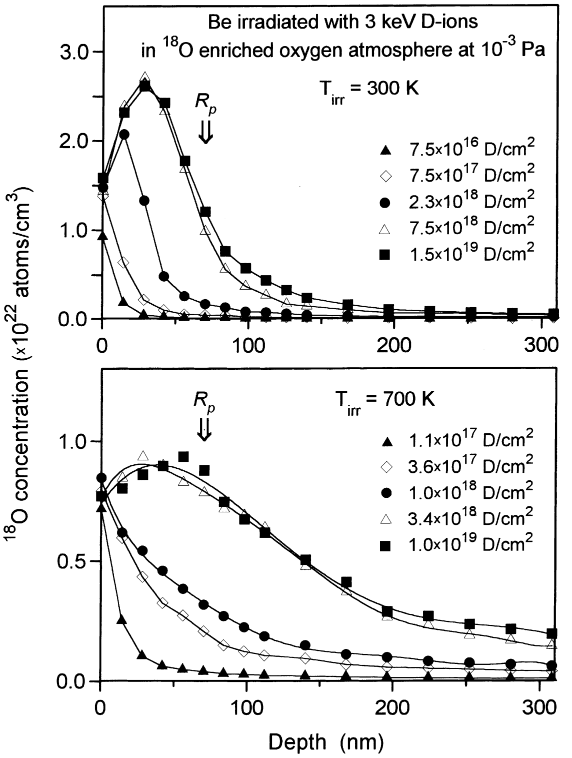

Fig. 4. Depth profiles of ^{18}O in Be irradiated with D-ions at 300 and 700 K in ^{18}O enriched oxygen atmosphere at pressure of 10^{-3} Pa. The arrows indicate the mean projected range, R_p, of the implanted D-ions.

Be bulk increases by a factor of about 2 with the P_{oxygen} increase from 10^{-5} to 10^{-3} Pa (Figs. 3 and 4).

SIMS measurements have revealed that fluence dependencies of $^{18}O^{-}$and $Be^{18}O^{-}$secondary ion yields on the depth are very similar. It pointed out that ^{18}O atoms are chemically bonded to beryllium atoms.

The evolution of ^{18}O content in Be under D-ion bombardment at 300 and 700 K is characterized by a stepwise increase (Fig. 5). At the first accumulation stage (at fluences below (5–7) × 10^{17} D/cm^2), the oxygen amount at saturation was observed to increase with P_{oxygen}. At the second stage of oxygen accumulation (at fluences above (5–7) × 10^{17} D/cm^2) the open porosity formation and oxidation of a new-formed Be surface lead to a marked increase of the oxygen content. The amount of ^{18}O incorporated into the ion stopping zone under D-ion irradiation to a fluence of 1 × 10^{19} D/cm^2 depends on the oxygen pressure and reaches a value varied from 1 × 10^{17} to 2 × 10^{17} D/cm^2 for 300 K and from 6 × 10^{16} to 2 × 10^{17} D/cm^2 for 700 K (Fig. 5).

Values of the initial ^{18}O incorporation rate at the first accumulation stage, as those were estimated for the different oxygen pressures and irradiation temperatures (Fig. 5), are given in Table 1. It should be remembered that percentage of ^{18}O atoms in the incorporated oxygen equals 0.8.

A strong oxygen pressure dependence was found for the initial ^{18}O incorporation rate. For $P_{\text{oxygen}} = 10^{-3}$ Pa the initial ^{18}O incorporation rates at 300 and 700 K are practically equal in value. For lower pressure, the in-

Table 1
Initial rates of incorporation of ^{18}O atoms into Be (O-atoms/D-ion) under irradiation with 3 keV D-ions in ^{18}O enriched oxygen atmosphere at T_{irr} of 300 and 700 K

	$P_{\text{oxygen}} = 10^{-5}$ Pa	$P_{\text{oxygen}} = 10^{-4}$ Pa	$P_{\text{oxygen}} = 10^{-3}$ Pa
$T_{\text{irr}} = 300$ K	0.07 ± 0.02	0.140 ± 0.05	0.16 ± 0.05
$T_{\text{irr}} = 700$ K	<0.02	0.09 ± 0.03	0.15 ± 0.05

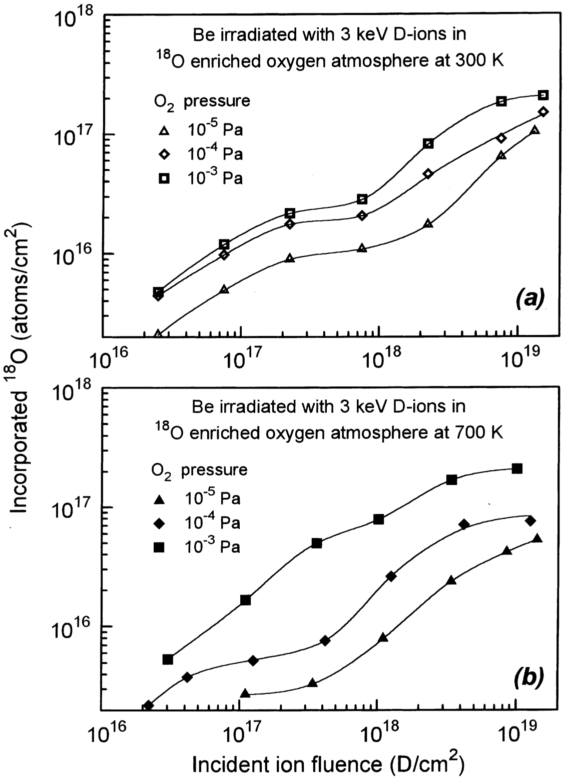

Fig. 5. Content of ^{18}O in Be after the irradiation with D-ions at 300 and 700 K in ^{18}O enriched oxygen atmosphere at pressures indicated as a function of the ion fluence.

corporation rate at 700 K is far less than that one at room temperature.

Some possible processes of the oxygen incorporation into and through existing beryllium oxide layer under ion bombardment at the first accumulation stage can be pointed out. (i) Dissociation of oxygen molecules on the oxide surface. Oxygen atoms or ions would diffuse much easier than molecules through the oxide layer thereby enhancing the incorporation rate. (ii) Radiation enhanced adsorption, causing a larger surface oxygen coverage due to electronic charging of the surface or to an increased number of oxygen adsorption sites on the surface produced by ion sputtering. (iii) Recoil implantation and/or radiation enhanced diffusion of oxygen atoms through defects created under irradiation.

It seems likely that the increase of implantation temperature will cause the number of oxygen adsorbed on BeO surface to decrease (especially for P_{oxygen} below 10^{-4} Pa) and will cause the oxygen incorporation rate to reduce.

The processes (i)–(iii) would be of major importance for the oxygen incorporation at low D-ion fluences. At high fluences, the formation of an open porosity over the D-ion stopping range increases the area of the oxygen interaction with beryllium atoms and hence the oxygen amount in the bulk. The rate of the oxygen–beryllium interaction is thought to be limited by oxygen flow through the system of open channels and depends on the oxygen pressure [16].

4. Conclusions

It has been found that the irradiation of beryllium with D-ions in O_2 atmosphere at 300 and 700 K leads to oxygen incorporation into the sample. The total amount of incorporated oxygen increases stepwise with D-ion fluence. At the first accumulation stage, the oxygen atoms are incorporated into BeO layer and metal layer adjacent to the oxide. The initial incorporation rate of oxygen and the saturated amount of oxygen increase with the oxygen pressure and decrease with the irradiation temperature.

At the second accumulation stage, the development of interconnected gas porosity in the Be matrix and penetration of oxygen molecules through the system of open pores result in the oxidation of new-formed beryllium surface; in so doing the marked increase of the oxygen content in the ion stopping zone takes place. The maximum content of oxygen incorporated into the bulk increases with the oxygen pressure and decreases when the irradiation temperature increases from 300 to 700 K.

Acknowledgements

Work supported by the US Department of Energy under Contract LF-7292 with Sandia National Laboratories.

References

[1] Technical Basis for the ITER Interim Design Report, Cost Review and Safety Analysis, ITER EDA Documentation Series, No.7, IAEA, Vienna, 1995.
[2] M.C. Billone, M. Dalle Donne, R.G. Macaulay-Newcombe, Fusion Eng. Des. 27 (1995) 179.
[3] K.K. Kelley, J. Amer. Chem. Soc. 61 (1939) 1217.
[4] J.T. Hurd, R.O. Adams, J. Vac. Sci. Technol. 6 (1969) 229.
[5] D.E. Fowler, J.M. Blakely, Surfa. Sci. 148 (1984) 265.
[6] V.Kh. Alimov, R.Kh. Zalavutdinov, A.E. Gorodetsky, A.P. Zakharov, J. Nucl. Mater. 220–222 (1995) 947.
[7] R.A. Langley, J. Nucl. Mater. 85&86 (1979) 1123.
[8] V.N. Chernikov, V.Kh. Alimov, A.V. Markin, A.P. Zakharov, J. Nucl. Mater. 228 (1996) 47.
[9] B. Hoffmann, H. Baumann, F. Rauch, K. Bethge, Nucl. Instrum. and Meth. B 28 (1987) 336.
[10] B. Hoffmann, H. Baumann, F. Rauch, K. Bethge, Nucl. Instrum. and Meth. B 36 (1989) 30.

[11] B. Hoffmann, H. Baumann, F. Rauch, K. Bethge, Nucl. Instrum. and Meth. B 36 (1989) 157.

[12] A.E. Gorodetsky, R.Kh. Zalavutdinov, V.Kh. Alimov, D.B. Bogomolov, A.P. Zakharov, Poverkhnost 8 (1996) 62 (in Russian).

[13] G. Holmén, H. Jacobsson, Appl. Phys. Lett. 53 (1988) 1838.

[14] V.Kh. Alimov, R.Kh. Zalavutdinov, A.E. Gorodetsky, A.P. Zakharov, J. Nucl. Mater. 231 (1996) 69.

[15] W. Linnik, Ein Apparat für Mikroskopisch-Interferometrische Untersuchung Reflektierender Objekte (Mikrointerferometer), Comptes Rendus de l'Académie des Sciences de l'URSS, 1 (1933) 18.

[16] P.C. Carman, The Flow of Gases in Porous Media, Butterworths Scientific, London, 1956.