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Effect of FLiBe Infiltration Pressure on Microstructure of Matrix for TMSR Fuel Elements (FEs)

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Abstract. The matrix graphite of fuel elements (FEs) with infiltration of 2LiF-BeF_2(FLiBe) at different pressures varying from 0.4 MPa to 1.0 MPa, has been studied by X-ray diffraction (XRD), scanning electron microscope (SEM) and positron annihilation lifetime (PAL) measurement. The result of XRD reveals that diffraction patterns of FLiBe appear in matrix graphite infiltrated with FLiBe at a pressure of 0.8 MPa and 1.0 MPa. The surface morphology from SEM shows that FLiBe mainly distributes within macro-pores of matrix graphite. PAL measurement indicates that there are mainly two positron lifetime components in all specimens:τ_1~0.21 ns and τ_2 ~0.47 ns, ascribed to annihilation of positrons in bulk and trapped-positrons at surface, respectively. The average positron lifetime decreases with infiltration pressure, due to the decrease in annihilation fraction of positrons with surface after infiltration of FLiBe into macro-pores.

Introduction

Recently, Molten Salt Reactor (MSR), one of the most advanced and promising Generation IV nuclear reactors has attracted more attention due to its inherent safety and economic competiveness [1.2.3]. The first MSR in the world was built by Oak Ridge National Laboratory (ORNL) in early 1960's [4]. One design of the Thorium Molten Salt Reactor (TMSR), proposed by Shanghai Institute of Applied Physics (SINAP) in 2011, will utilize 2LiF-BeF_2 (FLiBe) as coolant and graphitic spheres containing TRISO coated particles as fuel elements (FEs).The main ingredients of FEs is matrix graphite[3.5] (volume fraction>90%) because of its excellent performance (neutron irradiation resistance, high temperature tolerance, good thermal conductivity, low thermal expansion coefficient and good mechanical stability). However, the matrix has a porous nature structure and it will contact directly with FLiBe during operation, thus the infiltration of FLiBe into matrix graphite would be one of the most important technological issues to be concerned and resolved for TMSR.

Positron annihilation (PA) [6.7.8] is a sensitive tool to study the open structures (vacancy, cluster, voids) and surface in condensed matter. Because open structures and surface often act as positron trapping sites with negative charge and very low electrons density, which could trap positrons easily and give an increased positron lifetime. There are some positron annihilation studies on graphite and carbon system both from theoretical calculation and experiment since 1980's [9-11], but no reports on graphite infiltrated with salts. In this work, matrix for TMSR FEs with infiltration of FLiBe at different pressures varying from 0.4 MPa to 1.0 MPa has been studied for the first time by XRD, SEM and PAL, in order to confirm the effect of FLiBe infiltration pressure on microstructure of matrix.

Experimental

Sample preparation. Specimens in this study were cut from matrix graphite spheres provided by INET, Tsinghua University. Raw materials of matrix are natural-graphite, electro-graphite and phenol formaldehyde. They were firstly compressed to be a ball with a diameter of 6 cm, followed by carbonization at 800℃ and purification at a temperature up to 1900℃ [3,5]. After these heat treatments, the matrix graphite sphere has a density of 1.70~1.77 g/cm^3, a total porosity of 20% and an anisotropic factor of about 1.0~1.1. Five pairs of specimens (Φ10×2 mm) were infiltrated with FLiBe at 700℃ under pressures varying from 0.4 MPa to 1.0 MPa for 20 hours. One pair of specimens without infiltration was measured for comparison. The weight gain (wt. %) for specimens due to FLiBe infiltration was varied from 0 to 10.8% with the increase of pressure. Details of these specimens are listed in Table1.

Table 1. Weight gain for specimens with various infiltration pressures

Sample No.	1	2	3	4	5	6
Pressure [MPa]	0	0.4	0.5	0.6	0.8	1.0
Weight gain [%]	0	0	0	3.1	8.8	10.8

Characterization. XRD is a very sensitive method to determine the graphite structure, crystal size, interlayer spacing and degree of graphitization [12.13]. The interlayer spacing d_{002} could be derived from XRD patterns through Bragger diffraction equation. The degree of graphitization G can be calculated by the equation: G= (0.3440-d_{002})/ (0.3440-0.3354). The mean lateral size L_a and stacking height of basal plane L_c could be calculated by using Scherrer equation. The crystallite structure of specimens in this study was characterized by XRD with the diffraction range (2θ) from 15 ° to 95°. SEM (MERLIN Compact) was performed to study the surface morphology and distribution of FLiBe in matrix before and after infiltration. PAL was carried out by using fast-fast coincidence scintillators with a time resolution of 240 ps at full width at half maximum (FWHM). The ^{22}Na positron source was sandwiched between two pieces of identical pellets. About 2×10^6 counts were accumulated for each lifetime spectrum.

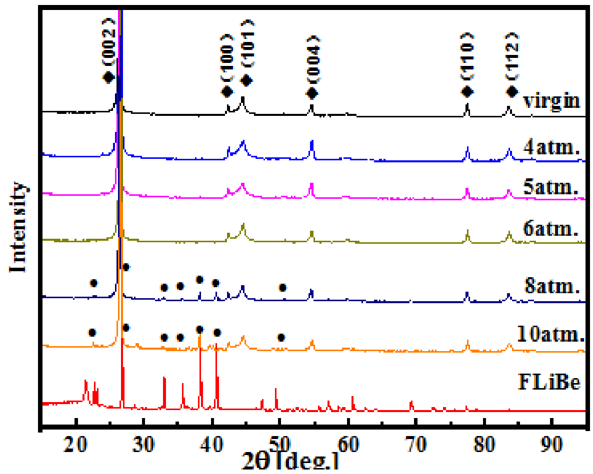

Fig. 1 XRD pattern of matrix before and after infiltration
◆ indicates Graphite ● indicates FLiBe

Results and discussion

Microstructure changes of matrix observed by XRD and SEM.

The XRD patterns of specimens are shown in Fig.1. Apparently, each specimen has six obvious characteristic diffraction peaks(2θ) at 26.44°, 42.23°, 44.40°, 54.56°, 77.38° and 83.49°, corresponding to (002), (100), (101), (004), (110) and (112) diffraction planes of graphite [12.13]. In addition, the peak location and FWHM of (002) plane is similar to each specimen, which suggests that the FLiBe infiltration has not destroyed the crystal structure of matrix. However, in respect of matrix graphite infiltrated at 0.8 MPa or 1.0 MPa, some new diffraction peaks appear at 2θ ranges 20° ~ 50°, which are assigned to the FLiBe diffraction peaks. The interlayer spacing d_{002}, graphitization G, the mean grain size L_a and L_c calculated for matrix crystallite before infiltration is about 0.3370 nm, 81.1%, 160 nm and 40 nm, respectively. After infiltration, no difference in these parameters is observed, which reveals that FLibe have not entered the inner crystal lattice of matrix.

However, XRD could not give information about the distribution of FLiBe in matrix, thus the surface morphology of matrix before and after infiltration was employed by SEM. The SEM results of virgin matrix are shown in Fig.2 (a) and (b), which reveal that the matrix has many large graphite lamellas and micrometer-sized pores locating at surface or interfaces between graphite lamellas. Fig.2 (c) and (d) show the matrix infiltrated at 1.0 MPa has some hundred-nanometer sized FLiBe particles locating at open pores. The results of SEM shown in Fig.2 indicate that FLiBe has occupied large open pores rather than the inner of crystallite, consistent with the XRD analysis.

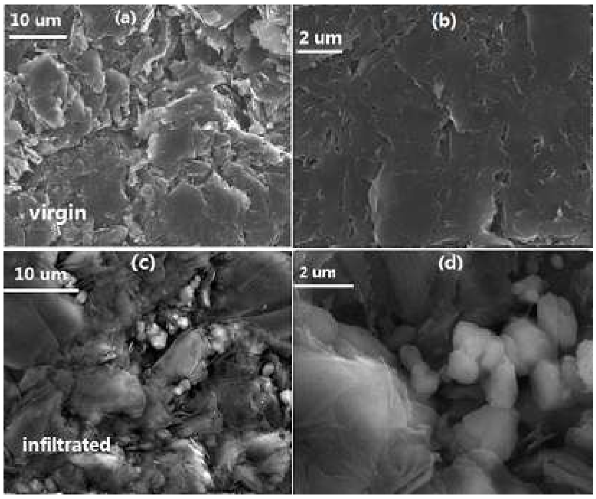

Fig. 2. SEM for virgin matrix(a-b) and matrix infiltrated at 1.0Mpa (c-d) with various magnification

Results of PAL measurement.

The variations of each specimen's lifetime and intensity are plotted in Fig.3. There are three lifetime components for each specimen. For specimens without FLiBe infiltration, the short-lived component $\tau_1 \sim 0.21$ ns corresponds well with calculated lifetime of free positrons in graphitic lattice (0.209 ns)[11], thus we assign τ_1 to the bulk positron lifetime in graphite crystallite. The middle-lived component τ_2 ~0.47 ns agrees well with the reported surface trapped positrons in graphite[9]. The long-lived component τ_3 ~3.5 ns is the o-Ps annihilation within voids, indicating the presence of large pores. In addition, these three components of lifetime almost stay constant with the increase of infiltration pressure or weight gain. It is commonly accepted that the second component τ_2 is resulted from positrons annihilation at surface or interfaces of crystallite, or internal surface of open spaces like pores in graphite. Since the mean grain size of crystallite L_a is about 160 nm, very close to the free positron diffusion length ~100 nm, a fraction of positrons will annihilate within grains while the other positrons will diffuse to surface or interfaces and then annihilate there.

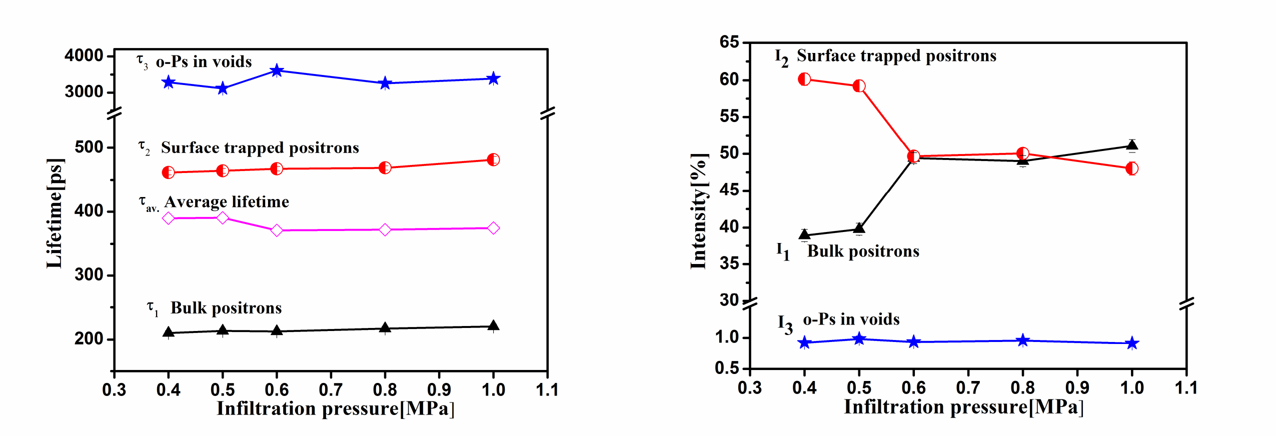

Fig. 3. Positron lifetime (left) and intensity (right) of matrix graphite with various infiltration pressures

However, intensity of bulk positrons(I_1) and surface trapped positrons(I_2) are strongly influenced by the infiltration pressure. With the increase of inflatration pressure, I_1 increases from 39% to 51% while I_2 decreases from 60% to 48%. There are two possibilities to explain the large variation of I_1 and I_2. One possibility is that some positrons will annihilate with LiF and BeF_2 infiltrated to pores, but due to the reported lifetime of positrons in alkali/alkaline earth fluorides τ_1~0.2 ns (bulk) [14.15], quite similar to τ_1 in graphite, thus the lifetime value τ_1 has no obvious change in Fig.3(left) but I_1 increases in Fig.3(right). Another possibility is that the inner surface of large open pores is reduced after occupation of FLiBe. Thus the fraction of positrons trapped at surface decreases while the fraction of positrons annihilated within bulk increases. Therefore, average lifetime $\tau_{av.}$ is reduced from 390 ps for specimen without infiltration to 370 ps for specimens with FLiBe infiltration. It should be noted that τ_3 has a very low intensity (I_3 ~0.9%), which suggests that fraction of o-Ps forming in voids is few ascribed to the chemical quenching or inhibition of Ps formation in graphite[10]. Further work needs to be done to study the positron annihilation enviroment and verify the fraction of positrons annihilated with graphite and LiF/BeF_2.

Summary

Effect of FLiBe infiltration on phase, morphology and defects of matrix for TMSR FEs is characterized by XRD, SEM and PAL measurement. No changes in microstructures was observed for matrix with the pressure lower than 0.6 MPa, indicating matrix would be a promising structural material for TMSR FEs (P_{max}~0.5 MPa). As infiltration pressure increased from 0.6 MPa to 1.0 MPa, much FLiBe penetrates to large open pores of matrix. PAL measurement shows that there are mainly two positron components in matrix with lifetime of τ_1~0.21 ns and τ_2 ~0.47 ns. They are ascribed to annihilation of positrons in crystallites bulk and surface or interface, respectively. In addition, a decrease in average lifetime with infiltration pressure was observed, which may due to the decrease in fraction of positrons trapped at surface while increase in fraction of positrons annihilated with bulk.

Acknowledgements

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