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Steam chemical reactivity of Be pebbles and Be powder ☆

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Abstract

This paper reports the results of chemical reactivity experiments for Be pebbles (2 and 0.2 mm diameter) and Be powder (14–31 μm diameter) exposed to steam at elevated temperatures, 350–900°C for pebbles and 400–500°C for powders. We measured BET specific surface areas of 0.12 m^2/g for 2 mm pebbles, 0.24 m^2/g for 0.2 mm pebbles and 0.66–1.21 m^2/g for Be powder samples. These experiments showed a complex reactivity behavior for the material, dependent primarily on the test temperature. Average H_2 generation rates for powder samples, based on measured BET surface areas, were in good agreement with previous measurements for fully dense consolidated powder metallurgy (CPM)-Be. Rates for the Be pebbles, based on measured BET surface areas, were systematically lower than the CPM-Be rates, possibly because of different surface and bulk features for the pebbles, especially surface layer impurities, that contribute to the measured BET surface area and influence the oxidation process at the material surface. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Evaluation of the safety hazards for advanced fusion devices and breeder-blanket concepts includes an assessment of the failures of plasma-facing-component (PFC) and tritium breeder-blanket materials due to various accident scenarios. If beryllium is used as the first-wall PFC material or as the neutron multiplier material for the breeder-blanket, then accident scenarios that result in water or steam exposure of the Be are of particular concern because steam interacts exothermically with hot beryllium to produce hydrogen and BeO. Experimentally derived, chemical reactivity data for various forms of Be are used in accident simulations to assess the consequences of such accident scenarios. In previous studies, we have reported the results of steam chemical reactivity for several forms of Be, including fully dense, consolidated powder metallurgy (CPM) Be discs and cylinders [1,2], plasma-sprayed Be plates of variable density [3], and irradiated CPM-Be cylinders [4,5].

In this paper, we present the key results of materials characterization analyses and chemical reactivity experiments for Be pebbles and Be powder that are exposed to steam at elevated temperatures. Be pebbles have been proposed as the neutron multiplier material for the European helium cooled pebble bed (HCPB) Demo Blanket [6] and the reference breeding blanket for the International Thermonuclear Experimental Reactor (ITER) [7]. Reactivity of Be powder is of interest to evaluate the consequences of steam interaction with Be powder debris generated in plasma devices by mechanisms such as plasma-disruption-induced vaporization or sputtering of Be surfaces [8]. A detailed description of this work has been reported [9,10].

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2. Experimental details

2.1. Specimen description

We tested Brush–Wellman Be pebbles with nominal 2 and 0.2 mm diameters. The larger size pebbles were obtained from an intermediate Be ore processing step in which beryllium fluoride is reduced by magnesium metal to molten beryllium and magnesium fluoride. These pebbles were recovered from a crushed solidified cake resulting from this process and subsequently sieved to provide 'spherical' particles with nominal 2 mm diameters. The smaller Be pebbles were made by inert gas atomization and centrifugal atomization, yielding a product that is nearly spherical and with purity levels comparable to that for other commercial Be products. These particles were also sieved to provide the nominal 0.2 mm diameter material.

Microstructural and microchemical analyses have been reported previously for the pebble material [6]. The larger pebbles usually show indentations on the surface, a variability of coarse pores, with some pebbles having large voids, and a very small microporosity that is usually oriented along the crystal axis showing a very fine dendritic or cellular structure. In general, the porosity of the small pebbles is always smaller than that of the large pebbles. Metallographic structure of both small and large pebbles shows the presence of large grains, in some cases as large as the pebble diameter. Chemical analysis of the pebbles reveals much higher impurity concentration levels in the large pebbles compared to that in the small pebbles [6]. For the 2 mm pebbles, the external surface is usually covered by a 2 μm thick SiO_2 layer and/or a fluorine layer (probably BeF_2) having a thickness less than 2 μm.

Five different grades of Be powder were characterized and tested. These samples, with nominal diameters ranging from 14 to 31 μm were produced by the technique of disc abrasion. Be content ranged from 97.7% to 99.1% with oxygen being the dominant chemical impurity. Additional information for these materials has been reported by Davydov et al. [8].

2.2. Measurement systems

Specific surface areas for the test specimens were measured using a Kr gas adsorption technique. The adsorbed gas data were analyzed by the method of Brunauer et al. [11], commonly referred to as the BET method.

Chemical reactivity experiments were conducted with a system developed to measure hydrogen generation rates for unirradiated and irradiated Be exposed to steam [1]. 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 ethylene glycol trap 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. Kinetic 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 ^4He and mass-40 for Ar.

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.

3. Measurements and results

Results of the BET analyses for the test samples are summarized in Table 1. These results were obtained from multiple analyses for samples of each material. The uncertainties in the specific surface area values are estimated to be between 5% and 10%, based on complementary gas adsorption measurements with a surface area standard.

Steam chemical reactivity experiments were performed at various temperatures for the pebbles and powders: at 10 temperatures between 350°C and 900°C for 2 mm Be pebbles; at nine temperatures between 350°C and 800°C for 0.2 mm Be pebbles; and at 400°C and 500°C for the Be powder samples. Sample material was placed in 4 cm long by 3 cm wide by 0.5 cm deep ceramic crucibles that were located at the center of the reaction chamber hot zone for a test. Pebble and powder material was distributed uniformly over the bottom of the crucible. Steam exposure times were 300–340 min for most experiments. Typical system parameters were line pressure (∼680 Torr or 0.9 MPa), Ar carrier-gas flow

Table 1
BET specific surface area analyses

Sample type	Nominal diameter	Specific surface area (m^2/g)
2 mm pebble	2 mm	0.12
0.2 mm pebble	0.2 mm	0.24
CBP-56-1 powder	31.3 μm	0.69
CBP-56-2 powder	30.1 μm	0.66
CBP-56-3 powder	29.1 μm	0.67
CBP-30-1 powder	14.1 μm	1.21
CBP-30-2 powder	19.1 μm	1.05
DBP-30 powder	20.5 μm	1.04

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 to 50,000 ppm.

In Figs. 1 and 2, we show the chemical reactivity kinetic behavior of 0.2 mm Be pebbles exposed to steam at 400°C and 550°C, respectively. Fig. 1 shows parabolic H_2 generation kinetics, typical for all materials tested at 400°C and below. Fig. 2 shows paralinear H_2 generation kinetics, a sequential combination of parabolic and linear components, typical for 0.2 mm pebble samples tested between 450°C and 600°C, 2 mm pebble samples tested between 450°C and 700°C, and powder samples tested at 500°C. Reactivity kinetics comprised a sequential combination of paralinear and accelerating components for 0.2 mm pebbles at 700°C and for 2 mm pebbles at 800°C. Autocatalytic behavior for which the reaction chemical heat contributes to and enhances the reaction rate was observed for 2 mm pebbles tested at 900°C and 0.2 mm pebbles tested at 800°C. Mechanisms for these reactivity kinetics have been discussed by Petti et al. [12].

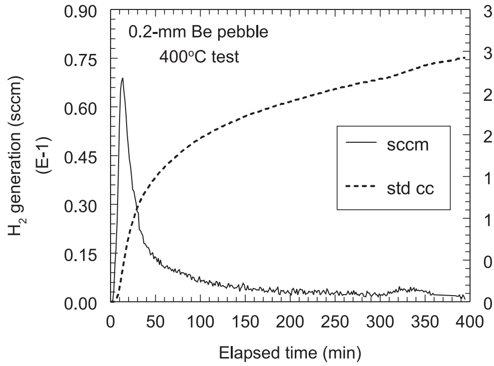

Fig. 1. H_2 generation kinetics for 0.2 mm Be pebble exposed to steam at 400°C.

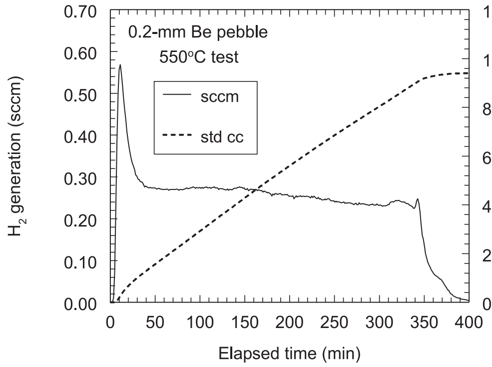

Fig. 2. H_2 generation kinetics for 0.2 mm Be pebble exposed to steam at 550°C.

A summary of average H_2 generation rates for the pebble and powder samples is presented in Fig. 3 along with the results of previous measurements for fully dense CPM-Be discs and cylinders [1,2,13]. Pebble data are designated by 2.0 mm Be-WG, -G and by 0.2 mm Be-WG, -G. Powder data are designated by R-Be PWDR-WG, -G. Previous results for fully dense CPM-Be are designated by INEL92-WG, -G, [13], INEL96-WG1, -G1, -WG2, and -G2, [1,2]. In the legend labels, mass spectrometer gas measurement results are identified with a G and values derived from weight-gain measurements are identified with WG. 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 surface areas of the samples prior to the experiment. For the fully dense CPM samples, we used the geometric surface areas as derived from specimen dimensional measurements. BET surface areas were used in the computation of the H_2 generation rates for the pebble and powder samples. Straight lines are drawn through the data for the different sample types to indicate the general trends in chemical reactivity for different temperature ranges. Values plotted for the powder data, R-Be PWDR-WG, -G, correspond to six-set averages of the rates obtained from experiments for each of the six powder types identified in Table 1.

In Fig. 4, we plot average hydrogen generation rates as a function of nominal powder diameter for each of the six powder sample types that were tested in separate experiments. Note that the rate values have units of cc/min g, in contrast to l/m^2 s, as shown in Fig. 3. This plot shows a systematic increase in the powder reactivity as the particle diameter decreases indicating the increase in

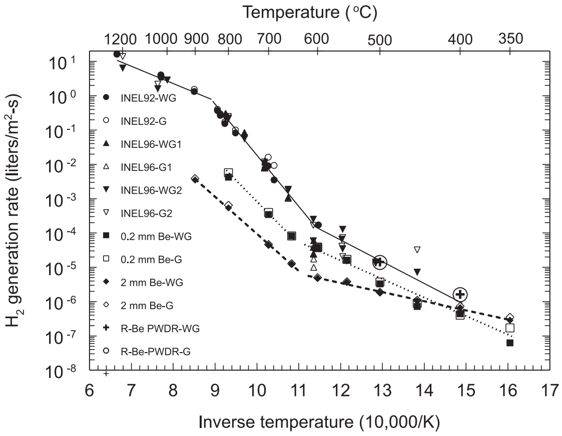

Fig. 3. Comparison of average H_2 generation rates for Be pebble and powder material with those for fully dense CPM-Be.

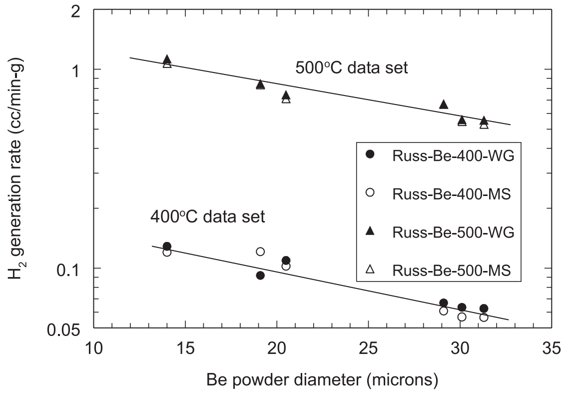

Fig. 4. H_2 generation rates for Be powder as a function of nominal powder diameter.

total surface area for a sample, as the particle size becomes smaller.

Fig. 5 presents parabolic rate constants for H_2 generation, as derived from the pebble-, powder- and CPM-Be kinetic H_2 generation data for temperatures of 600°C and below, the temperature region for which parabolic or paralinear behavior was observed. Parabolic rate constants, k_p, are defined by Eq. (1):

$$(V_c/A)^2 = k_p^* t, \tag{1}$$

where V_c is the cumulative quantity of hydrogen generated at an elapsed time t for a specimen with surface area A. In the computation of the rate constants, geometric surface areas were used for the CPM-Be data and BET surface areas were used for the pebble and powder data. The constants were computed using a cumulative hydrogen value corresponding to an elapsed time of 35 min, an appropriate value in the region of parabolic kinetics before linear kinetics are operative. Straight lines are drawn through the data to guide the eye and indicate the trends for each data set.

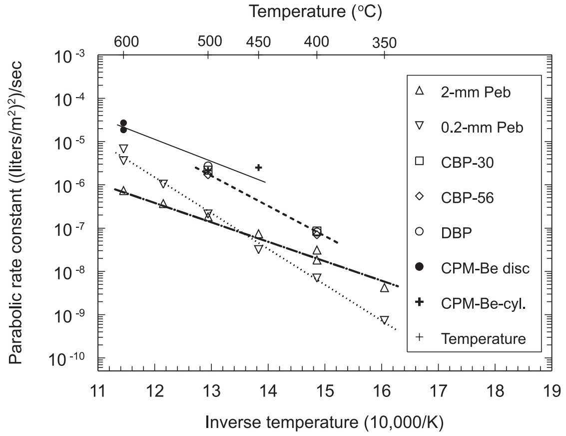

Fig. 5. Comparison of H_2 generation, parabolic rate constants for Be pebble, Be powder and fully dense CPM-Be.

4. Discussion and conclusions

In this paper, we have presented the results of steam reactivity measurements for Be pebble and powder material, and we have compared those results to data for fully dense, CPM-Be cylinder and disc samples. The results indicate, as shown in Figs. 3 and 5 that H_2 generation rates for the powder material based on BET surface area are quite consistent with the CPM-Be data. In contrast, the rates for 2 and 0.2 mm diameter Be pebbles based on BET surface area are systematically lower than corresponding CPM-Be H_2 generation rates.

We believe that the differences for the pebble data can be attributed primarily to differences in the surface and microstructural features for the pebble material, as compared to the CPM-Be machined samples. As we noted in Section 2, both the 2 and 0.2 mm pebble material have microstructural and surface topographical features that are substantially different for the pebbles. In addition, the bulk and surface impurity composition for the pebble material was substantially different from the CPM-Be material, especially for the 2 mm pebble material that had an ~2 μm thick impurity surface layer of SiO_2 and/or BeF_2. The impact of such surface features and impurities could contribute to the BET surface area, as measured by gas adsorption techniques, but also affect the oxidation process at the material surface, resulting in some ambiguity between the BET surface area and the reactive surface area. If the reactive surface area is less than the BET surface area, then the derived H_2 generation rates for the pebble material based on BET surface area could be smaller than they should be.

In conclusion, this work has contributed new experimental results of the reactivity of Be pebbles and powder exposed to steam at elevated temperatures. However, the work suggests the need for additional experiments, materials characterization and modeling analyses to better understand the reactivity behavior for different forms of Be exposed to steam over a wide temperature range. In particular, experiments are required to elucidate the influence of bulk and surface impurities and other surface and microstructural features on both the BET surface area determinations and on oxidation behavior for materials exposed to steam.

Acknowledgements

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