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Chemical reactivity of SiC fibre-reinforced SiC with beryllium and lithium ceramic breeder materials

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Abstract

SiC fibre-reinforced SiC fabrics (f-SiC/SiC) are considered for structural materials of advanced fusion blanket concepts. Priority tasks are compatibility studies of SiC with Li breeder ceramics and the Be neutron multiplier. Isothermal and anisothermal powder reactions by DTA up to 1220°C were examined between Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3, respectively, and SiC and SiC/SiO_2 mixtures, respectively. The SiC/SiO_2 mixture simulated the chemical state of Nicalon fibres. Solid state reactions between SiC and Be pellets were studied by capsule experiments. The reaction products Be_2C and Si were observed between the initial phases after annealing at 800°C and 900°C. A parabolic time law with a chemical diffusion coefficient $\tilde{D} = 2.6 \times 10^{-15}$ m^2/s of Be in the products was deduced at 900°C. Additional oxygen released from SiO_2 as a component of the simulated fibres oxidised the reaction products via the gas phase by formation of a Be_2SiO_4 layer. All reactions are kinetically hindered below 700°C. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The helium-cooled pebble bed blanket (HCPB) is one of the concepts considered in the European fusion programme as a DEMO relevant blanket [1]. The most important limitations of this concept are the low temperatures of the helium coolant ($\leqslant 450$°C), and consequently an uneconomical efficiency, and the neutron activation of the used ferritic–martensitic steels. To alleviate these problems, new first wall structural materials have been proposed and are being investigated within the European programme as possible candidates for advanced concepts. Among them are SiC fibre-reinforced SiC fabrics (f-SiC/SiC) in their hermetically sealed form. They are characterised by very low neutron activation and a reasonable stability at higher blanket operating temperatures [2,3]. Therefore, compatibility studies of SiC materials with the considered breeder materials Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3 and with the neutron multiplier beryllium above 700°C are considered high priority.

Two series of compatibility tests were started to elucidate these subjects: (1) Powder reaction experiments were made by isothermal annealings at 700°C and by differential thermal analysis (DTA) up to 1220°C of the breeder materials Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3 with SiC and SiC + SiO_2 (in order to simulate the oxygen containing fibres). (2) Stacks of polished SiC/Be/SiC pellets were isothermally annealed at different temperatures followed by X-ray microanalysis of the formed reaction product layers.

2. Experimental

2.1. Materials

Stoichiometric Li_4SiO_4 was manufactured by Schott Glaswerke (Mainz, Germany) through air-spraying between 1350°C and 1400°C to form single-phase granules up to 1 mm diameter. The material was then powdered, re-compacted and annealed at 900°C for 10 min in air. Details are reported in [4]. Li_2ZrO_3 and Li_2TiO_3 (purity >99%) were supplied by Alfa Aesar, Johnson Matthey

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(Karlsruhe, Germany) and were also annealed at 900°C for 10 min in air. The β-quartz modification of SiO_2 (purity 99.999%) was obtained from the same supplier. Hexagonal α-SiC powder with <5 μm grain size was purchased from H.C. Starck (Goslar, Germany); impurities: O = 1.1%, Al < 0.1%, Fe < 0.05%, Ca < 0.02%. Cubic β-SiC tiles were bought from Elektroschmelzwerk Kempten (Kempten, Germany); purity 99.78%; they were cut into quadratic pieces with 8 mm diagonal; density: >97% th.d.; roughness: 8 μm, maximum to minimum. The single-phase character of all materials was checked by X-ray diffraction. Beryllium disks of 8 mm diameter and 0.5 mm thickness were manufactured by W.C. Heraeus (Hanau, Germany). The chemical analysis of the supplier gave >99.83% Be. Details are reported in [5].

2.2. Procedure

Compacted SiC–Li ceramics powders were taken for the compatibility studies. To simulate the reaction behaviour of the Li breeder ceramics with SiC fabrics containing the Nicalon fibres composed of SiC and amorphous SiO_2 [6], compacted equimolar $SiC–SiO_2–Li$ ceramics powder mixtures were used.

Selected annealing experiments were made under static argon at 700°C. A 404/3 DTA unit (Netzsch, Selb, Germany) was used to investigate the kinetics of the powder reactions under flowing argon at 1 bar total pressure. The temperature calibration was made with the melting points [7] of aluminium ($T_m = 660.3$°C), gold ($T_m = 1064.4$°C) and nickel ($T_m = 1453$°C). The heating mode and the cooling mode were applied at a rate of 2 K/min for the calibrations and for the measurements to distinguish between heterogeneous reactions and reversible transition phenomena. Sample masses were 150–200 mg for all DTA experiments. The time constant of the DTA unit was calculated according to the tangent method [8]; it is less than 0.5 min of samples in this mass range and allows peak separation of one degree difference. X-ray diffraction work was carried out on all reacted samples with a Guinier camera (Nonius, model FR 522, Solingen, Germany) using Cu $K\alpha_1$ radiation ($\lambda = 154.060$ pm) and calibration with an internal NaCl standard (lattice parameter $a = 564.02$ pm).

Isothermal compatibility tests between polished Be and β-SiC were made in gas-tight molybdenum capsules screwed together with Mo plugs. Tantalum and ZrO_2 spacers of different thicknesses were used in the capsule to apply compression to the SiC–Be–SiC stacks. Annealings were made between 700°C and 900°C for a period up to 70 days. Thereupon the plug was removed after each experiment, the open capsule was impregnated with araldite and was axially separated. A metallographic cut was prepared therefrom. The isothermal SiC–Be diffusion couple experiments in molybdenum capsules were modified in one run by the presence of a SiO_2 pellet which acts as an oxygen source. It was not in direct contact with beryllium and simulated the oxygen partial pressure caused by the presence of SiO_2 in the Nicalon fibres. The formed layers were checked with a Siemens X-ray diffractometer.

The quantitative chemical analysis of Be, C, O and Si in μm areas was done in the reaction zones of the annealed samples using the X-ray microanalyser JEOL JRXA-50/JSM-6400 of IMF I in the Hot Cells of the Centre. For this purpose, a special diffraction crystal had been installed in one of the X-ray spectrometers which facilitates the direct beryllium analysis. The synthetic $Mo–B_4C$ multilayer crystal in its final version has a lattice spacing $2d = 22.2$ nm and a spectral resolution $\Delta\lambda/\lambda = 0.066$. A full width at half maximum $\Delta E = 7.2$ eV and a detection limit $c_{min} = 0.2\%$ for Be Kα radiation ($\lambda = 11.35$ nm) in Be were measured under optimised conditions [5]. The Vickers hardness of the reaction layers was measured.

3. Results and discussion

No reactions were observed by room temperature X-ray diffraction between Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3, respectively, and α-SiC after isothermal annealing at 700°C for two weeks under static argon. However, traces of reaction products (e.g., Li_2SiO_3) were detected after annealing of α-SiC with SiO_2 additions and the Li ceramics under the same conditions. The results for the dynamic annealing of the same materials at higher temperatures by DTA are described in the following sections.

3.1. Compatibility of Li_4SiO_4 with SiC and simulated Si–O–C fibres

No solid state reaction was observed between α-SiC and Li_4SiO_4 up to about 1000°C. However, an endothermic reaction became evident by DTA above 1000°C up to the maximum experimental temperature of 1150°C due to increasing Li, O_2 and Li_2O evaporation from solid Li_4SiO_4 [9]. The process results altogether in the formation of solid SiO_2 which reacts with Li_4SiO_4 to Li_2SiO_3. This phase was detected in smaller amounts by room temperature X-ray diffraction. SiC remains unaffected. First melting in the $SiC–Li_4SiO_4–Li_2SiO_3$ three-phase field was observed at 1025°C, that is the eutectic temperature of the $Li_4SiO_4–Li_2SiO_3$ sub-system [4].

The reaction between the compacted α-SiC, SiO_2 and Li_4SiO_4 powders (mole ratio 1:1:1) started at 760°C and was terminated at about 1000°C. This broad temperature interval is due to the presence of α-SiC taking charge of a stable diluent. The reactants SiO_2 and Li_4SiO_4 disappeared completely. The reaction products observed by X-ray diffraction are Li_2SiO_3 and small amounts of free Si. The mass loss of the sample is about 4% after heating to a maximum temperature of 1150°C. The lowest melting was observed at about 1015°C, possibly the Li_2SiO_3–Si eutectic. The beginning of the solid state reaction between Li_4SiO_4 and SiO_2 without the presence of α-SiC as a topochemical barrier was observed previously at 750°C, the reaction ended at 800°C [10].

3.2. Compatibility of Li_2ZrO_3 with SiC and simulated Si–O–C fibres

The DTA results have shown that a solid state reaction between α-SiC and Li_2ZrO_3 started at 1100°C, but it was not terminated at the maximum temperature of 1200°C on the evidence of room temperature X-ray diffraction. The products are ZrC and Li_2SiO_3 according to the reaction $SiC + Li_2ZrO_3 = ZrC + Li_2SiO_3$. The Gibbs energy of reaction is $\Delta_r G^\circ = -22$ kJ/mol at 1127°C [7]. First melting was stated at 1145°C.

The reaction between the compacted α-SiC, SiO_2 and Li_2ZrO_3 powders (mole ratio 1:1:1) started at about 1070°C and was not terminated at 1190°C. The reaction products observed by room temperature X-ray diffraction are Li_2SiO_3 and monoclinic ZrO_2. The reactants SiO_2 and Li_2ZrO_3 disappeared completely. SiC remained in lower amounts. First melting was stated at 1145°C which is reversible. The mass loss of the sample is about 2% after heating to a maximum temperature of 1200°C.

3.3. Compatibility of Li_2TiO_3 with SiC and simulated Si–O–C fibres

The DTA results have shown that a solid state reaction between α-SiC and Li_2TiO_3 started at 1160°C, but it was not terminated at the maximum temperature of 1220°C on the evidence of room temperature X-ray diffraction. The products are TiC and Li_2SiO_3 according to the reaction $SiC + Li_2TiO_3 = TiC + Li_2SiO_3$. The Gibbs energy of reaction is $\Delta_r G^\circ = -84$ kJ/mol at 1127°C [7].

The reaction between the compacted α-SiC, SiO_2 and Li_2TiO_3 powders (mole ratio 1:1:1) started at about 1020°C and was not completely terminated at 1220°C. The reactants SiO_2 and Li_2TiO_3 disappeared completely. The reaction products observed by room temperature X-ray diffraction are mainly Li_2SiO_3 and TiO_2 (anatas), Li_2TiSiO_5 ($T_m = 1207$°C [11]) and TiC in low concentrations and a further phase of unknown X-ray diffraction pattern as well as residues of α-SiC. Sticking of the sample to the Al_2O_3 crucible wall indicated partial melting. The mass loss is about 2% at the maximum temperature of 1220°C.

3.4. Compatibility between SiC and Be

No reaction between β-SiC and Be was observed at 700°C after 10 days. A thin reaction layer of about 50 μm thickness was observed between SiC and Be after annealing at 800°C for 34 days. Most of the present experiments were performed at 900°C. X-ray microanalysis revealed that the reaction layer is two-phase and is composed of interconnected Be_2C and Si. The presence of these phases was confirmed by X-ray diffraction. The thickness is 50 μm after 10 days, 70 μm after 14 days, 140 μm after 34 days and 190 μm after 70 days. The reaction zone occurs by beryllium diffusion into the SiC pellet. Cracks that have formed in SiC perpendicular to the surface remain visible in the reaction product layer. There is a gap between this layer and the beryllium foil which decreased in thickness during reaction. A microstructure of the Be_2C–Si reaction zone is illustrated in Fig. 1. The thickness is proportional to the square root of time, see Fig. 2. The material transport of

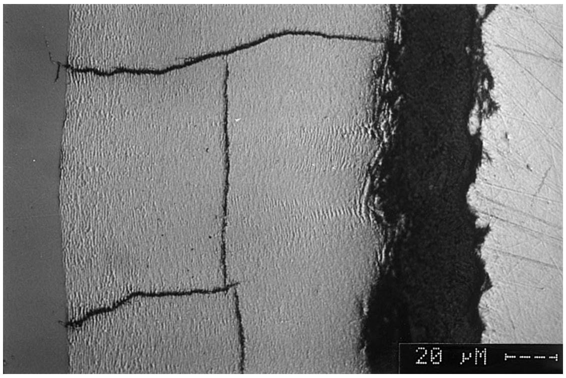

Fig. 1. Microstructure of the 120 μm thick two-phase Be_2C–Si layer between SiC (left) and Be after reaction at 900°C for 34 days.

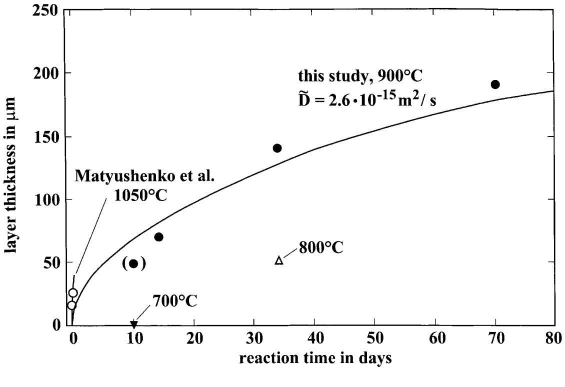

Fig. 2. Thickness of the formed Be_2C–Si layer between SiC and Be as a function of the reaction time. A parabolic curve was fitted to the 900°C data.

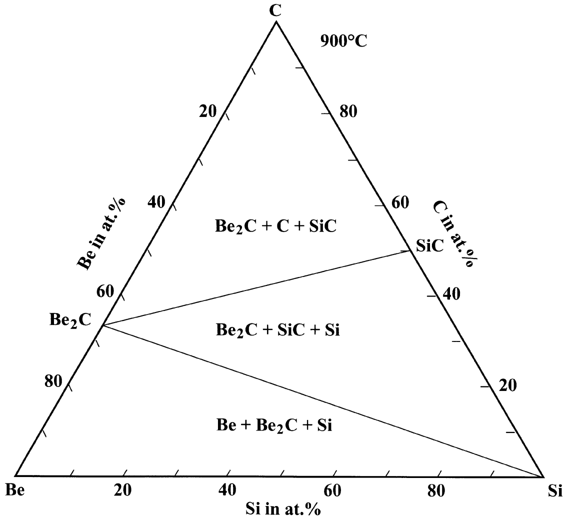

Fig. 3. Isothermal section of the phase diagram of the ternary Be–C–Si system at 900°C.

Be is uni-directed. The fitted chemical diffusion coefficient $\tilde{D}$ of Be in the reaction zone is $\tilde{D} = 2.6 \times 10^{-15}$ m^2/s at 900°C.

An isothermal section of the phase diagram of the ternary Be–C–Si system at 900°C can be derived from these observations, see Fig. 3. Tie lines exist between Be_2C and Si and between Be_2C and SiC. The Be–SiC couple is thermodynamically unstable. However, the reaction is kinetically hindered at 700°C. A ternary phase does not exist. The results of the Vickers hardness measurements (1 N load) at room temperature after the 900°C annealings are, SiC: 2055 HV, Be_2C–Si: 1250 HV, Be_2SiO_4: 1990 HV, Be: 165 HV.

3.5. SiC–Be compatibility at low oxygen partial pressure

The Nicalon fibres (f-SiC) contain about 10–15 mass% oxygen in the form of amorphous SiO_2 [6]. Though direct contact of the fibres within the f-SiC/SiC fabrics with beryllium is not expected, it is thermodynamically possible that this metal reacts with oxygen containing species via the gas phase. Therefore, a SiC–Be compatibility experiment was performed in an austenitic steel capsule in a low oxygen partial pressure environment for 10 days at 900°C. The oxygen partial pressure was simulated by a SiO_2 pellet in the stack sequence SiO_2–SiC–Be–SiC–ZrO_2. After reaction a 40-µm thick two-phase Be_2C–Si layer was observed on the SiC surface adjacent to the Be foil and was overcoated by a 10-µm thick Be_2SiO_4 layer as SiO_2 was the oxygen source. The Si/SiO_2 oxygen potential is given by $\Delta G(O_2) = RT \times \ln p(O_2) = -683$ kJ/mol O_2 at 1173 K [7]. The reaction proceeds in two steps

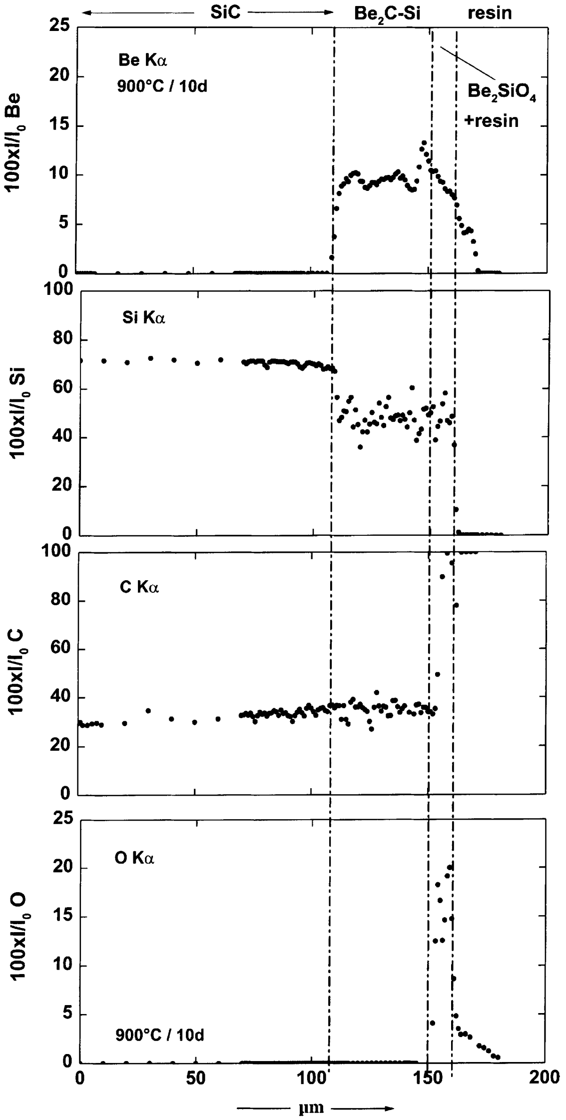

Fig. 4. Be, Si, C and O step scans by X-ray microanalysis across the Be_2C–Si and Be_2SiO_4 reaction layers between SiC and Be (Be is not shown on the right) in a low oxygen partial pressure environment after annealing at 900°C for 10 days.

$$\begin{array}{l} Be_2C + \frac{3}{2}O_2 = 2BeO + CO \\ 2BeO + Si + O_2 = Be_2SiO_4 \\ \hline Be_2C + Si + \frac{5}{2}O_2 = Be_2SiO_4 + CO \end{array}. \qquad (1)$$

Using the Gibbs energy of formation data of Be_2C, Be_2SiO_4 and CO from [6], the Gibbs energy of reaction, Eq. (1), results in $\Delta_r G = -105$ kJ/mol at 1173 K. Fig. 4 illustrates the reaction layer sequence SiC/Be_2C–Si/Be_2SiO_4/araldite filled gap which results from X-ray microanalysis by step scans of uncorrected relative intensities I/I_0 of Be, Si, C and O. The adjacent Be foil on the right side is not shown in the figure.

4. Conclusions

The powder reactions of SiC and SiC + SiO_2, respectively, with Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3, respectively, illustrate the different reaction behaviour between the structural materials and the Li ceramics. There are no indications of SiC and Li_4SiO_4 reactions up to 1000°C, whereas a rapid reaction starts at 760°C between Li_4SiO_4 and SiO_2, a component of the Nicalon fibres, also at indirect contact of the phases. The reactions of SiC with Li_2ZrO_3 and Li_2TiO_3, respectively, begin above 1070°C.

The Be–SiC couple is thermodynamically unstable in the Be–C–Si system. Solid state reactions revealed a Be_2C–Si layer formation at 900°C with a parabolic rate law and a chemical diffusion coefficient of the diffusing element Be to be $\tilde{D} = 2.6 \times 10^{-15}$ m^2/s. An overcoating of a Be_2SiO_4 layer was observed already at very low oxygen partial pressures. These reactions are kinetically hindered at 700°C.

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