Elemental characterisation of beryllium and electrical behaviour of their pebbles beds

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Abstract

The temperature dependence of the electrical resistivity of a 1 mm single-size pebble bed is presented as a function of different applied pressures. The pebble bed was maintained in a He + 0.1 vol.% H_2 flowing atmosphere. In agreement with previous studies, the resistivity displays two distinct regimes under the applied load. The first one is characterised by a strong reduction in the resistivity and is likely correlated with the mechanical rearrangement of the pebbles during the first compression phase. The load range of this regime is strongly reduced when the temperature is increased. The second regime is characterised (in a semilogarithmic plot) by a linear decrease of the resistivity with the applied load. The ultimate reached resistivity was 3.0×10^{-4} Ωm under a pressure of 53 MPa at all temperatures from 20 to 800 °C. The slope of the resistivity curve decreases with temperature, which can be likely correlated with an increase in the plasticity of the pebbles.
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1. Introduction

The electrical behaviour of a beryllium pebble bed is of relevant interest considering its possible use as a neutron multiplier in a ceramic breeder blanket for a fusion power reactor. Solid breeding blankets with lithium ceramics as breeder and stainless steel as structural material need beryllium as a neutron multiplier to increase the tritium breeding ratio performance. As beryllium becomes brittle and swells under neutron irradiation, its use in the form of small pebbles offers various advantages [1]. In fact, the temperature differences are small within small pebbles, thus the stresses caused by thermal gradients and by different swelling rates (swelling is temperature dependent) are considerably reduced.

In the event of plasma disruptions the eddy currents induced in the blanket structure have to pass through the breeding blanket and their distribution will depend on the electrical resistivity of the entire module. Since beryllium pebbles occupy a large fraction of the module volume, and pure beryllium has a high electrical conductivity, high electromagnetic loads would have to be expected if beryllium pebble beds would behave like solid material. However, the oxide scale present on the beryllium pebbles surface and the limited contact between the pebbles due to the bed porosity lead to a resistivity which is about two orders of magnitude higher than that of steel [2].

The electrical resistivity of single-size and binary beryllium pebbles beds (2 and 0.1–0.2 mm) were already measured at ambient atmosphere as a function of temperature and externally applied mechanical load. In this study the possible influence of the reducing atmosphere, which could have an impact on the oxygen distribution

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on the Be surface, on the resistivity will be addressed. The beryllium 1 mm pebbles are accommodated in a typical purge gas environment, using $He + 0.1$ vol.% H_2 as foreseen in the blanket design.

2. Experimental details

The material used in this study consists of mono-sized spherical beryllium pebbles with 1 mm diameter supplied by NGK Insulators Company. The pebbles were produced by the rotating electrode process. Optical microscopy reveals a smooth surface with large grains (average grain size 100–300 μm). Some of the pebbles exhibit a hole in their centre [3].

Broad and microbeam techniques were used in the analysis of the Be pebbles. In order to investigate in detail the surface composition avoiding sample preparation and the influence of the curvature of the pebbles on the analysis, we studied several pebbles using a nuclear ion microprobe. A 1.6 MeV He^+ beam with about 6 μm diameter was used for Rutherford backscattering spectrometry (RBS) analysis in order to extract information on light elements (C and O). A 2.0 MeV proton beam with about 3 μm in diameter was used to scan the pebbles surface and to obtain particle induced X-ray emission (PIXE) maps and spectra for elements with atomic numbers higher or equal to that of Mg. The backscattered particles and X-rays were collected with a surface barrier particle detector and a Si(Li) detector, respectively. Although, in the used nuclear microprobe set-up, PIXE and RBS spectra can be obtained simultaneously with any kind of bombarding particle, the RBS analysis with a He beam gives a better depth resolution than a proton one (depth analysis range of about 2 μm for a 1.6 MeV He beam to 20 μm for a 2.0 MeV proton beam) while for PIXE analysis X-ray cross-sections are higher for protons than for He beams with similar energy. However the actual nuclear microprobe set-up does not allow absolute quantitative PIXE analysis and so a traditional broad beam set-up was used for elemental chemical analysis. In this case, the Be pebbles were submitted to acid digestion at room temperature in Teflon vessels with Supra-Pure chloridic acid. Known amounts of Y were added in order to be used as an internal standard for absolute concentration determinations. All handling and chemical reactions were done inside a chemical hotte for user safety. Broad beam PIXE targets were prepared by pipeting 10 μl of the resulting solution on a Mylar foil and irradiated with a 2.3 MeV proton beam with 5 mm diameter. A more detailed description of the usual procedure for acid digestion preparation can be found elsewhere [4].

The resistivity measurements have been performed enclosing the pebble column in an insulating alumina tube with a diameter D of 10 mm and a height H of 14 mm. This guarantees a value of D/r of 20 (r is the pebble radius) needed to eliminate the influence of geometric parameters such as end-effects on the experimental results. During the filling process the bed was vibrated to obtain a packing factor of about 65%. The force is applied by a pneumatic lift through a pressure gauge, which is used to measure the pressure. A thermocouple in contact with the pebbles monitors continuously the pebbles temperature. This set-up allows us to heat the pebble using a heating coil surrounding the alumina tube. A constant current of 180 mA was applied and the voltage drop along the Be pebble bed column was measured under different applied loads. The flux of the purging gas mixture ($He + 0.1$ vol.% H_2) was kept at a rate of 50 l/h during the measurements. The gas was kept flowing during heating and cooling of the pebble bed.

3. Results and discussion

3.1. Chemical analysis

Several pebbles were studied in order to have a clear picture of the impurity content and its distribution. As an example, an RBS spectrum of a virgin pebble is shown in Fig. 1. Oxygen is clearly identified on the pebble surface. The analysis of the oxygen peak reveals a maximum concentration of oxygen close to 25 at.% extending to a depth of 70 nm. This value is below the pure BeO composition (50 at.%) and can be due to a Be–BeO two-phase scale the porosity of the surface or the presence of other impurities. At higher depths the oxygen concentration decreases to lower values. These results are in close agreement with our findings for the 2 mm Be pebble [2]. Furthermore, the extension of the spectrum to higher channels indicates the presence of other impurities in the pebble. The spectrum obtained from a
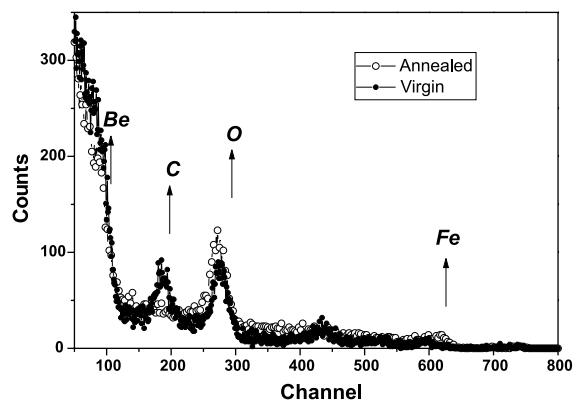

Fig. 1. Nuclear microprobe RBS spectra obtained with a 1.6 MeV He^+ beam, of a virgin and an annealed 1 mm Be pebble treated at 600 °C under a flowing $He + 0.1$ vol.% H_2 mixture.

pebble after annealing at 600 °C under the flux of the purge gas mixture (He + 0.1 vol.% H$_2$) is also included in the Fig. 1. Although the annealed pebbles show some different behaviour the general trend is the reduction of the surface carbon content and an almost constant oxygen profile. PIXE elemental maps obtained with the nuclear microprobe beam for the Be annealed pebbles indicate that some surface precipitates may be formed under the working conditions. Similar results were found after the 800 °C annealing.

For the elemental composition of the beryllium pebbles for elements with higher atomic number ($Z > 11$) both proton broad beam and microbeam analysis were used. Acid digestion of six different pebbles was performed and broad beam PIXE used for quantitative analysis of Ti, V, Cr, Mn, Fe, Ni and Cu. As chloridic acid was used in the acid digestion instead of the usual nitric acid (nitric acid has only a mild reaction with the Be pebbles) the Cl content makes impossible to detect Mg, Al and Si whereas the use of Y as internal standard increases the uncertainty in the concentration values for Zr, Au and U. For that reason the proton microprobe spectra were used to get information on the Mg, Al, Si, Zr, Au and U contents using the Fe amount determined in broad beam PIXE analysis for concentration normalisation. The spectrum in Fig. 2 shows the characteristic X-ray emissions of the elements present in a Be pebble. The average concentration and standard deviation results obtained in the analysis are reported in Table 1. Some care should be taken when comparing the acid digestion with reported quantitative results of the nuclear microprobe. In fact, the acid digestion results represent the entire pebble concentration whereas the nuclear microprobe results represent a mean value on the volume probed by the beam (depth about 20 μm). However, RBS analysis shows an altered surface of only 70 nm that is very small when compared to the total
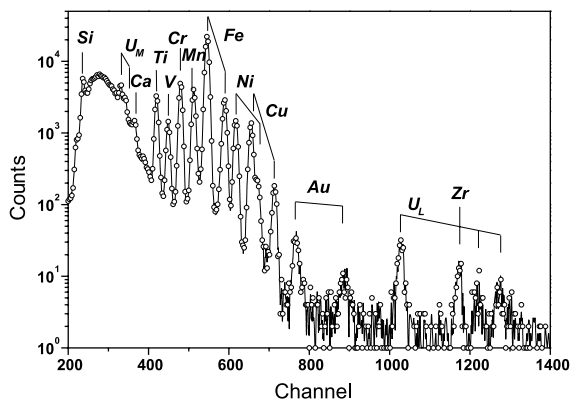
Table 1
Elemental concentration of 1 mm Be pebbles obtained by combined broad and microbeam PIXE analysis as referred in the text

Element	Concentration (μg/g)
Mg	116 ± 30
Al	376 ± 35
Si	305 ± 27
Ti	42 ± 9
V	19 ± 3
Cr	102 ± 12
Mn	104 ± 13
Fe	1050 ± 122
Ni	153 ± 27
Cu	113 ± 51
Zr	31 ± 9
Au	20 ± 2
U	103 ± 28

The reported errors are the standard deviations obtained from the six analysed samples.

proton range indicating that the PIXE microprobe analysis should be representative of the whole pebble.

3.2. Electrical resistivity

The resistivity of the pebble bed as a function of the load for two representative temperatures is displayed in Fig. 3. The existence of two distinct regimes are evident in both cases. During the first regime the pebble bed resistivity decreases drastically to about 4×10^{-4} Ω m under the applied load. This initial drastic drop of the electrical resistivity is due to the formation of electrical contacts between the pebbles, promoted by the mechanical arrangement of the pebble bed as a consequence of the applied load. The slope of the curve describing this regime increases sharply with the temperature. We can explain this behaviour assuming that the plasticity of the Be pebbles increases with temperature and a small load is sufficient to obtain the complete compaction of the pebbles.

In the second regime, the resistivity of the bed decreases slowly and linearly (in a semilogarithmic plot) with the applied pressure. The hysteresis of the resistivity is also shown in the figure. This irreversible effect is mainly seen for the lowest pressures indicating that the initial applied pressure provides the mechanical contact, which is responsible for the first decrease in the resistivity. The lower value of the electrical resistivity (3.0×10^{-4} Ω m) remains similar for all temperatures up to 800 °C.

Although the experiments were performed in a reducing atmosphere the BeO layer remains stable having no influence on the overall electrical behaviour of the pebble bed for temperatures up to 800 °C.

Fig. 2. Nuclear microprobe PIXE spectrum obtained with a 2.0 MeV proton beam, of a virgin 1 mm Be pebble indicating the main impurities present.
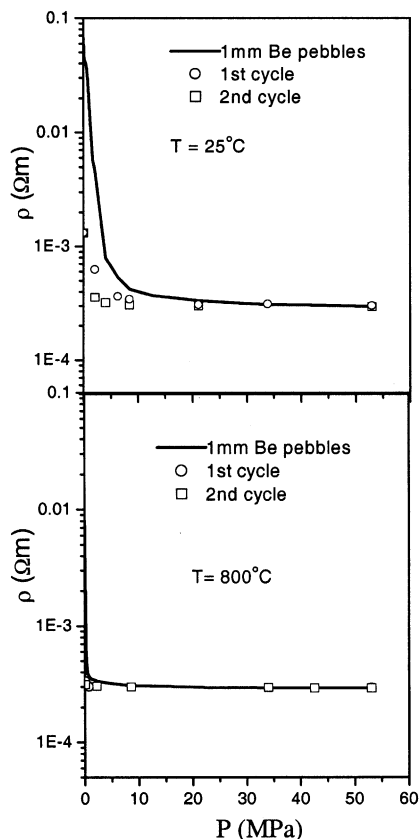
Fig. 3. Electrical resistivity of the Be pebble bed at room temperature and at 800 °C as a function of the applied pressure under a flowing He + 0.1 vol.% H_2 mixture.

4. Conclusions

The metallographic characterisation of the pebbles indicates the presence of a certain amount of BeO precipitates distributed on the pebble surface as well as along the grain boundaries, which contributes to an increase of the effective electrical resistivity of the pebble bed when compared to pure Be. The RBS analysis with the nuclear microprobe reveals that the oxygen distri-bution depth extends up to 70 nm with a maximum concentration value of 25 at.% corroborating the existence of a Be–BeO mixed surface layer. At room temperature the electrical resistivity measurements indicate the presence of two regimes for the electrical resistivity of the Be pebble bed. The first one corresponds to the mechanical rearrangement of the pebble bed and results in a drastic decrease of the pebble bed resistivity with the applied load. The range of this regime decreases with temperature. The second regime is linear (in a semilog-arithmic plot) with the pressure and could be related with the increase of the contact area between the pebbles under the effect of the external pressure. After mechanical cycling the bed shows an irreversible behaviour and the electrical resistivity never reaches its initial value for zero pressure. Although it is impossible to reproduce the envisaged conditions of the fusion power reactor our results are in agreement with the trends foreseen by theoretical calculations [5].

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