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Tritium Release from Advanced Beryllium Materials after Loading by Tritium/Hydrogen Gas Mixture

Vladimir Chakin[a], Rolf Rolli[a], Anton Moeslang[a], Petr Kurinskiy[a], Pavel Vladimirov[a], Christopher Dorn[b], and Igor Kupriyanov[c]

[a]*Karlsruhe Institute of Technology, Institute for Applied Materials, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*
[b]*Materion Beryllium & Composites, 6070 Parkland Boulevard, Mayfield Heights, Ohio 44124-4191 U.S.A.*
[c]*Bochvar Russian Scientific Research Institute of Inorganic Materials, Rogova str., 5, 123098 Moscow, Russia*

Comparison of different beryllium samples on tritium release and retention properties after high-temperature loading by tritium/hydrogen gas mixture and following temperature-programmed desorption (TPD) tests has been performed. The best properties showed both the I-220-H grade produced by hot isostatic pressing (HIP) having the smallest grain size and pebbles with 1 mm diameter produced by fluoride reduction method (FRM) having a highly developed inherent porosity. It should be noted that all uses of the term "porosity" in this paper refer to presence of pores in materials due to their manufacturing processes. This is not to be confused with radiation-induced porosity, which, as the term suggests, is found in the material as a result of its exposure to radiation.

Keywords: titanium beryllide; tritium release; thermal desorption

1. Introduction

It is planned for beryllium to be used as the neutron multiplier material in the European Helium Cooled Pebble Bed (HCPB) concept for a breeding blanket design for DEMO [1]. Tritium release and retention properties are the key issues for successful application of beryllium in the blanket. Under neutron irradiation, large amounts of tritium and helium are produced in beryllium. Clearly, the best possibility in current conditions to simulate fusion relevant parameters is performing an irradiation test with investigated materials in a materials test reactor. There is, however, another method which allows the saturation of beryllium samples by tritium without neutron irradiation [2]. It is a high-temperature loading of the samples in a tritium/hydrogen gas mixture. By using this method, it is possible to investigate and to rank advanced beryllium materials on tritium release and retention behavior without irradiation and, accordingly, with comparatively lower time costs. In this study, a wide range of beryllium materials is investigated by using the loading method and following temperature-programmed desorption (TPD) tests.

2. Experimental

In this study, several kinds of beryllium materials have been investigated. Beryllium grades I-220-H, O-30-H, and S-65-H have been consolidated by hot isostatic pressing (HIP) by Materion Beryllium & Composites (MBe&C), U.S.A. The samples were prepared as cylinders with dimensions of 4 mm in diameter and 2 mm in height. These beryllium grades differ from each other by grain size and beryllium oxide (BeO) content. The second kind of material is beryllium pebbles with irregular shape produced by Bochvar Institute, Russia by a crushing method (CM) from beryllium pieces with subsequent mechanical processing by an attritor. Three different types of pebbles were tested, with grain sizes of 10-30 μm, 30-60 μm, and >100 μm, respectively. The third kind of material is beryllium pebbles with a regular, round shape, differing by production method and diameter. In particular, pebbles produced by the rotating electrode method (REM) with diameters of 0.5 mm, 1 mm, and 2 mm from NGK Insulators in Japan, and pebbles fabricated by the fluoride reduction method (FRM) with diameters of 1 mm and 2 mm from MBe&C were used. In addition, MBe&C supplied a piece of beryllium single crystal in the form of a 5 mm cube which was also investigated in this study.

The tritium/hydrogen loading of the samples was performed in the $^{1}H_2$ + 500 appm $^{3}H_2$ gas mixture at 873 K for 6 h at 4 bar. By performance of the TPD tests, a permanent heating mode with a ramp rate of 0.117 K/s up to 1373 K followed by 3 h exposure at the maximum temperature was used [3]. The gas mixture of high-purity helium with a small addition of hydrogen (^{4}He + 0.1 vol.% $^{1}H_2$) was applied as a purge gas to transport the released species from the furnace with the beryllium samples to a proportional counter (PC). A Zn-bed was placed between the furnace and the PC. The Zn-bed was permanently heated up to 663 K which permitted the conversion of tritiated water to tritium gas to avoid the absorption of the tritiated water into the pipes and into the PC. For the same reason, all gas pipes in the manifold were heated up to 573 K during the TPD tests. So, the released tritium reaches the PC mainly in the form of $^{1}H^{3}H$ [3].

3. Results

3.1. Tritium release and retention

Fig. 1 shows the tritium release rate versus testing temperature for beryllium grades fabricated by HIP as

vladimir.chakin@kit.edu

well as for beryllium single crystal. All samples have quite a broad single peak at high temperatures with a long shoulder to lower temperatures. For all materials, the high-temperature peaks are located at 1260-1302 K, and the shoulders begin around 500-600 K.

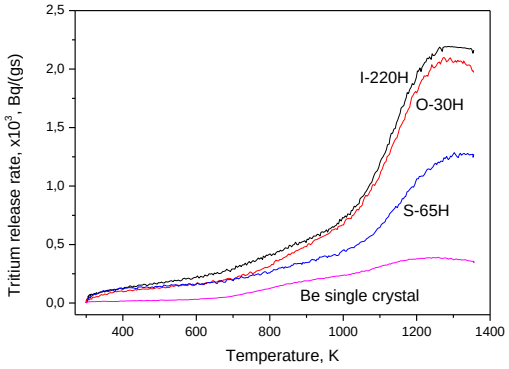

Fig. 1. Tritium release rate for beryllium grades produced by HIP and for beryllium single crystal.

Fig. 2 shows the total tritium release for HIPed beryllium grades and for beryllium single crystal. I-220-H (the grade with the smallest grain size and highest BeO content) has the greatest amount of total release. Both O-30-H and S-65-H have comparatively lower total release values, and S-65-H has the lowest total release and correspondingly, the largest grain size. This demonstrates, therefore, an inverse dependence of the total tritium release on the grain size for these HIPed beryllium grades. It seems logical that the beryllium single crystal has the lowest total release, since it has inherently no grain boundaries.

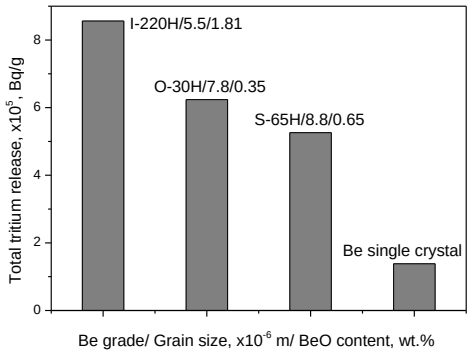

Fig. 2. Total tritium release for beryllium grades produced by HIP and for beryllium single crystal.

Fig. 3 shows tritium release rates for beryllium pebbles of irregular shape made by CM. The pebbles of grain sizes 30-60 µm and >100 µm have single peaks which are practically coincident with each other, and they are also very similar in shape to the peaks from Fig. 1 for the HIPed beryllium grades. The tritium release rate curve for the pebbles of grain size of 10-30 µm differs significantly from that for the pebbles with the larger grain size. The tritium release starts immediately from the beginning of the TPD test, i.e. from even just a small increment above room temperature after heating, and continues with increasing rate until reaching a broad peak. Despite the difference in the behavior of the release rate for pebbles with grain size of 10-30 µm, however, the peaks for all three pebble types are grouped closely at temperatures in the region of 1251-1308 K.

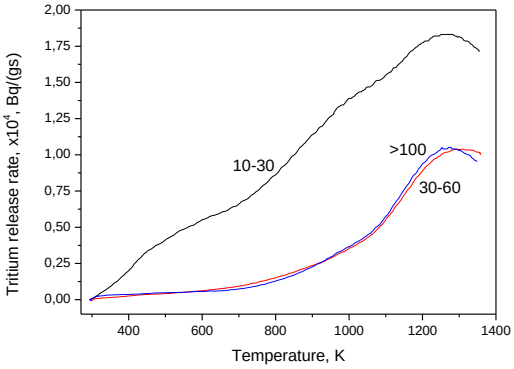

Fig. 3. Tritium release rates for pebbles prepared by CM. Grain sizes are shown in µm.

For the pebbles made by CM, the highest total tritium release detected was for the pebbles with the 10-30 µm grain size, which also happened to be the smallest (see Fig. 4). With increasing grain size, therefore, the total tritium release decreases.

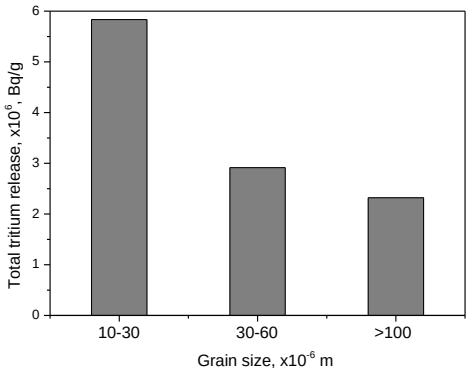

Fig. 4. Total tritium release for pebbles prepared by CM.

Fig. 5 shows the tritium release rate for beryllium pebbles of different diameters produced by REM. The most facilitated tritium release occurs from the 0.5 mm pebbles where tritium begins to leave the material starting from room temperature at a high rate. For 1 mm and 2 mm pebbles, the release occurs with close rates up to 650-700 K. Then, at higher temperatures, the release from the 1 mm pebbles is comparatively faster than from the 2 mm pebbles. The major peak for all three pebble sizes is located within the temperature range of 1302-1348 K. It should be noted that there are two additional peaks at lower temperatures for the 0.5 mm pebbles. These peaks occur at ~350 K and ~900 K. For both 1 mm and 2 mm pebbles, the peak at the lowest temperature is absent, and the peak at ~900 K is weakly expressed.

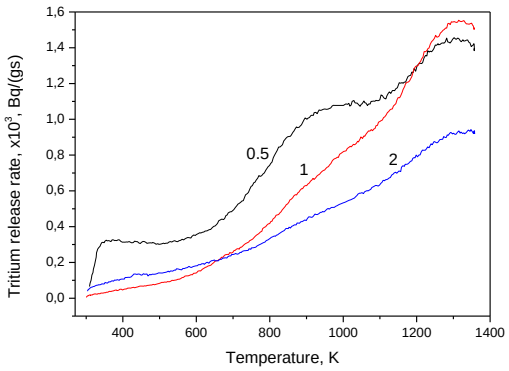

Fig. 5. Tritium release rate for beryllium pebbles with different diameters produced by REM. Diameters are shown in mm.

Total tritium release for the beryllium pebbles produced by REM is strongly dependent on the pebble diameter (see Fig. 6). Specifically, the highest total tritium release is from the 0.5 mm pebbles, and, therefore, the lowest release is from the 2 mm pebbles.

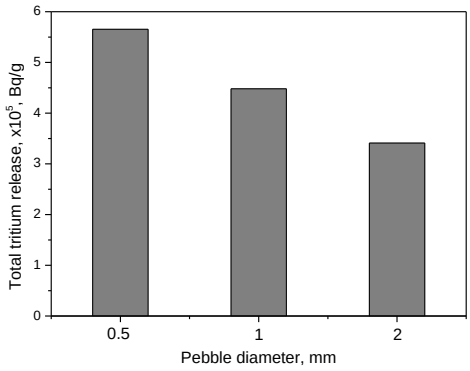

Fig. 6. Total tritium release for beryllium pebbles with different diameters produced by REM.

It would be interesting to compare 1 mm-diameter pebbles produced by different methods, since the 1 mm beryllium pebbles produced by REM are currently considered as the reference material for HCPB breeding blanket concepts for fusion reactors. The comparison of 1 mm pebbles produced by REM and FRM on tritium release behavior is represented in Fig. 7. The REM batch with greater content of porosity demonstrates a most facilitated tritium release starting immediately from room temperature. For temperatures higher than 1000 K, however, the release occurs comparatively faster from the FRM pebbles. In addition, the major peak for the FRM pebbles is at the lower temperature (1269 K) compared to that for the REM pebbles (1315-1323 K).

Fig. 8 shows total tritium release for the 1 mm beryllium pebbles produced by REM and FRM. The highest total tritium release is from the FRM pebbles, but for the REM pebbles with the higher amount of porosity, the total release amount is close to that of the FRM pebbles.

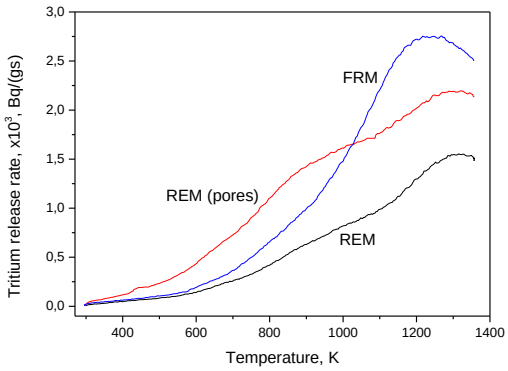

Fig. 7. Tritium release rate for 1 mm-diameter beryllium pebbles fabricated by REM and FRM. "REM (pores)" indicates the presence of a higher relative density of pores compared to the "REM" batch with a significantly lower amount of pores.

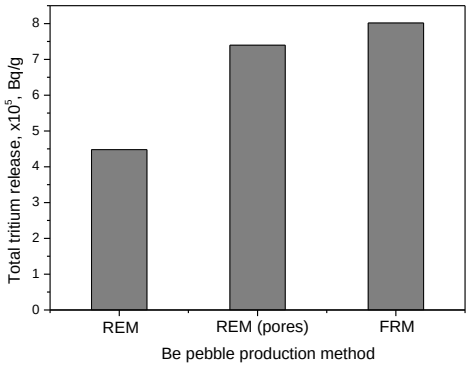

Fig. 8. Total tritium release for beryllium pebbles of 1 mm diameter produced by REM and FRM.

Comparing the highest total tritium release values for different kinds of beryllium materials and samples (see Figs. 2, 4, 6, 8), it can be concluded that the highest total release is from the I-220-H beryllium grade made as a cylinder of 4 mm diameter and 2 mm high. The total release from the FRM pebbles with 1 mm diameter has a slightly lower value.

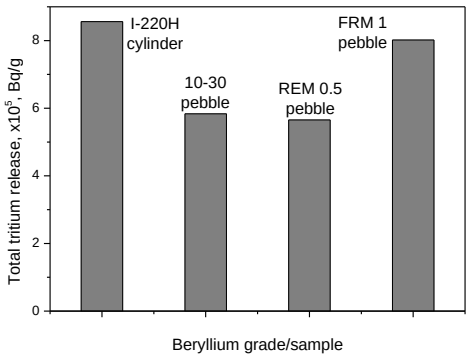

Fig. 9. Comparison of total tritium release for various beryllium samples and pebbles.

3.2 Microstructure

Fig. 10 shows the microstructure of I-220-H beryllium grade. There are visible fine grains (Fig. 10a) and numerous inclusions (most likely BeO particles) which are located primarily in the grain boundaries (Fig. 10b).

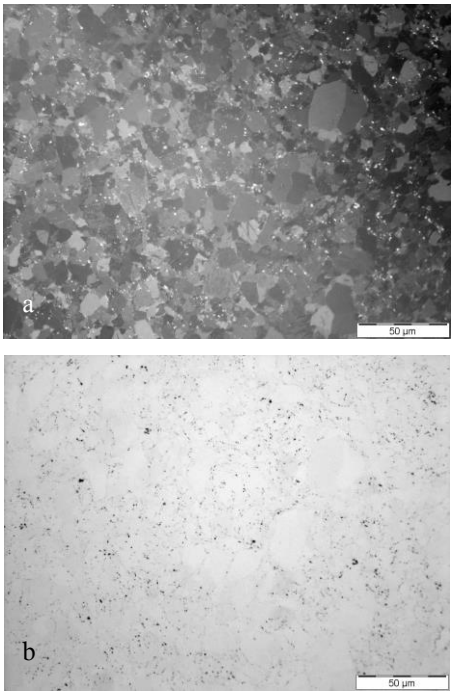

Fig. 10. Optical micrograph of a cross-section of I-220-H beryllium: a) in polarized light, b) the same area, in general light.

The O-30-H beryllium grade was consolidated by HIP from atomized powder (Fig. 11). This explains the presence of spherical grains and low BeO content in the microstructure. There is a very high degree of variation in the grain sizes. Some individual grains are up to 60 µm in diameter, and numerous fine grains around the larger grains are smaller than 10 µm.

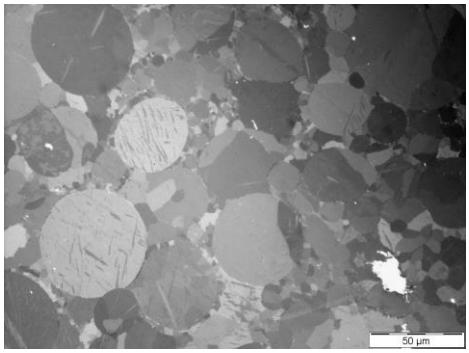

Fig. 11. Optical micrograph in polarized light of cross section of O-30-H sample.

The microstructure of S-65-H beryllium grade (Fig. 12) is similar to that of I-220-H. S-65-H, however, has comparatively larger grain size, and the amount of BeO particles is considerably less than that in I-220-H.

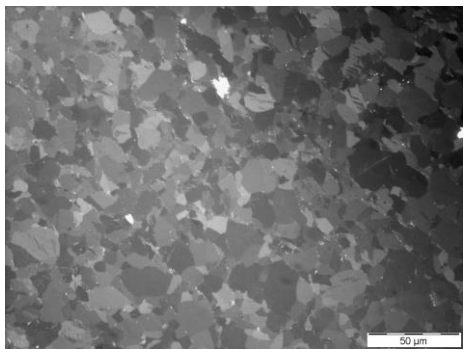

Fig. 12. Optical micrograph in polarized light of a cross-section of S-65-H beryllium.

Fig. 13 shows a general view of beryllium pebbles produced by CM. The pebbles have an irregular, "potato-like" shape. The sizes of the pebbles are mainly between 1 mm and 2 mm.

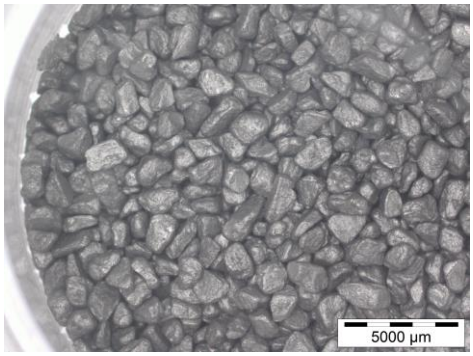

Fig. 13. General view of beryllium pebbles with grain size of 10-30 µm produced by CM.

Fig. 14 shows the microstructure of beryllium pebbles produced by CM with grain size of 10-30 µm.

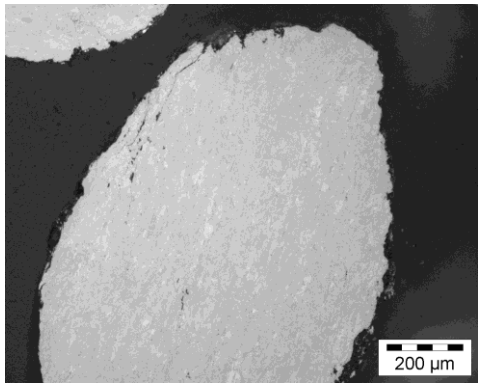

Fig. 14. Optical micrographs in polarized light of the cross-section of a beryllium pebble produced by CM with grain size of 10-30 µm.

A general view of beryllium pebbles with a diameter of 1 mm produced by REM is shown in Fig. 15. In appearance, these pebbles have been selected to have the closest to a true spherical shape with a smooth, shiny surface.

Fig. 16 shows a cross-sectional image of a 1 mm pebble produced by REM. The main feature of the pebble's microstructure is the presence of coarse grains.

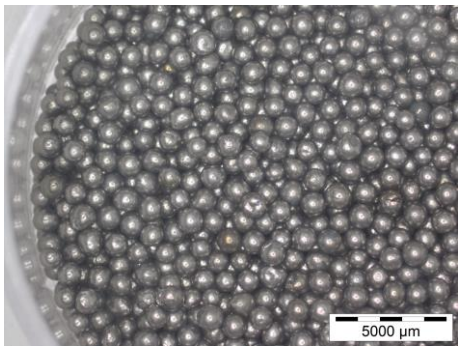

Fig. 15. General view of beryllium pebbles of 1mm diameter produced by REM.

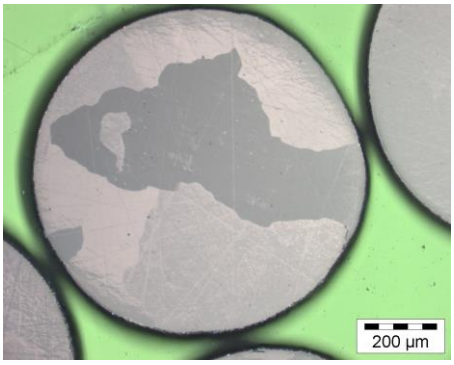

Fig. 16. Optical micrograph in polarized light of the cross-section of a beryllium pebble of 1mm diameter produced by REM.

It should be noted that there is one batch of 1mm REM beryllium pebbles which was made by using a variety of production parameters (Fig. 17) that resulted in much higher porosity in the pebbles' microstructure. As a rule, these pebbles have a large amount of shrinkage in areas close to the pebble's center and many pores more or less uniformly distributed in the coarse grains as well.

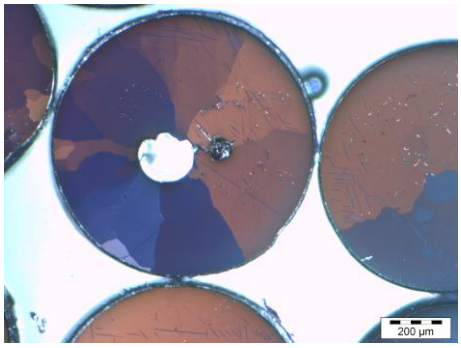

Fig. 17. Optical micrograph in polarized light of the cross-section of beryllium pebbles of 1 mm diameter produced by REM from a batch with comparatively higher porosity.

Fig. 18 presents a general view of 1 mm beryllium pebbles produced by FRM. In contrast to the REM pebbles, they do not have a true spherical shape, and the surface is matte and frequently with indentations. Cross-sections of several FRM pebbles (Figs. 19, 20) also demonstrate that the shape of the pebbles is not always perfectly spherical, as well as the presence of numerous pores. The pores are arranged in chains or large conglomerates, or uniformly distributed in the microstructure.

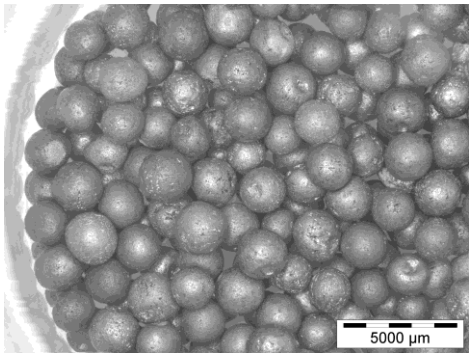

Fig. 18. General view of beryllium pebbles of 2 mm diameter produced by FRM.

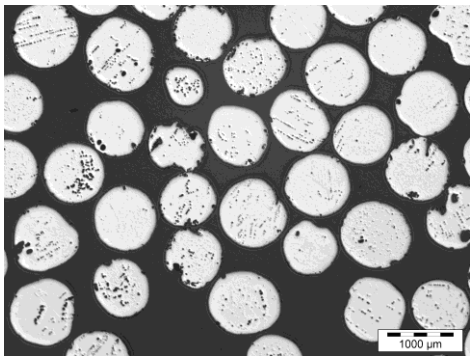

Fig. 19. General view of cross-sections of beryllium pebbles of 1mm diameter produced by FRM.

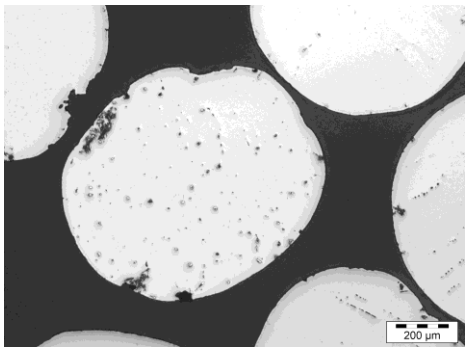

Fig. 20. Optical micrograph of cross-sections of beryllium pebbles of 1 mm diameter produced by FRM. The presence of numerous inherent pores can be seen in the microstructure.

Fig. 21 shows the microstructure of the FRM pebbles in polarized light. There are coarse grains similar to the grains in the REM pebbles (see Fig. 16). The FRM pebbles have, however, comparatively many more pores and a more developed twinning structure. The twins are mainly located near to the external surface of the pebbles and look like parallel or intersecting lines.

Loading of the FRM pebbles with tritium/hydrogen gas mixture at 873 K for 15 h leads to microstructural changes (Fig. 22). The twins almost disappear. The coarse grains are converted in the smaller grains. The loading temperature is more than half the melting point of beryllium, therefore permitting recrystallization to start and inducing the transformation of the grain boundary structure.

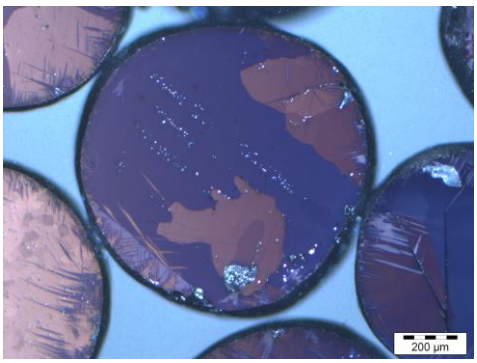

Fig. 21. Optical micrograph in polarized light of cross-sections of beryllium pebbles of 1 mm diameter produced by FRM.

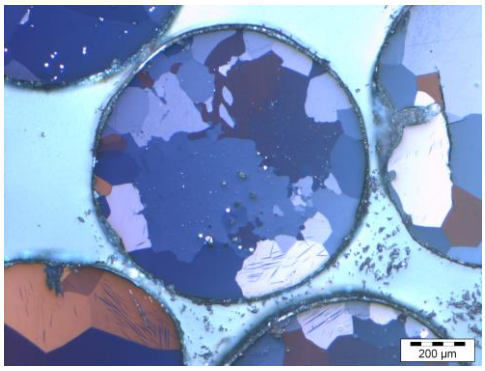

Fig. 22. Optical micrograph in polarized light of cross-sections of 1 mm diameter beryllium pebbles produced by FRM after loading with tritium/ hydrogen gas mixture at 873 K for 15 h.

4. Discussion

High-temperature loading with the tritium/hydrogen gas mixture occurs through the outer surface of a beryllium pebble (or cylinder-sample, as applicable) either directly through the bodies of first-layer grains or along the boundaries which come to the surface (Fig. 23a). Clearly, the mobility of tritium atoms (and hydrogen atoms, of course) moving along boundaries is comparatively much higher than that through the grain body. Only a short time after starting the loading, therefore, the tritium atoms can penetrate along the boundaries into the whole pebble volume reaching the presence of the tritium at the boundaries in sufficient amounts to start the motion of these atoms into the grain bodies. As a result, the possible negative impact of the BeO layer, which is always present on the beryllium sample's surface, is not considered. After dissociation of the tritium molecules outside the pebble, the tritium atoms penetrate through the BeO layer to start their movement into the beryllium pebble. Thickness of the BeO layer can be up to 0.15µm [2].

The BeO layers on the beryllium samples in this study have approximately equal thickness. The time of penetration through the oxide layer is, therefore, about the same for each sample. Another point worth noting regards the state of the tritium in the grains after saturation of the beryllium sample by tritium/hydrogen. The tritium and hydrogen should form small bubbles in the beryllium as was observed in the near-surface layers after implantation of deuterium [4-6]. So, as a result of loading at the same parameters, the beryllium samples end up with a similar microstructure with their primary defects' being gas bubbles which differ by their size and density according to the grain size in each sample.

Another possible outcome for the moving tritium is for it to be captured by the pores in the beryllium microstructure. These pores already exist in the pebbles after their production and have comparatively larger sizes (see Figs. 17, 19-21) than the bubbles which are formed after tritium/hydrogen saturation. The single major peak in the TPD testing is caused by release of trapped tritium/hydrogen from the small bubbles and pores. So, the total tritium release value is defined by the amount of tritium/hydrogen which penetrated the bubbles/pores under the loading and then, accordingly, left the bubbles/pores as well as the pebbles during the TPD testing. In other words, the total tritium release is the result of a beryllium sample's ability to both absorb and retain the loaded tritium.

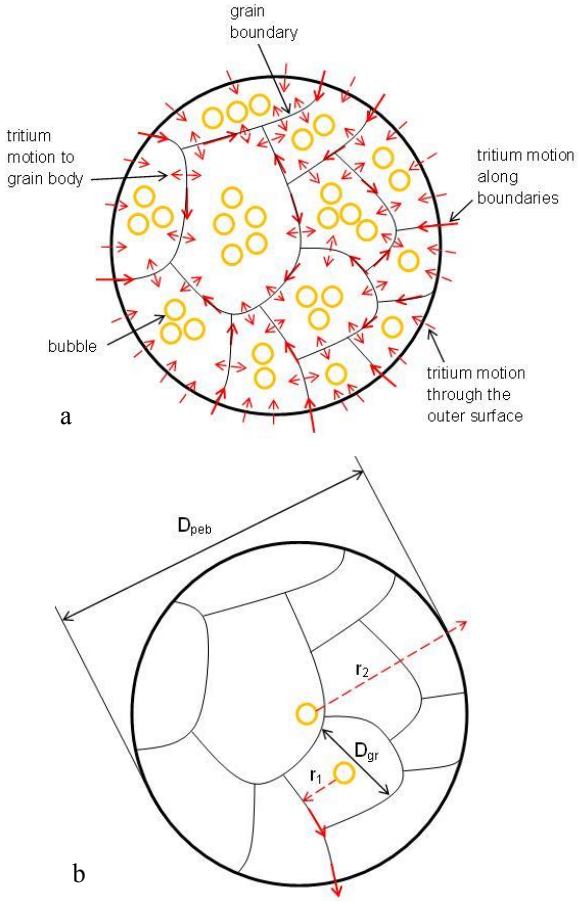

Fig. 23. Possible paths of tritium/hydrogen atoms into a beryllium pebble during thermal loading (a) and their outward motion during the TPD test (b).

Fig. 23b shows a schematic for possible paths of tritium/hydrogen inside the pebbles during the TPD test. Most likely, the tritium leaving the bubbles/pores and reaching the nearest grain boundary prefers to move further along the boundary to the outer surface of the pebble. In that case, a key structural parameter for characterization of this motion can be considered as $r_1 \sim$

$D_{gr}/2$ where D_{gr} is the average grain size. It can be supposed, however, that the tritium may also leave the pebble by moving directly to the outer surface, bypassing the available boundaries. In this case, the key parameter is $r_2 \sim D_{peb}/2$ where D_{peb} is the pebble diameter. The essential point is whether r_1 or r_2 defines the ability of a beryllium piece (pebble, sample, etc.) to retain its tritium.

Generally speaking, if the tritium atoms freed from structural traps take a two-stage path (in the beginning, a slow path to the nearest boundary, then a faster path along the boundaries to the surface of the piece), it would indicate that the r_1 parameter (or the grain size) is more important for comparison of different beryllium forms/grades. Alternatively, one may also consider a case in which the r_2 parameter (or the characteristic size, e.g. the pebble diameter) is more preferable for this purpose.

In this study, the results permit the assumption that the r_1 parameter plays a more significant role in this matter compared to r_2. This assumption, however, demands more experimental substantiations. At least, comparing the I-220-H sample (r_1 = 2.75 μm, r_2 = 1 mm), the 10-30 μm CM pebble ($r_1 \approx$ 20 μm, r_2 = 0.5-1 mm), the 0.5 mm REM pebble (r_1 = 100-250 μm, r_2 = 0.25 mm), and the 1 mm FRM pebble (r_1 = 100 μm, r_2 = 0.5 mm) (see Fig. 9), a conclusion in favor of the r_1 parameter can be made. In particular, for the highest retention samples such as the I-220-H and the 1 mm FRM pebble, the I-220-H has comparatively much smaller grain size (5.5 μm to 200 μm). At the same time, the I-220-H has the larger overall size compared to the FRM pebble (height of 2 mm vs. 1 mm diameter, respectively). Intuitively, it seems that smaller grain size is the more important factor than the overall size, although it is impossible to say that at this point in full confidence.

Potential impact of BeO content in the beryllium samples on tritium release/retention was not considered in the discussion up to this point. According to Scaffidi-Argentina, the chemical trapping of tritium/hydrogen at BeO inclusions with formation of beryllium hydroxide in beryllium is possible [7]. Data from Fig. 2 for O-30-H and S-65-H grades, however, did not confirm possible influence of BeO content on tritium retention. In particular, despite its comparatively lower BeO content, O-30-H showed a higher total tritium release than S-65-H. There is, therefore, a greater likelihood that the more significant factor in this case is the differing grain size of the beryllium grades.

5. Conclusions

After high-temperature loading of various beryllium grades with different sample shapes with a tritium/ hydrogen gas mixture, and following the subsequent TPD tests, some conclusions can be suggested as follows:

1. Among the beryllium grades produced by hot isostatic pressing (HIP) by Materion Beryllium & Composites, the I-220-H has the best tritium release and retention properties. That characteristic is most likely defined by the smaller grain size of I-220-H compared to other grades.

2. Among the pebbles of irregular shape with various grain sizes produced by the crushing method (CM) by Bochvar Institute, the pebbles with the smallest grain size (10-30 μm) demonstrate the comparatively better tritium release and retention behavior.

3. Among the beryllium pebbles with the regular round shape in diameters of 0.5 mm, 1 mm, and 2 mm made by the rotating electrode method (REM) by NGK Insulators, and by the fluoride reduction method (FRM) by Materion Beryllium & Composites, the FRM pebbles with 1 mm diameter show the better tritium release and retention properties.

4. Grain size can be considered as a key structural parameter for comparison and ranking of different beryllium materials on tritium release and retention properties. In particular, a beryllium grade with smaller grain size has a comparatively higher tritium release and lower tritium retention compared to the grades with larger grain size.

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References

[1] L.V. Boccaccini, L. Giancarli, G. Janeschitz, S. Hermsmeyer, Y. Poitevin, A. Cardella, E. Diegele, Materials and design of the European DEMO blankets, Journal of Nuclear Materials 329–333 (2004) 148–155.

[2] V. Chakin, A. Moeslang, P. Kurinskiy, R. Rolli, H.-C. Schneider, E. Alves, L.C. Alves, Tritium permeation, retention and release properties of beryllium pebbles, Fusion Engineering and Design 86 (2011) 2338–2342.

[3] V. Chakin, R. Rolli, P. Vladimirov, A. Moeslang, Tritium release from highly neutron irradiated constrained and unconstrained beryllium pebbles, Fusion Engineering and Design 95 (2015) 59–66.

[4] S.P. Vagin, P.V. Chakrov, B.D. Utkelbayev, L.A. Jacobson, R.D. Field, H. Kung, Microstructural study of hydrogen-implanted beryllium, Journal of Nuclear Materials 258-263 (1998) 719-723.

[5] V.N. Chernikov, V.Kh. Alimov, A.V. Markin, A.E. Gorodetsky, S.L. Kanashenko, A.P. Zakharov, I.V. Kupriyanov, Gas-induced swelling of beryllium implanted with deuterium ions, Journal of Nuclear Materials 233-237 (1996) 860-864.

[6] N. Yoshida, S. Mizusawa, R. Sakamoto, T. Muroga, Radiation damage and deuterium trapping in deuterium ion injected beryllium, Journal of Nuclear Materials 233-237 (1996) 874-879.
[7] F. Scaffidi-Argentina, Tritium and helium release from neutron irradiated beryllium pebbles from the EXOTIC-8 irradiation, Fusion Engineering and Design 58-59 (2001) 641-645.