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Li ceramic pebbles chemical compatibility with Eurofer samples in fusion relevant conditions

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Abstract

Information on the chemical compatibility between Li ceramic breeders and reactor structural materials is an important issue for fusion reactor technology. In this work, Eurofer samples were placed inside a Li ceramic pebble bed and kept at 600 °C under a reducing atmosphere obtained by the flow of a purging gas ($He + 0.1vol.\%H_2$). Titanate and orthosilicate Li pebble beds were used in the experiments and exposure time ranged from 50 to 2000 h. Surface chemical reactions were investigated with nuclear microprobe techniques. The orthosilicate pebbles present chemical reactions even with the gas mixture, whereas for the samples in close contact with Eurofer there is evidence of Eurofer elemental diffusion into the pebbles and the formation of different types of compounds. Although the titanate pebbles used in the chemical compatibility experiments present surface alterations with increasing surface irregularities along the annealing time, there is no clear indication of Eurofer constituents diffusion.

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1. Introduction

One of the concepts for the blanket of the fusion reactor is the solid breeder blanket. The proposed designs use lithium ceramics as breeders, beryllium for neutron multiplier and helium as coolant. Several ceramics are candidates for this application, lithium orthosilicate (Li_4SiO_4), lithium metatitanate (Li_2TiO_3) and lithium metazirconate (Li_2ZrO_3). The use of ceramic breeders, despite its relatively low thermal conductivity, presents several advantages. Among them is low chemical activity, which is important to get a good compatibility with the structural materials and coolant. From the safety point of view these materials also have good characteristics. However the presence of minor or trace elements can play a decisive role both on neutron activation and surface chemical behaviour and particular attention must be paid on material purity and manufacture contamination control. Furthermore the chemical compatibility with other materials at high temperatures must be completely assessed in order to develop the final designs.

In this work we used ion beam techniques to study the chemical compatibility of Li orthosilicate and Li titanate pebbles with Eurofer at 600 °C. The PIXE (Particle Induced X-ray Emission) and RBS (Rutherford Backscattering Spectrometry) techniques are well suited, not only due to their sensitivity, but also due to their spatial and depth resolution to monitor the composition and trace elements surface contamination of the ceramic pebbles.

2. Experimental conditions and results

Eurofer samples were placed inside a Li ceramic pebble bed and kept at 600 °C under a reducing

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atmosphere obtained by the flow of a purging gas composed of He + 0.1vol.%H_2. Titanate and orthosilicate Li pebble beds were used for the experiments and exposure time ranged from 50 to 2000 h. The annealing experiments were conducted at ENEA-Casaccia and analysis was done at ENEA and ITN for investigating the chemical compatibility between Li pebbles and Eurofer samples. The detailed description on the annealing experimental procedure as well as the geometry and composition of the used samples can be found elsewhere [1].

At ITN, ion beam nuclear microprobe techniques were used for the characterisation of the Li pebbles. In these experiments, an Oxford Microbeams® nuclear microprobe type set-up was used to focus a 2 MeV proton beam generated with a Van de Graaff accelerator. PIXE (Particle Induced X-Ray Emission) and RBS (Rutherford Backscattering Spectrometry) techniques were used simultaneously in the characterisation of the analysed samples.

X-ray spectra were accumulated with an 80 mm^2 Si(Li) detector and RBS spectra were collected with a Si surface barrier detector with an active area of 200 mm^2. Beam spatial resolution was set to 3 μm with beam currents close to 200 pA. The focused beam was raster scanned over the samples and two-dimensional X-ray elemental maps obtained. From those maps, some regions were chosen to perform point analysis. Basic data acquisition, manipulation and mapping were done with the OM-DAQ program [2]. PIXE spectra fitting and quantitative results were obtained with the GUPIX computer package [3] that accounts for matrix and secondary fluorescence corrections while for RBS spectra evaluation the NUSDAN [4] computer code was used.

The Li pebbles analysed for each of the annealing periods were divided in two subsets: one containing pebbles forming the pebble bed and the other one containing pebbles that were directly removed from the surface of the Eurofer samples. As a rule, from each of the subsets, three different pebbles were analysed by means of nuclear microprobe techniques.

3. Experimental results

3.1. Compatibility of Li_4SiO_4

Before ion beam analysis, the samples were observed with an optical microscope to try to identify any regions of interest. This should be particularly interesting in the case of the pebbles that were in close contact with the Eurofer samples. However no clear deformation from the sphericity or any other type of clear indication of the contact area could be found. So all the obtained spectra can be considered as random spectra and only some kind of average behaviour can be attributed to the analysed pebbles.

The RBS spectra obtained from a representative set of the analysed orthosilicate pebbles contained in the pebble bed but not in direct contact with the Eurofer are shown in Fig. 1(a). The spectra were obtained from a scan of 53×53 μm^2 in the centre of the pebbles. This analysis at the centre of the pebble reduces the problems of defining a certain geometry of analysis and at the same time reducing surface irregularities that could be raised by a simple point analysis, by averaging over a larger area. The most relevant result is the amount of C present at the surface of the samples which shows a small depletion on Si. Fig. 1(b) shows the same type of spectra but obtained for the orthosilicate pebbles that were in close contact with the Eurofer samples. The spectra in Fig. 1 show that a systematic behaviour can be established for both series of spectra (pebbles in close

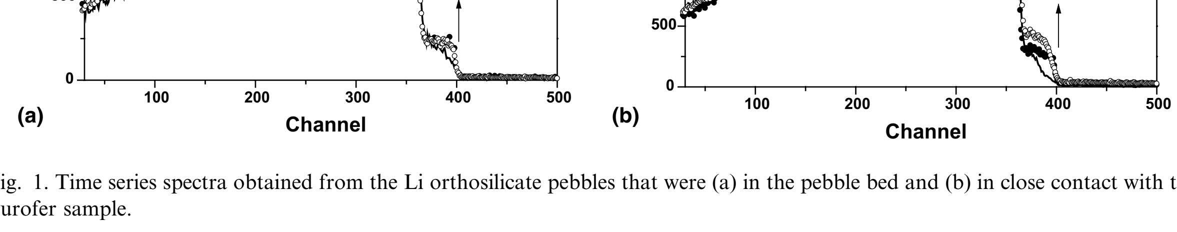


Fig. 1. Time series spectra obtained from the Li orthosilicate pebbles that were (a) in the pebble bed and (b) in close contact with the Eurofer sample.

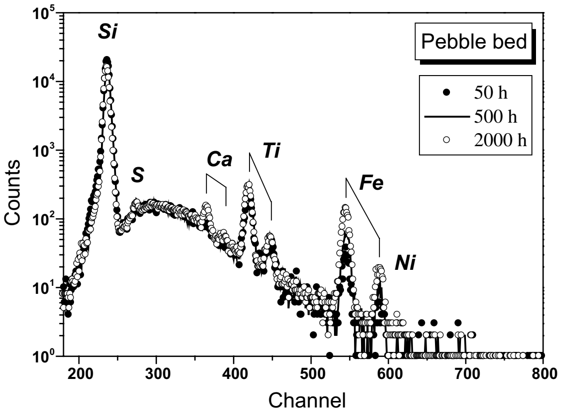
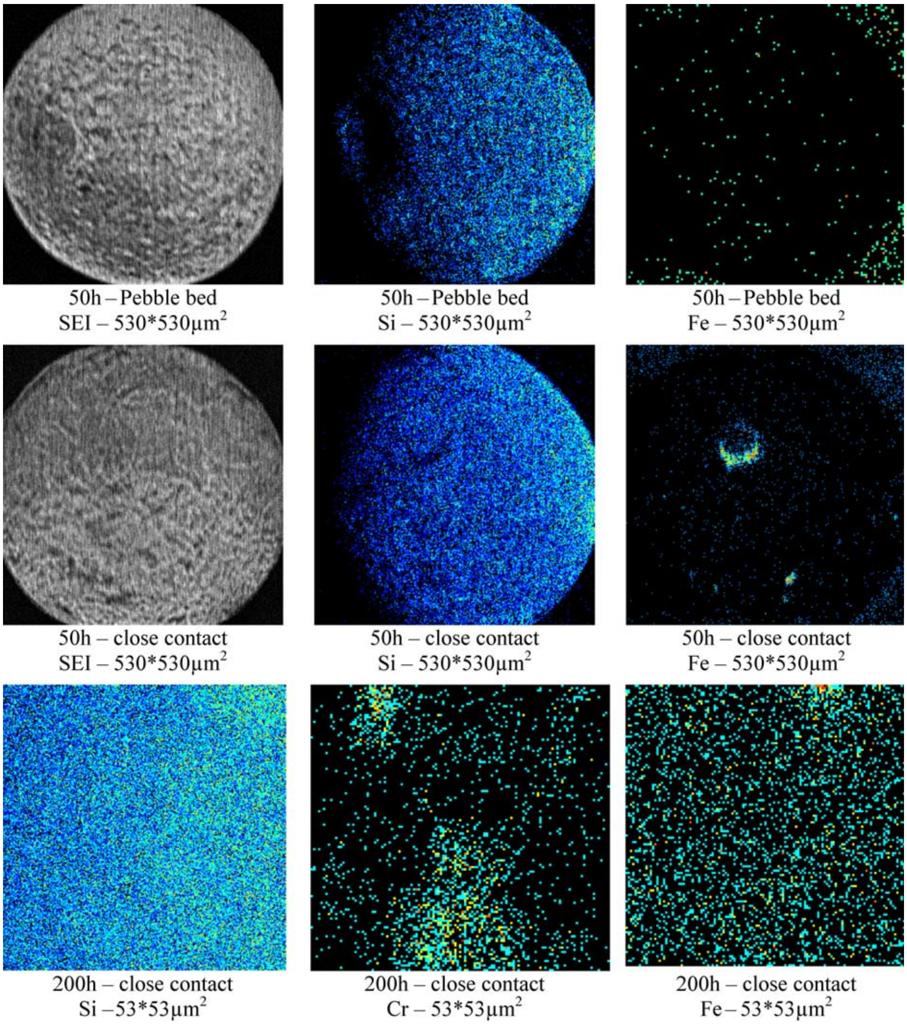


Fig. 2. PIXE time series spectra obtained from the Li orthosilicate pebbles that were in the pebble bed.

contact or in the pebble bed), with the C content being reduced with the annealing time. It is also evident from the RBS analysis of samples with 50 h of annealing time that the surface layer is composed only of C, Li and O whose extension varies from 500 to 800 nm on top of a Li_4SiO_4 substrate. This same type of composition was also referred for the Li pebbles used in the FZK experiments [5]. The annealing induces the removal of this layer with C and the appearance of a front layer with Si. The annealing time dependence of this effect is more easily noticed in the spectra of the close contact pebbles (Fig. 1(b)). This means that the removal of the layer with C is faster for the samples in the pebble bed than for the samples in close contact with the Eurofer. This probably indicates the contribution from the purging gas mixture that, on account of its different flow, reveals a higher



50h – Pebble bed
SEI – 530*530μm^2

50h – Pebble bed
Si – 530*530μm^2

50h – Pebble bed
Fe – 530*530μm^2

50h – close contact
SEI – 530*530μm^2

50h – close contact
Si – 530*530μm^2

50h – close contact
Fe – 530*530μm^2

200h – close contact
Si – 53*53μm^2

200h – close contact
Cr – 53*53μm^2

200h – close contact
Fe – 53*53μm^2

Fig. 3. (First and second table row) Secondary electron image (SEI), Si and Fe maps obtained from the 50 h annealed pebbles (first row – pebbles in the pebble bed; second row – pebbles in close contact with Eurofer). (Third table row) Si, Fe and Cr elemental maps of an orthosilicate pebble annealed for 200 h and that was in close contact with the Eurofer sample.

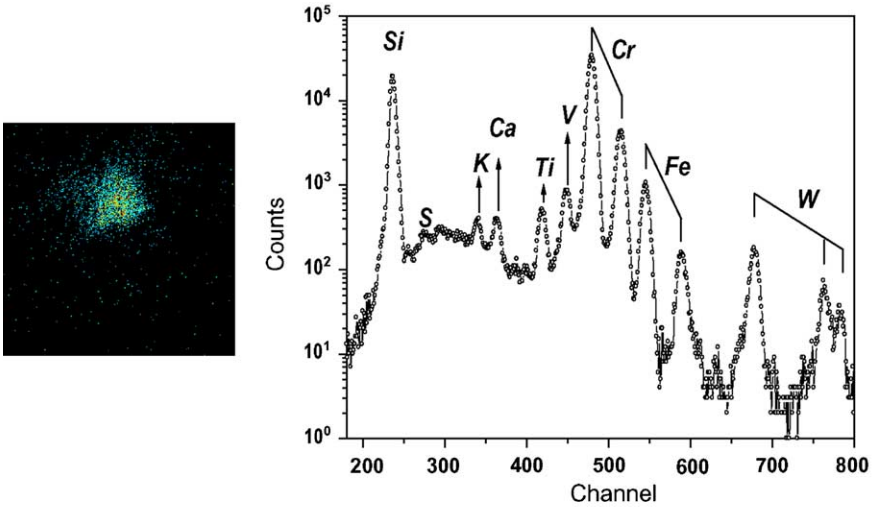


Fig. 4. 53×53 μm^2 Cr elemental map obtained from an orthosilicate Li pebble annealed during 200 h that was removed from the surface of the Eurofer sample (left), and PIXE point analysis spectra taken on the Cr region.

efficiency for the pebbles in the pebble bed than for the pebbles on top or close to the surface of the Eurofer sample.

In what accounts for PIXE, the spectra obtained from the Li pebbles in the pebble bed not in direct contact with Eurofer are show in Fig. 2. Apart from the occasional appearance of Ni in one sample, all the other spectra show only varying concentrations of S (60–140 μg/g), Ca (15–70 μg/g), Ti (140–250 μg/g) and Fe (40–240 μg/g). The samples in close contact with the Eurofer sample present PIXE spectra with a much wider variation on elemental contents indicating a reaction with the Eurofer sample constituents. As an example, Fig. 3 shows the secondary electrons images and some elemental maps obtained from a sample in contact with Eurofer and other in the pebble bed but not in direct contact. The surface topography is basically the same for the two samples but the increase in Fe content seems to be due to a localised contamination from the Eurofer steel.

The elemental maps from a sample exposed 200 h in close contact are also shown in Fig. 3. The increase in the Cr content observed in the PIXE spectra is shown in this figure to be due to the formation of large Cr precipitates. Although the Cr and Fe contamination should be due to the major constituents of the Eurofer samples, it is interesting to notice that they do not have the same spatial distribution. This is in accordance with the expected formation of Fe and Cr oxides [6,7].

As it cannot be assured that the analysed regions of the pebbles removed from the surface of the Eurofer samples are the ones that were really in close contact, a definite trend with time of exposure cannot be well established. In fact, it is one of the samples with an exposure of 500 h that exhibits the clearest indication of Eurofer constituent diffusion into the Li pebbles. This is evidenced by the Cr X-ray map shown in Fig. 4 and by the point analysis spectra taken from enhanced Cr region. The PIXE spectrum clearly shows elements as Cr, V, Fe and particularly W that can only be due to the diffusion of Eurofer constituents.

3.2. Compatibility of Li_2TiO_3

For the Li titanate pebbles the RBS results obtained before and after the exposure are shown in Fig. 5. The spectra show that there is no significant change in elemental composition during the annealing experiment. The surface colour change from white to blue that can be observed for the pebbles that suffered an annealing

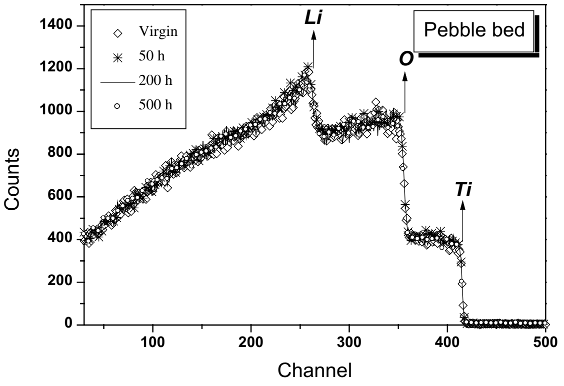


Fig. 5. RBS time series spectra obtained from the Li titanate pebbles present in the pebble bed during the chemical compatibility experiments with Eurofer samples.

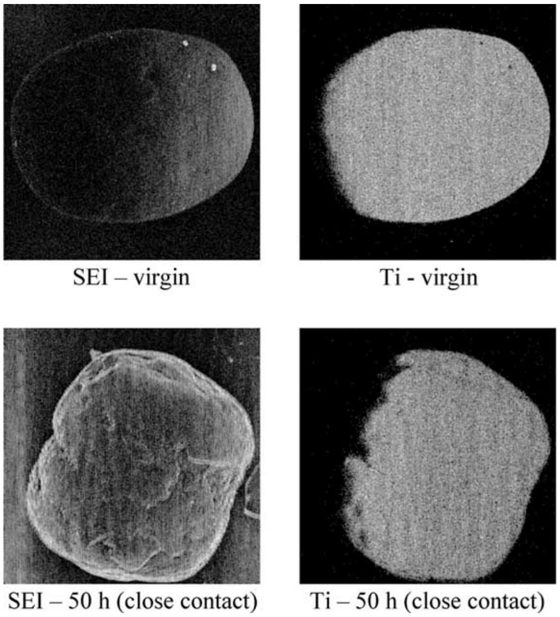


Fig. 6. SEI (secondary electrons images) and Ti elemental maps obtained from a virgin (top), and an annealed for 50 h in close contact with Eurofer (bottom) titanate pebbles. All images were obtained from a 1320×1320 μm^2 scan.

over 500 h, cannot be attributed to elemental composition variation.

Although the pebbles surface topography is altered during the exposure procedure, as can be seen in Fig. 6, elemental composition variation could only be found in some small zones of some pebbles due to Ce contamination (not shown in this manuscript). Among the possibilities for the colouration of the pebbles we would consider the phase transformations which are known to occur or the formation of different types of Ti oxides in the pebbles.

4. Conclusions

Microbeam analysis was used to characterise Li ceramic pebbles exposed to experimental conditions similar to the ones envisaged in a fusion reactor. Chemical compatibility experiments between Eurofer and Li ceramic pebbles were performed and ion beam techniques used for the characterisation of those pebbles. A carbon compound layer was observed on top of the Li orthosilicate material. It was observed that this layer, that extends up to ~800 nm from the pebble surface, is gradually removed as a function of annealing time. This effect is stronger for the orthosilicate pebbles in the pebble bed than for the ones that were removed directly from the surface of the Eurofer sample. The pebbles that were in close contact with the Eurofer indicate a clear diffusion into the pebbles of the constituent elements from the Eurofer. The heterogeneities found also reveal the different formation and localisation of compounds. For the Li titanate pebbles, a diffusion of Eurofer elemental constituents was not found. Apart from an increase in the irregularities of the pebble surface, chemical composition alterations that could justify the pebble colour change above 500 h of exposure were not found. This could be an indication that the colouration is related with phase transformation, including the formation of different Ti oxides.

References

[1] A. La Barbera, ENEA contribution to EFDA Technology Workprogramme, Task TTBB-005 deliverable D2, 2001.

[2] G.W. Grime, M. Dawson, Nucl. Instrum. and Meth. B 104 (1995) 107.

[3] J.A. Maxwell, W.J. Teesdale, J.L. Campbell, Nucl. Instrum. and Meth. B 95 (1995) 407.

[4] F. Watt, I. Orlic, K.K. Loh, C.H. Sow, P. Thong, S.C. Liew, T. Osipowicz, T.F. Choo, S.M. Tang, Nucl. Instrum. and Meth. B 85 (1994) 708.

[5] L.C. Alves, E. Alves, Final report EFDA Technology Workprogramme, Task TTBB-005 deliverable D9, 2002.

[6] M.W. Chase et al., JANAF Thermochemical Tables, 3rd Ed., J. Phys.-Chem. Reference Data, vol. 14, Suppl. 1, 1985.

[7] I. Barin, Thermochemical Data of Pure Substances, 2nd Ed., VCH, Weinheim, 1993.