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Steam-chemical reactivity for irradiated beryllium

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Abstract

This paper reports experimental results concerning the influence of neutron irradiation effects and annealing on the chemical reactivity of beryllium exposed to steam. The work entailed: (1) measurements of swelling, porosity and specific surface area for irradiated Be annealed at temperatures ranging from 700°C to 1200°C and (2) measurements of hydrogen generation rates for unirradiated Be, irradiated Be and irradiated-annealed Be exposed to steam at elevated temperatures. For irradiated Be, volumetric swelling increased from 14% at a 700°C anneal to about 56% at a 1200°C anneal. Gas-release measurements during annealing indicated the development of a surface-connected porosity network. Specific surface areas for irradiated-annealed Be increased with the anneal temperature. Steam-chemical reactivity was similar for irradiated and unirradiated Be at temperatures between 450°C and 600°C. For irradiated Be exposed to steam at 700°C, the reactivity accelerated rapidly and the specimen experienced a temperature excursion. Irradiated-annealed Be showed enhanced chemical reactivity related to its higher specific surface area.

1. Introduction

Evaluation of the safety hazards for the International Thermonuclear Experimental Reactor (ITER) includes an assessment of the failures of plasma-facing-component (PFC) materials due to various accident scenarios [1]. One scenario is a loss-of-coolant accident (LOCA) in which a water-line break injects steam into the torus vacuum vessel. This accident type is of concern for the ITER design because steam interactions with hot beryllium, the proposed first-wall PFC material, can produce hydrogen via the following reaction.

$$Be + H_2O \rightarrow BeO + H_2$$

Assessment of the consequences of such LOCAs is done by accident model-simulations [2] that use experimentally derived, chemical reactivity data for Be.

This paper presents the results of chemical reactivity experiments for unirradiated, irradiated and irradiated-annealed Be exposed to steam at elevated temperatures. The primary purpose was to evaluate the influence of neutron irradiation effects and swelling on steam-chemical reactivity for Be. The work included annealing experiments, during which tritium and helium release was measured, and specimen characterization measurements to obtain bulk densities, swelling, porosity, and specific surface areas for the annealed-irradiated Be. Initial results have been published previously [3]. The emphasis of the present paper is on characterization of annealed-irradiated Be and the influence of annealing on chemical reactivity. No other previous chemical reactivity studies have been reported for irradiated Be. However, many studies have investigated swelling and mechanical properties [4,5], swelling evolution [6–9], and gas-release behavior [10–13], phenomena that are related to the presence of entrapped tritium and ^{4}He produced in neutron-irradiated Be via nuclear transmutation reactions.

2. Experimental details

2.1. Specimen description

The Be specimens were fabricated using consolidated powder-metallurgy (CPM) techniques and Brush–Well-

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man SP-200-F powder (<44 micron particles; chemical composition in weight percent: Be(99.1%), BeO(0.9%), Fe(0.09%), C(0.08%), Al(0.04%), Si(0.03%), Mg(0.02%), and other metals(<0.04%)). To achieve fully dense material, the powder was cold isostatic pressed, sintered in a vacuum furnace at 1250°C for 4 h and hot isostatic pressed at 1000°C for 3 h with a pressure of 103 MPa. Dry-machining produced cylindrical test specimens with a 0.76-cm diameter and three different lengths, 0.635, 2.032, and 3.051 cm. No chemical etching was used to remove surface deformation layers from machining.

Irradiation of 0.635- and 2.032-cm long Be specimens took place in position 2B1 of the Experimental Breeder Reactor, EBR-II, a fission reactor with a fast neutron environment [14]. Nominal fast neutron fluences (>0.11 MeV neutrons) were estimated to range from 5.2×10^{22} to 6.7×10^{22} n/cm^2, values that are approximately a factor of 10 higher than those expected for Be components in ITER. The nominal irradiation temperature was 400°C.

2.2. Steam-chemical reactivity system

Chemical reactivity experiments were conducted with a system developed to measure hydrogen generation rates and tritium mobilization rates for irradiated Be exposed to steam [15]. The system comprised a flow-through, integrated assembly with components set up in an inert-gas glovebox and in a laboratory hood. Argon carrier gas was used to sweep reaction gases from the hot sample reaction chamber through a process line equipped with condensers, a cryotrap, instrumentation for gas analyses and an oxidizer and ethylene-glycol traps at the end of the process line. Steam, introduced upstream from the sample furnace, reacted with the hot specimen inside the quartz reaction chamber and was condensed downstream from the sample furnace.

Hydrogen generation rates and total quantities of H_2 generated were obtained from on-line mass-spectrometer measurements of the gas composition in the system process line. Mass peak signatures were mass-2 for H_2, mass-4 for ^{4}He and mass-40 for Ar. The contribution of HT to the QMS mass-4 peak was negligible relative to that of ^{4}He. Tritium measurements were made with an in-line ion chamber and by post-test analyses (liquid scintillation counting) for tritium in the condensed water and ethylene-glycol traps.

A precision balance (0.1 mg sensitivity) was used to measure the specimen mass before and after testing. These weight-gain (WG) measurements of the oxygen uptake by Be provided a second means to obtain the total hydrogen generated during a chemical reactivity test.

2.3. System for annealing experiments

Annealing experiments were conducted with a second flow-through, integrated assembly set up in a laboratory hood. This system consisted of an inlet gas manifold, a molybdenum-lined tube furnace, in-line instruments downstream from the furnace for analysis of the gas-stream composition and an in-line oxidizer and ethylene-glycol traps at the process line terminus. A 100-cm^3/min Ar carrier gas with approximately 1% H_2 was used in the annealing tests. Measurements of the gas composition in the process line were made with an on-line quadrupole mass spectrometer (QMS). Tritium measurements were made with an in-line ion chamber and by post-test analyses (liquid scintillation counting) of the tritium content in ethylene-glycol traps.

2.4. Techniques for physical property characterization

Measurements were made to characterize the density, porosity and specific surface area for the test specimens, both before and after annealing tests. Densities were obtained by two techniques: (1) measurements of the masses and of the diameters and lengths of the specimens and (2) water immersion density measurements. Porosity was determined from the water immersion measurements. Specific surface areas for the test specimens were measured using a Kr gas adsorption technique, with analysis of the adsorbed gas data by the method of Brunauer et al. [16], commonly referred to as the BET method.

3. Measurements and results

3.1. Annealing experiments

Two sets of annealing experiments were done for irradiated Be. Small cylinders were annealed at temperatures of 450°C, 600°C, 700°C, 800°C, 1000°C and 1200°C, with the thermal history patterned after that used in chemical reactivity tests for the irradiated Be. Approximate annealing temperatures and times were as follows: 450°C (300 min), 600°C (1440 min), 700°C (260 min), 800°C (185 min), 1000°C (100 min), and 1200°C (80 min). These times include ramp-up times of ~60 min for the two high temperature anneals and ~30–40 min for the other anneals. In addition, both long and short cylinders were annealed at a temperature of 1100°C for about 35 min, following a linear thermal ramp of 20°C/min. Tritium release rates were measured with the in-line ion chamber and ^{4}He release rates were measured with the QMS. Standard gas mixtures flowing in the process line were used to calibrate the QMS. The ion chamber was calibrated by assay of tritium in the ethylene-glycol traps using liquid-scintillation-counting.

Our gas analysis measurements indicated that tritium and helium gas-release behavior was a complex function of both temperature and time at temperature. Detailed

results of these measurements were reported earlier for the small Be specimens [3] so only the salient features of these measurements are summarized here. No measurable tritium and helium were observed from the specimens annealed at and below 600°C. Although tritium was released from the specimen at 700°C, no helium release was observed, probably because of insufficient detection sensitivity in the QMS analysis setup. Tritium release from the specimen annealed at 700°C exhibited a small steady release from the specimen, once it reached 700°C, followed by a rise to a substantially higher level, after an incubation time of about 60 min at 700°C. In contrast, the tritium release behavior for specimens annealed at temperatures of 800°C and above was characterized by relatively sharp release peaks (gas burst release). The largest peak corresponded to the time that the specimen first reached 800°C, and smaller release peaks occurred about 20 and 40 min after the initial release transient, again indicating incubation times associated with the gas-burst release behavior. For the small specimens annealed at 1000°C and 1200°C, prominent tritium release peaks were observed when the specimens reached 1000°C, with much smaller release peaks occurring during heatup. Comparable quantities of tritium were released from specimens annealed at 700°C and 800°C, and these quantities were about a factor of 10 below that released from the specimens annealed at 1000°C and 1200°C. The high temperature anneals released the entire inventory of tritium and helium. The tritium release behavior for the long and short specimens annealed at 1100°C was similar to that for the short specimen annealed at 1200°C. For anneal experiments of 800°C and above, the release of helium (^{4}He) was observed to be concurrent with the burst tritium release.

3.2. Material characterization

Measurements of the mass, density, length and diameter were made both before and after the anneal tests. The density of unirradiated Be was 1.854 g/cm^3 and the density of irradiated Be was 1.825 g/cm^3, prior to anneal tests, indicating a density loss of 1.6% during the EBR-II irradiation.

Fig. 1 presents the volumetric swelling for each specimen as a function of anneal temperature. Volumetric swelling was computed as $[(\rho_0 - \rho)/\rho] \times 100\%$, where ρ_0 is the density for unirradiated Be and ρ is the density of Be after irradiation and heat treatment. Differences in the values from the two measurement approaches are most likely due to inaccuracies in the dimensional measurements for highly swelled specimens with non-uniform dimensional changes.

Measurements of surface-connected (open) porosity were attempted for the irradiated-annealed Be by the liquid immersion approach. The results indicated no

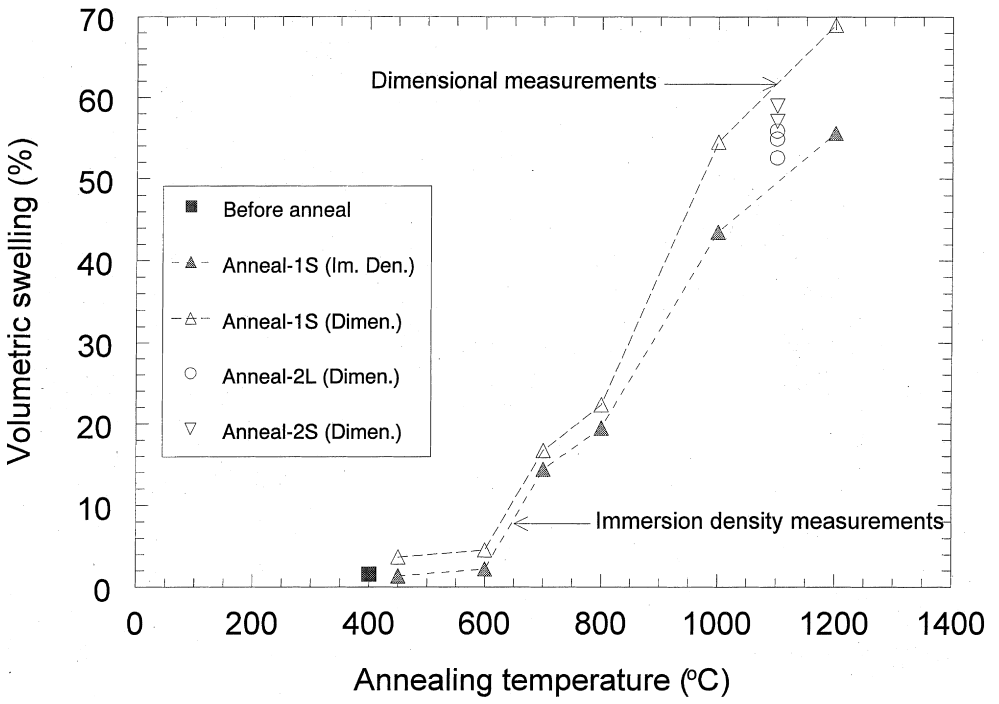

Fig. 1. Volumetric swelling of irradiated Be specimens as a function of anneal temperature.

appreciable porosity, even though the density changes were large.

Specific surface area measurements were made for the irradiated-annealed specimens and for unirradiated CPM-Be specimens of varying density. Fig. 2 shows that measured BET specific surface areas for the irradiated-annealed Be specimens were much less than those measured for the control Be specimens of varying density. The points plotted for the irradiated-annealed Be correspond to measurements on the short specimens annealed at the indicated temperatures.

3.3. Steam-chemical reactivity experiments

Steam-chemical reactivity experiments were performed at various temperatures: at 10 temperatures between 450°C and 1200°C for unirradiated Be; at 450°C, 500°C, 600°C, and 700°C for irradiated Be specimens; and at 400°C, 500°C and 600°C for irradiated-annealed specimens. Typical system parameters were: line pressure (~680 Torr or 0.9 MPa), Ar carrier-gas flow rate (100 cm^3/min), steam flow rate (2500 cm^3/min for a water throughput of 2 cm^3/min), steam-generator temperature (350°C). For these conditions, the system response time was about 6 min and the H_2 detection sensitivity was about 3 ppm of H_2 in Ar. The on-line QMS was calibrated using Ar–H_2 standard gas mixtures in which the H_2 contents varied from 50 ppm to 50 000 ppm.

A summary of the measured H_2 generation rates is presented in Fig. 3, along with the results of previous measurements by Smolik et al. for fully dense CPM-Be [17] and for porous Be [18]. The results are presented as average values in that they correspond to the total quantities of H_2 generated during an experiment divided by the steam exposure time and the geometric surface area of the specimen prior to the chemical reactivity experiment. Geometric surface areas were derived from specimen dimensional measurements. Mass-spectrometer gas measurement results are identified with a G and values derived from weight-gain measurements are designated with a WG. Results for unirradiated Be cylinders are identified by INEL96-G2, -WG2 and for unirradiated Be discs by INEL92-G, -WG. Straight lines are drawn through the data for unirradiated Be to indicate the general trends in chemical reactivity for three different temperature ranges. Results for irradiated Be cylinders are designated by INEL96IR-G1, -WG1 and for irradiated-annealed Be cylinders by INEEL97IRA-G1, -WG1, -G2, and -WG2. The INEEL97IRA-G1 and -WG1 data represent reactivity trends at 500°C as a function of different anneal temperature, and the INEEL97IRA-G2 and -WG2 data represent reactivity trends as a function of steam-reactivity temperature for specimens annealed at 1100°C. Previous measurements

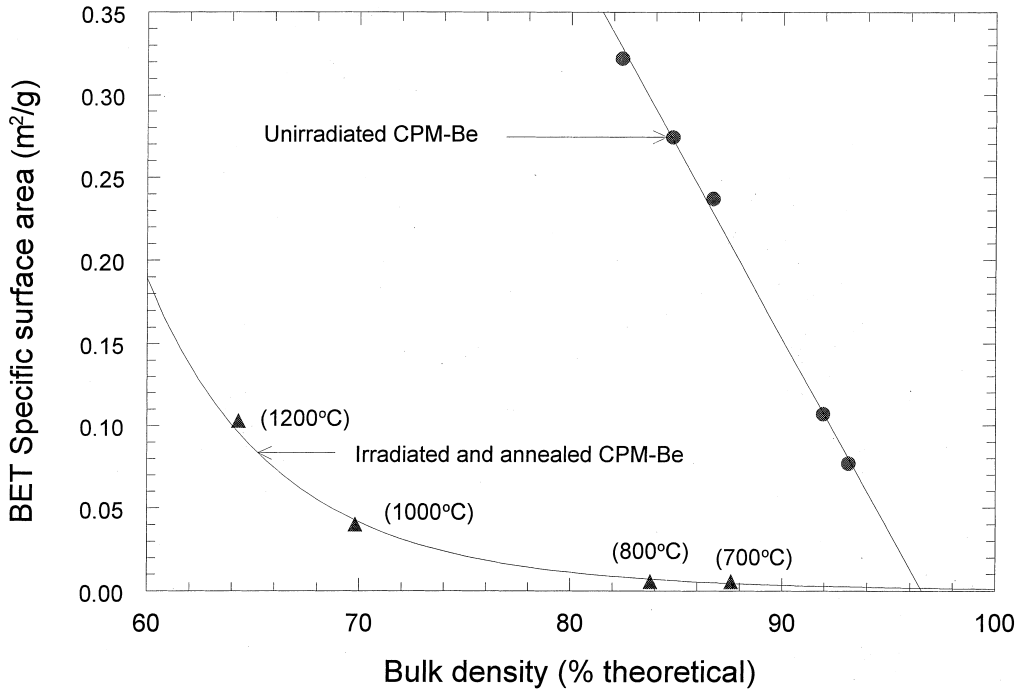

Fig. 2. Bulk density and specific surface area correlation for unirradiated and annealed-irradiated CPM-Be.

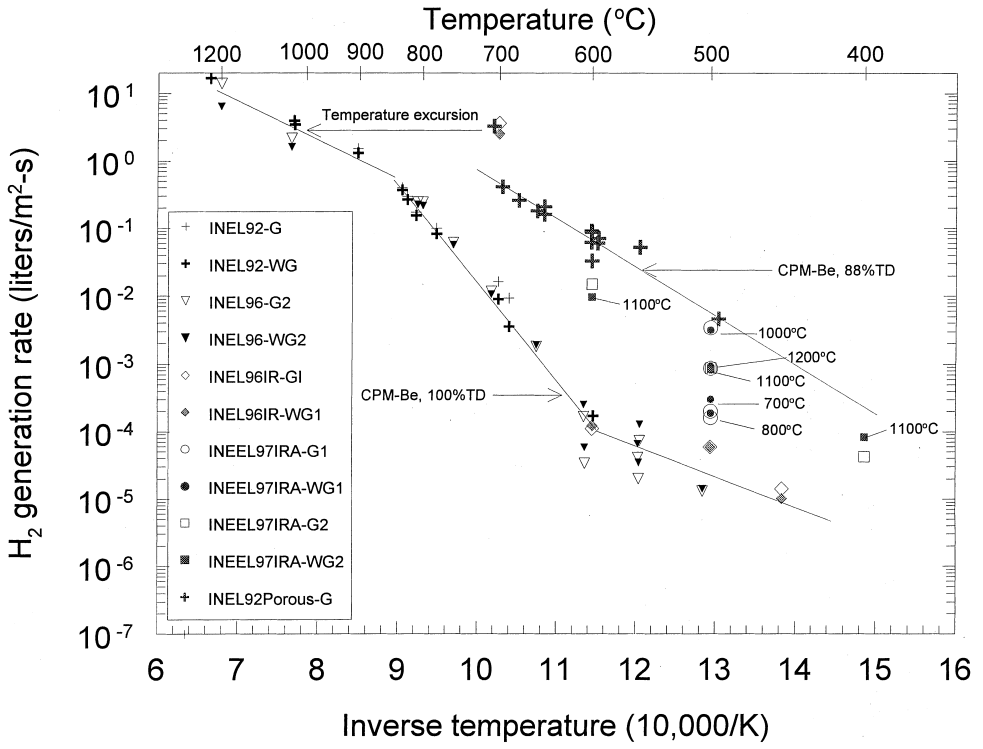

Fig. 3. Average H_2 generation rates relative to geometric surface area for unirradiated (INEL92-G, -WG; INEL96-G2, -WG2), irradiated (INEL96IR-G1, -WG1), irradiated-annealed (INEEL97IRA-G1, -WG1, -G2, -WG2) and porous (INEL92Porous-G) CPM-Be. G and WG identify mass-spectrometer-gas and weight-gain data, respectively.

by Smolik et al. [18] for porous Be having a bulk density of 88% are identified as INEL92Porous-G, -WG, with a line to indicate the trend.

These results show a variation in the observed H_2 generation rates, dependent on the type and condition of the test specimens, the anneal temperature, and the temperature of the steam-exposure experiment. For test temperatures from 450°C to 600°C, the H_2 generation rates for irradiated Be are similar to those for unirradiated Be, although there is an indication of a higher rate for irradiated Be tested at 500°C. A significant difference was observed in reactivity of the irradiated Be tested at 700°C. H_2 generation accelerated very rapidly for this specimen, and the specimen experienced a temperature excursion to above 1000°C. As discussed previously, Anderl et al. [3], swelling and development of a surface connected-porosity for this specimen resulted in an acceleration of the reactivity, leading to a temperature excursion for the sample and the high H_2 generation.

H_2 generation rates for irradiated-annealed Be were much higher than those for unirradiated or irradiated Be. With the exception of the data point corresponding to a specimen annealed at 1000°C, the results (INEEL97IRA-G1, -WG1) indicate a systematic increase in reactivity for irradiated Be annealed at progressively higher temperatures. The deviation of the 1000°C anneal result from this trend may be due to the generation of a surface-connected porosity with a higher specific surface area. Results for irradiated Be annealed at 1100°C and tested at 400–600°C show a systematic increase in reactivity with test temperature. In general, H_2 generation rates for the irradiated-annealed Be are much lower than rates observed for unirradiated, porous CPM-Be.

The observed differences in chemical reactivity of the unirradiated and irradiated Be, compared to the reactivity for irradiated-annealed Be and porous Be, can be accounted for, to a great extent, by the higher specific surface areas for the annealed and porous materials. This is demonstrated by Fig. 4 that presents the H_2 generation rate data with values for the irradiated-annealed and porous Be normalized to the measured BET surface areas derived using the results from Fig. 2. We note that the surface-area correction brings the H_2 generation data in much better agreement, indicating the significance of surface-area determinations. However, the corrected data for the porous Be data at test temperatures near 700°C are somewhat lower than those for the control material indicating that the surface area correction may become less significant as the test temperature increases above 600°C.

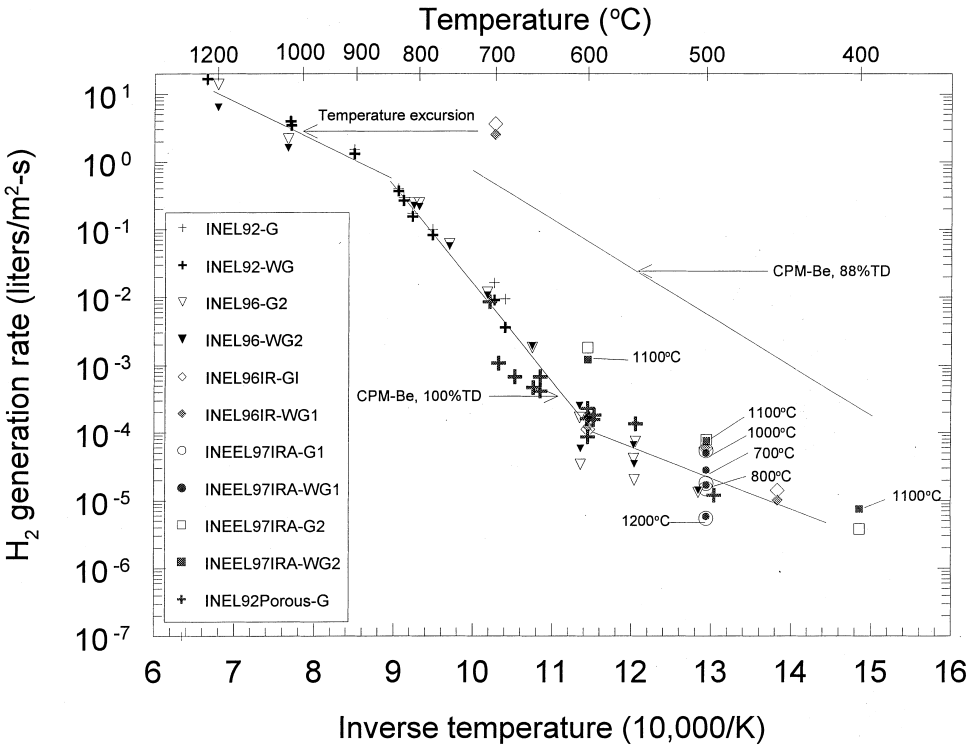

Fig. 4. Average H_2 generation rates relative to BET surface area. See Fig. 3 for legend description.

4. Conclusions

Neutron irradiation of Be influences its chemical reactivity with steam, and the magnitude of the effect is dependent on steam exposure temperature. For test temperatures between 450°C and 600°C, the general trend in H_2 generation rates for irradiated Be was similar to that for unirradiated Be, although the rates for irradiated materials tested at 500°C and below could be a little higher. More dramatic increases in the chemical reactivity for irradiated Be were observed at a test temperature of 700°C. At this temperature, the H_2 generation rate accelerated very rapidly and the specimen experienced a temperature excursion to 1000°C or higher. This behavior is attributed to the development of swelling and a surface connected-porosity for the specimen that resulted in enhanced reactivity and heat deposition in the material causing the temperature excursion and the accelerating H_2 generation.

Annealing of irradiated Be at temperatures of 700°C and higher produced enhancements in the chemical reactivity for annealed Be relative to unirradiated and irradiated Be. The reactivity enhancement could be accounted for by differences in the specific surface areas for the tested materials. Annealing of the irradiated material at temperatures of 700°C and higher produced a surface-connected porosity that resulted in the increased specific surface area.

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