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Recovery Behavior of Neutron-irradiation-induced Defects in Monolithic SiC and SiC_f/SiC Composites

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Abstract

Silicon carbide (SiC) and continuous silicon carbide fiber-reinforced silicon carbide matrix (SiC_f/SiC) composites have been used extensively in nuclear applications because of their excellent nuclear, mechanical and thermal properties. In this study, several types of SiC and SiC_f/SiC composites have been neutron-irradiated simultaneously at moderate fluence of 2.0-2.5×10^{24} n/m^2 (E>0.1 MeV) at low irradiation temperature (333-363 K) for 60 days. Radiation effects, recovery behavior and microstructures on those specimens were investigated in order to understand the fundamental responses after neutron irradiation. Results showed that high purity SiC was swelled approximately 1.2% while length change of SiC containing additives was 0.1% larger than those of the high purity SiC due to the irradiation. Further, SiC_f/SiC composites were less swelled than monolithic SiC. Investigation on the recovery behavior by isothermal and isochronal annealing showed that high purity SiC and SiC containing 12 wt% sintering additives recovered completely. Activation energies for volume recovery during annealing were obtained for each specimen. Observations of the microstructures of irradiated SiC clarified that most of the defects induced by the irradiation were Frenkel defects and no black spot defect or dislocation loop has been perceived. The recovery mechanisms of examined SiC were discussed.

Thesis Outline

Chapter 1:

Introduction

This chapter is described to give a fundamental knowledge about the structures and properties of the main materials, silicon carbide (SiC) and silicon carbide fiber-reinforced silicon carbide (SiC_f/SiC) composites. Furthermore, their applications are introduced briefly, and the radiation effects that occurred on these materials are explained and clarified. The purposes of this study are to define the neutron radiation effects on highly pure SiC and SiC containing sintering additives and their recovery behavior by post-irradiation annealing.

1.1 Silicon carbide (SiC)

Sintering, direct conversion, gas phase reaction, and polymer pyrolysis are common fabrication methods of SiC ceramic. One of the most well-known gas phase reaction is chemical vapor deposition (CVD) technique. It is able to produce a highly crystalline, stoichiometric, and high-purity β-SiC at comparatively lower temperature (1173-1373 K). Another method is liquid phase sintering (LPS) applied for a hot-pressing technique to manufacture a vigorous and dense SiC at lower temperatures. However, utilization of sintering additives such as alumina (Al_2O_3) and yttria (Y_2O_3) is able to deteriorate the mechanical properties of SiC at higher temperatures. Similar disadvantage has been introduced by Prochazka, i.e., the pressureless sintering process using boron as additive for SiC, showed an unstable behavior under neutron irradiation attributed to the large (n,α) cross-section of the ^{10}B isotope.

SiC has magnificent properties and has been used in harsh environment due to its resistance to high-temperatures, heavy loads, and corrosion. Due to its excellent mechanical and chemical properties, SiC has been preferred to be used in combustion components, magneto hydro dynamic (MHD) generator, aerospace engine parts, pump components, and as a component in TRISO fuels for high temperature gas-cooled reactors. TRISO fuels stand for tristructural-isotropic fuel, a type of micro fuel particles commonly used in pebble bed reactor (PBR), and thousands of the particles are dispersed into graphite pebbles. It consists of a fuel kernel composed of uranium oxide (UO_2) in the center and coated with four layers. One of the layers is SiC utilized in TRISO-fuel to retain the fission products at elevated temperatures and to give the particle more structural integrity.

In spite of their excellent engineering ceramic properties, SiC possesses its own major deficiency, i.e., inherent brittle nature that can lead to a high probability of catastrophic failure under excess load. Therefore, to ensure sufficient mechanical properties and reliability, the proposed materials for future in various application parts are SiC fiber-reinforced SiC (SiC_f/SiC) composites composed of infiltrated SiC matrix into SiC fiber preforms woven into 2D, or preferably a 3D fabric.

1.2 SiC_f/SiC composites

SiC_f/SiC composites have potentials to produce an efficiently transfer heat, tritium retention, and high damage tolerance under neutron irradiation. There are several approaches to fabricate SiC_f/SiC composites by chemical vapour infiltration (CVI) and nano-infiltration and transient eutectoid (NITE) processes. Long manufacturing time, residual porosity, and less dense are the disadvantages of CVI process. On the other hand, sintering additives used to densify the composite in NITE process will lead to secondary phases which is not resistant to radiation damage.

Other methods to fabricate the composite are liquid silicon infiltration (LSI) or melt infiltration (MI) method and polymer impregnation and pyrolysis (PIP) method. In addition, electrophoretic deposition (EPD) is a promising method proposed by Yoshida et al. to be a feasible process in a way to control the fiber/matrix interface and the microstructures of SiC composite with high productivity. Since SiC_f/SiC composites have been developed to improve the properties and reliability of monolithic SiC, thus the composite has been proposed by Riley et al. as a potential fusion reactor blankets material due to low decay heat properties and able to minimize on tritium breeding. Moreover, the composites are capable to retain in extreme irradiation environment at higher-temperatures up to 1573 K and neutron fluence up to 70 dpa. Furthermore, SiC composites have been proposed as one of the candidates for fusion reactor components as a first wall in the ITER broader approach (BA) activities, as an attempt to enhance the plant efficiency due to its outstanding radiation/heat resistance, and combined with tungsten as a material for divertor.

1.3 Neutron irradiation effects on SiC and SiC_f/SiC composites

Numerous researchers have been conducted from low to high neutron fluences with various temperatures for high purity SiC such as Chemical Vapor Deposition (CVD)-SiC and SiC with sintering additives such as Nano-infiltration Transient Eutectoid (NITE)-SiC. It is well known that β-SiC shows an isotropic swelling due to neutron irradiation and are saturated up to 10^{24} n/m^2 below 1273 K and the saturated swelling decreases with increasing the irradiation temperature. In terms of atomic microstructures observed with TEM, at lower irradiation temperatures, Suzuki et al. reported that black spot defects were distributed throughout the SiC grains after irradiated at 4.8×10^{25} n/m^2. This result was supported by Katoh et al. that SiC contains black spots or tiny interstitial clusters after neutron irradiated at 6×10^{25} n/m^2. As the irradiation temperatures increase, those black spots have been matured and growth significantly coarser if compared to those formed at lower irradiation temperatures. In addition, SiC continued to swell at the higher irradiation temperatures (1773–1873 K) due to the significant of void formation.

SiC composite behaviors after neutron irradiation depend on types of fibers such as low oxygen-content Hi-Nicalon fiber and high crystalline Tyranno SA3 fiber. Snead et al. reported that SiC composites which used Hi-Nicalon fibers were swelled approximately 0.46% and 0.56% after neutron-irradiated up to 1.1×10^{25}n/m^2 at 658 K and 533 K, respectively, while SiC that used Tyranno SA3 fiber was swelled about 0.98% after ion-irradiation up to 3 dpa at 873 K. Under heavy neutron irradiation, it has been reported that the fiber and the matrix would detach or decouple owing to the fiber shrinkage and matrix swelling. It may be attributed to the crystallization of amorphous fibers, while crystalline matrix is swelled due to irradiation-induced defects.

1.4 Recovery behavior of SiC

The operating temperature in fission reactors would be achieved until 1473 K as in gas-cooled fast reactor, while it can reach up to 1673 K in fusion reactors. Defects seem to be annihilated during irradiation at elevated temperatures. It means that, swelling of neutron-irradiated SiC induced by interstitials atoms and vacancies is recovered simultaneously at high temperature during nuclear reactor operations. This behavior has been studied by Suzuki et al. by post-irradiation annealing to estimate the irradiation temperature. It is specified that SiC exposed to doses up to 1.0×10^{27} n/m^2 at temperatures from 703 K to 823 K were started to recover from similar temperature with the irradiation temperatures after post-annealing up to 1273 K for 1 h. Yamazaki et al. reported that dilatometer method can be applied for length change measurement at elevated temperatures. This technique can measure continuous change of specimen length during heat treatment for long period. It is noted that the recovery of length is mostly dominated by recombination of interstitial atoms and vacancies

1.5 Purposes of this research

In this study, the dimensional stability after neutron irradiation for several types of SiC and SiC composites was clarified. Several experiments regarding to recovery behavior of SiC were conducted and the activation energies for volume recovery were determined. Plenty of observations of the specimens' surfaces also has been conducted. Lastly, the atomic arrangement in crystals on their irradiation responses were investigated using TEM. Below are the main points for each chapter;

Chapter 1: Introduction

This chapter describes the overview of key properties of SiC and SiC_f/SiC composites and their nuclear applications. The problems of these materials have been explained briefly, particularly when they are applied under severe environments such as fission/fusion reactor. Thus, several data from previous studies about neutron irradiation effects on those materials were reviewed in this chapter. The unsolved problems of SiC and SiC_f/SiC have been clarified and finally the objectives of this study were described.

Chapter 2: Neutron Irradiation Swelling of SiC and SiC_f/SiC for Advanced Nuclear Applications

In this chapter, the basic radiation effects on various types of SiC and SiC_f/SiC composites were investigated after medium fluence neutron irradiation at low irradiation temperatures. Macroscopic length, lattice parameters, and their microstructure were analyzed in order to understand their radiation stability using pre- and post-irradiated specimens.

Chapter 3: Recovery behavior of high purity cubic SiC polycrystals by post-irradiation annealing up to 1673 K

In this chapter, recovery behavior of two kinds of high purity SiC was investigated and explained clearly. The unirradiated and irradiated specimens were annealed up to 1673 K continuously using precise dilatometer and the length could be in-situ measured simultaneously. Activation energies have been determined by first order model to understand the defects stability. It is suggested that the recovery is mostly proceeded by the recombination of interstitial atoms and vacancies.

Chapter 4: Defect-annihilation behavior of neutron-irradiated SiC ceramics densified by liquid-phase-assisted method after post-irradiation annealing

This chapter defines the recovery behavior of SiC containing large amount of sintering additives by the similar method which was described in Chapter 3. For these specimens, secondary phases formed by heat treatment during fabrication or post-irradiation annealing have to be considered since the recovery behavior is different from the high purity SiC. However, from the calculation of activation energies, it is clarified that they exhibit similar recovery mechanism and the recovery mostly involve the recombination of point defects.

Chapter 5: Radiation damage analysis in SiC by transmission electron microscopy.

The objective of this chapter was to clarify the changes in microstructure and atomic arrangement of several SiCs after irradiated at low temperatures by transmission electron microscopy (TEM). In addition, specimens treated by post-irradiation annealing were also investigated. From the observations, the defects behavior and their stabilities after neutron irradiation and after heat treatment experiments, observed in Chapter 2-4, are discussed.

Chapter 6: Conclusions

The whole results obtained from Chapter 1 to 5 were summarized.

Chapter 2:

Neutron Irradiation Swelling of monolithic SiC ceramics and SiC_f/SiC composites

In this chapter, the basic neutron irradiation effects on various type of SiC and SiC_f/SiC composites were evaluated by their microstructure changes after medium neutron irradiations at low irradiation temperatures. Macroscopic lengths, lattice parameters, and microstructure were analyzed in order to understand their radiation stability.

Although numerous reports have discussed the irradiation effects on SiC, neutron-irradiated SiC with high purity at low irradiation temperature has never been described in details. Furthermore, irradiation effects on SiC with impurity were also investigated to recognize the influence of sintering additives on irradiation resistance. In addition, presence of SiC fibers in SiC matrix with various method certainly give significant role to maximize high tolerance. In this chapter, seven types of monolithic SiC ceramics or SiC_f/SiC composites fabricated by different processes were irradiated in the BR2 reactor up to a fluences of 2.0-2.5×10^{24} n/m^2 (E>0.1 MeV) at 333-363 K. Changes in their macroscopic lengths, lattice parameters and microstructure before and after the neutron irradiation were measured to clarify the basic irradiation effects on each SiC-based material.

2.1 Introduction

Reports on neutron irradiation effects of SiC and SiC_f/SiC composites have been limited in the literatures, particularly under medium neutron fluencies and at relatively low irradiation temperatures. Nevertheless, these materials are proposed to be applied at central region in fusion power reactors, where high neutron fluences and high temperature environments inevitably exist. Hence, it is valuable to obtain basic irradiation response of the materials after a mild irradiation condition. From these specimens, estimations of irradiation response of materials up to high temperature by post-irradiation annealing experiments can be investigated.

In this study, seven types of SiC ceramics and SiC_f/SiC composites (PureBeta, Chemical vapour deposition (CVD)-SiC, Liquid phase sintering (LPS)-SiC, Nano-powder Infiltration and Transient Eutectoid (NITE) A and B, SiC_f/SiC of chemical vapor infiltration (CVI), NITE and electrophoretic deposition (EPD) methods) with different fabrication processes were irradiated in the BR2 reactor (Belgium) up to a fluences of 2.0-2.5×10^{24} n/m^2 (E>0.1 MeV) at 333–363 K. Then the attention was put on the differences of monolithic materials and composites under the same irradiation condition. This study was conducted at low conditions to understand the behavior of point defects that induced by neutron irradiation and eventually gives fundamental information of microstructure evolution. Thus, changes in macroscopic length, lattice parameters and microstructure before and after the neutron irradiation were measured using point or flat type micrometers, X-ray diffractometer (XRD) and scanning electron microscope (SEM) to observe and clarify basic irradiation effects on each material.

2.2 Experimental procedures

2.2.1 Materials

Seven SiC-based materials were chosen in this study. They can be categorized into two groups, monolithic SiC ceramics and SiC_f/SiC composites. Group SiC consists of PureBeta-SiC (β-SiC), CVD-SiC and NITE-SiC, and group SiC_f/SiC composites consist of the composites fabricated by CVI, NITE and EPD processes.

2.2.2 Neutron irradiation, macroscopic length, lattice parameters and SEM observation

All the specimens were concurrently neutron-irradiated in the BR2 reactor in Belgium up to a fluences of $2.0\sim2.5\times10^{24}$ n/m^2 (E>0.1 MeV, 0.20~0.25 dpa) at 333-363 K, and they were exposed for 60 days. Macroscopic lengths of unirradiated and irradiated specimens were measured using a point type and a flat type micrometer at room temperature. Macroscopic volume change was calculated based on the changes in the macroscopic length, the thickness and the width changes. The length direction was parallel to SiC fabrics in the case of the composites.

Lattice parameters were determined by X-ray diffraction (XRD) technique. XRD with a CuKα source (40 kV, 40 mA) was performed with Philips PW-1700 diffractometer equipped with a graphite monochromator at room temperature. In order to observe the microstructure of SiC_f/SiC composites after sustaining intermediate neutron irradiation, scanning electron microscopy (SEM, Hitachi S-3500) was conducted by applying 20 kV with various magnifications.

2.3 Conclusions

Monolithic SiC ceramics and SiC_f/SiC composites fabricated by different processes were concurrently neutron-irradiated in the BR2 reactor up to a fluence of 2.0~2.5×10^{24} (E>0.1 MeV) at 333-363 K. Changes in macroscopic lengths and lattice parameters were measured. The results are summarized as follows:

(1) High purity SiC ceramics showed slightly smaller swelling than the SiC ceramics with oxide sintering additives.

(2) The group of SiC_f/SiC composites showed less swelling than the group of monolithic SiC ceramics due to smaller swelling of SiC fibers.

(3) Within various SiC_f/SiC composites tested in this study, swelling of the composites fabricated by EPD method was the smallest.

Chapter 3:

Recovery behavior of high purity cubic SiC polycrystals by post-irradiation annealing up to 1673 K

Previous chapter described how neutron irradiation can affect two kinds of SiC (high purity and sintering additives) and SiC_f/SiC composites at low irradiation temperature on their microstructures. The results showed that all the specimens were swelled 1.0-1.3% owing to the formation of point defects and less swelling of SiC composite specimens showed. Furthermore, it is well-known that increasing the irradiation temperature will decrease the swelling of SiC due to enhanced recombination of Frenkel defects of high temperatures as explained in Chapter 1. Thus, the idea of current researches is developing experiments to study the recovery behavior by annealing the irradiated specimens up to 1673 K. This chapter explains the mechanism of the recombination of interstitials and vacancies in high purity SiC by post-irradiation annealing technique.

Changes in macroscopic lengths were examined by post-irradiation thermal annealing using a precision dilatometer up to 1673 K with a step-heating method. The specimen was held at each temperature step for 6 h and the change in length of the specimen was recorded continuously during each isothermal annealing step from 373 K to 1673 K with 50 K increments. The recovery curves were analyzed with the first order model, and rate constants at each annealing step were determined.

3.1 Introduction

In the present work, recovery behavior assessment by post-irradiation annealing was conducted to clarify recovery stages of high purity monolithic β-SiC (PureBeta and CVD-SiC) polycrystals, which were the same specimens as in the previous study. Post-irradiated isochronal annealing up to 1673 K and in-situ length change measurement at isothermal annealing for 6 h with increment of 50 K from room temperature under helium environment was performed using a precision dilatometer to confirm recovery stages in those specimens.

3.2 Experimental procedures

3.2.1 Materials

In this study, high purity β-SiC polycrystals, PureBeta-SiC, and CVD-SiC were used to evaluate the recovery behavior by post-irradiation thermal annealing. Both of these materials were machined into bar shape with the size of 25 mm x 4 mm x 2 mm. Microstructure of unirradiated and irradiated specimens from both types have been observed by scanning electron microscopy (SEM).

3.2.2 Neutron irradiation and post-irradiation annealing

PureBeta-SiC and CVD-SiC specimens were concurrently neutron-irradiated in the BR2 reactor in Belgium up to a fluences of 2.0–2.5×10^{24} n/m^2 (E>0.1 MeV, 0.20~0.25 dpa) at 333-363 K for 60 days. Prior to post-irradiation annealing, both unirradiated and irradiated specimens were cut into half (25 mm x 2 mm x 2 mm) with a diamond cutter.

The annealing behavior was investigated with a precision dilatometer (DIL 402C, NETZSCH, Germany). Length changes for both specimens were in-situ measured continuously from room temperatures up to 1673 K with a step heating temperature interval of 50 K in helium atmosphere. Pushrod movement can detect the specimen length changes. Thermocouple (Type-S; Pt 10%Rh–Pt) located next to the heating element (SiC-heating element) was used to control the temperature in the furnace.

After completing the annealing, macroscopic lengths and lattice parameters of both irradiated specimens were determined with a point type micrometer and by X-ray diffraction (XRD) technique at room temperature, respectively.

3.2.3 Rate of recombination and activation energy

Presence of point defects is corresponding to the volume change (ΔV) of the specimen after the neutron irradiation, and the recovery of crystal after thermal annealing is based on migration of these defects and annihilation through recombination of interstitial atoms and vacancies. From understanding the material behavior and mechanism of defects annihilation, activation energy for recombining interstitial atoms and vacancies from Frenkel pairs formed in irradiated specimens can be estimated by first order reaction and an Arrhenius equation.

3.3 Conclusions

High purity PureBeta-SiC and CVD-SiC were concurrently neutron-irradiated in the BR2 reactor up to a fluence of 2.0~2.5×10^{24} (E>0.1 MeV) at 333-363 K. Recovery behavior by post irradiation annealing up to 1673 K were measured, and the results are summarized as follows;

1. Recovery of defects induced by neutron irradiation in high purity β-SiC have four stages with different activation energies. At 373-573 K, the activation energy of PureBeta-SiC and CVD-SiC were in the range of 0.17-0.24 eV and 0.12-0.14 eV, 0.002-0.04 eV and 0.006-0.04 eV at 723-923 K, 0.20-0.27 eV and 0.26-0.31 eV at 923-1223 K, and 1.37-1.38 eV and 1.26-1.29 eV at 1323-1523 K, respectively.
2. Below 1223 K the recombination possibly occurred for closely positioned C and Si Frenkel pairs and no long-range migration is essential. Nearly three-fourths of defects induced by neutron irradiation were recovered by this mechanism. In addition, at 1323-1523 K, recombination of slightly separated C Frenkel pairs and more long-range migration of Si interstitials would occur for PureBeta-SiC and CVD-SiC specimens. Migration of both vacancies should restricted up to ~1523 K.
3. Comparing to hexagonal α-SiC, high purity β-SiC was recovered more quickly in the lower annealing temperature range less than 873 K, particularly less than 573 K.

Chapter 4:

Defect-annihilation behavior of neutron-irradiated SiC ceramics densified by liquid-phase-assisted method after post-irradiation annealing

Numerous studies on the recovery behavior of neutron-irradiated high-purity SiC have shown that most of the defects formed in it are annihilated by post-irradiation annealing if the neutron fluence is less than 1×10^{26} n/m^2 (>0.1 MeV) and the irradiation is performed at temperatures lower than 973 K. However, the recovery behavior of SiC fabricated by the nanoinfiltrated and transient eutectic phase (NITE) process is not well understood. In this chapter, the effects of secondary phases on the irradiation-related swelling and recovery behavior of monolithic NITE-SiC after post-irradiation annealing were studied. As explained in Chapter 2, the NITE-SiC specimens were irradiated in the BR2 reactor at fluences of up to 2.0–2.5×10^{24} n/m^2 (E > 0.1 MeV) at 333–363 K and the results showed that the specimens were swelling up ~1.3%, and the value is 0.1% higher than the increase seen in concurrently irradiated high-purity SiC.

The recovery behaviors of the specimens after post-irradiation thermal annealing were examined using a precision dilatometer; the specimens were heated at temperatures up to 1673 K using a step-heating method. The recovery curves were analyzed using a first-order model, and the rate constants for each annealing step were obtained to determine the activation energy for volume recovery. The experiment technique and analyzing data are precisely similar with previous chapter, which has been conducted on high purity SiC.

4.1 Introduction

Since NITE-SiC composites have been proposed as candidate materials for fusion reactor components in the ITER-broader approach (BA) activities, in an attempt to enhance plant efficiency, the behavior of monolithic SiC constituting the matrix of such composites, should be explained through post-irradiation annealing. Thus, neutron-irradiated monolithic NITE-SiC specimens containing sintering additives in different amounts were annealed at temperatures of up to 1673 K in a precision dilatometer, in order to scrutinize their recovery behaviors. We could also estimate the stability of the defects induced by neutron-irradiation using the thermal annealing up to high-temperatures. Further, the effects of the secondary phases in the two specimens containing different amounts of additives on their recovery behaviors were examined and compared with that of high-purity SiC.

4.2 Experimental procedure

4.2.1 Materials

Two types of liquid-phase sintered SiC ceramics with ultrafine (average particle size of 30 nm) β-SiC powder (Marketech International Inc., USA) prepared by the NITE process at Kyoto University were examined. The specimens were prepared such that they contained the additives in two different volumes, i.e., they contained either 12 wt% or 18 wt% of yttria (Kojundo Chemical Industries Ltd., Japan), silica (Kojundo Chemical Industries Ltd., Japan)), and alumina (Sumitomo Chemical Industries Ltd., Japan). In this chapter, these samples are referred to as NITE-A and NITE-B, respectively.

4.2.2 Neutron irradiation and post-irradiation annealing

NITE-A and NITE-B were simultaneously neutron-irradiated in the BR2 reactor of SCK·CEN in Belgium at fluences of 2.0–2.5 × 10^{24} n/m^2 (E>0.1 MeV, 0.20–0.25 dpa). The temperature of the specimens was kept at 333–363 K, and the duration of irradiation was 60 days. Before being subjected to post-irradiation annealing, the irradiated specimens were cut into half; the dimensions of the resulting halves were 25 mm × 1.5 mm × 2 mm.

The recovery in length after post-irradiation annealing was examined using a precision dilatometer (DIL 402C, NETZSCH, Germany). The changes in the lengths of the irradiated specimens were measured continuously in a He atmosphere, from room temperature to 1673 K, in a step-wise manner at intervals of 50 K and kept for 6 h at each step.

4.2.3 Data analysis

After the completion of the annealing process, the crystalline phases of the specimens were determined by X-ray diffraction (XRD) measurements performed at RT on a Philips PW-1700 diffractometer equipped with a graphite monochromator and a CuKα source (40 kV, 40 mA). The microstructures of the annealed specimens were observed using scanning electron microscopy (SEM, Hitachi S-3500). In addition, to determine the compositional profiles of the specimens after annealing, a JEOL JXA-8500F electron probe micro analyzer (EPMA) equipped with wavelength dispersive spectrometers was used at 15 kV/50 nA. The rate of volume shrinkage and the corresponding activation energy were estimated by assuming a first-order reaction and applying the Arrhenius equation as described previously.

4.3 Conclusions

The NITE-SiC specimens containing the total amount of 12 wt% or 18 wt% of alumina, yttria and silica as sintering additives swelled by ~1.3% after neutron irradiation in the BR2 reactor; the irradiation was performed at fluences of 2.0–2.5 × 10^{24} (E > 0.1 MeV) at 333–363 K. An analysis of their recovery behaviors following post-irradiation annealing at temperatures of up to 1673 K was conducted. The results can be summarized as follows;

1. The NITE-SiC specimens swelled slightly more than those of high-purity SiC.
2. The NITE-A specimen recovered completely at ~1573 K; however, it started to shrink at 1673 K, owing to the volatilization of the oxide phases. The NITE-B specimen, on the other hand, did not recover completely, since a secondary phase (YAG) underwent crystallization during the annealing process.
3. The recovery of the NITE-SiC specimens was based mainly on the recombination of C and Si Frenkel pairs, which were very closely sited or slightly separated at temperatures lower than 1323 K as well as the recombination of slightly separated C Frenkel pairs and the migration of C and Si interstitials at temperatures lower than 1573 K; these processes are essentially similar to those responsible for the recovery of pure SiC.

Chapter 5:

Radiation damage analysis in SiC microstructure by transmission electron microscopy

Chapter 2 explains that several types of SiC and SiC_f/SiC composites were swelled owing to neutron-induced Frenkel defects, and these defects profoundly influence the microstructure of SiC. Meanwhile, in Chapter 3 and 4, recovery behaviors have been investigated for high purity SiC and SiC containing sintering additives, respectively, and the mechanism of recombination of interstitial atoms and vacancies has been understood clearly. However, it is inadequate not to perform an experiment regarding to the microstructure by TEM. As a result, it can verify the atomic arrangement after neutron irradiation and post-irradiation annealing of SiC. In this chapter, similar specimens that have been used through previous chapters were observed by TEM, except for SiC_f/SiC composite specimens.

The crystal lattice of all specimens (unirradiated, irradiated and post-irradiated annealing) were observed under a Hitachi H-9000 instrument with accelerating voltage of 300 kV. Several photos have been taken and the films were developed and scanned, consecutively. In the case to take a clear figure by using a high resolution electron microscopy (HREM), figures were captured directly from a TV screen using a LightCapture software. Figures of all specimens were compared and analyzed.

5.1 Introduction

The purpose of this study is to evaluate an atomic micrograph using high purity SiC and SiC containing sintering additive by TEM after neutron-irradiation at intermediate fluence with low irradiation temperature. Irradiated specimens after annealing which showed recovery also has been observed to investigate the microstructure changes and to clarify the defects stability. Further, the effects of secondary phase on atomic arrangement of SiC after neutron irradiation and post-irradiation annealing were discussed.

5.2 Experimental procedure

5.2.1 Materials

In this chapter, high purity β-SiC polycrystals, PureBeta-SiC, and CVD-SiC were used. Furthermore, SiC that contained either 12 wt% or 18 wt% of alumina, silica and ytrria as sintering additives were applied in this research, too. Specimens were simultaneously neutron-irradiated in the BR2 reactor of SCK·CEN (Belgium) at fluences of 2.0–2.5 × 10^{24} n/m^2 (E>0.1 MeV, 0.20–0.25 dpa). The irradiation temperature of the specimens was 333–363 K and the duration of irradiation was 60 days. For post-irradiation annealing experiments, irradiated specimens from both types of SiC were annealed from RT to 1673 K, in a step-wise manner at intervals of 50 K and were kept for 6 h at each step. Each of the specimens with different conditions (unirradiated, irradiated and post-irradiation annealed) was observed by transmission electron microscopy (TEM).

5.2.2 TEM observation

The transmission electron microscope used in the present study was Hitachi H-9000 instrument (Fig. 7) at an accelerating voltage of 300 kV with filament current of 8 μA in vacuum (1 x 10^{-7} torr and 0.5 x 10^{-5} Pa for the specimen chamber and an ion pump, respectively) to investigated the microstructure of the unirradiated and irradiated specimen. Further, high-resolution electron microscopy (HREM) technique was used to observe atomic configuration of each specimen.

5.3 Conclusions

Microstructures of unirradiated, irradiated and post-irradiation annealed of PureBeta SiC, CVD-SiC, NITE-A and NITE-B were investigated by transmission electron microscopy (TEM) with accelerating voltage of 300 kV. Further, high-resolution electron microscopy (HREM) technique was used to observe atomic configuration of each specimen. The results were summarized as follows;

1. Black spot defects or dislocation loops have not been observed for all specimens after moderate neutron irradiation at low irradiation temperature.
2. Black spots and/or dislocation loops were found in SiC grains of PureBeta SiC and CVD-SiC after post-irradiation annealing due to the surviving interstitials tend to agglomerate by themselves rather than recombine with vacancies.
3. From HREM images, no significant difference of atomic arrangement between unirradiated and irradiated specimen.

4. NITE-A and B were swelled mostly due to the presence of point defects and amorphization of YAG phase after the neutron irradiation. No significant effect of sintering additives on atomic orientation of SiC was observed after the neutron irradiation, since they were mostly formed as amorphous YAG outside SiC grains.
5. Anomaly shape of YAG grains were found in NITE-A and B when amorphized YAG phases underwent recrystallization and combined with other crystalline YAG by post-irradiation annealing.

Chapter 6:

Conclusions

6.1 Thesis conclusions

In the order to evaluate the fundamental neutron irradiation effects, seven SiC-based materials were chosen in this study. They can be categorized into two groups, monolithic SiC ceramics and SiC_f/SiC composites. Group SiC consists of PureBeta-SiC (β-SiC), CVD-SiC and NITE-SiC, and group SiC_f/SiC composites consist of the composites fabricated by CVI, NITE and EPD processes. All the specimens were concurrently neutron-irradiated in the BR2 reactor in Belgium up to a fluences of 2.0~2.5×10^{24} n/m^2 (E>0.1 MeV, 0.20~0.25 dpa) at 333-363 K, and they were exposed for 60 days. Firstly, macroscopic lengths and lattice parameters were measured. Then recovery behavior of high purity SiC and SiC contained sintering additives were investigated. Finally, the microstructures and atomic order of irradiated specimens and annealed specimens were analyzed by TEM and HREM. The overall conclusions of the present research consisted of four parts (Chapter 2-5) were summarized as follows;

Chapter 2: Neutron Irradiation Swelling of monolithic SiC ceramics and SiC_f/SiC composites

Changes in macroscopic lengths and lattice parameters of monolithic SiC ceramics and SiC_f/SiC composites fabricated by different processes were measured. It is important to distinguish neutron irradiation effects on high purity SiC and SiC contained sintering additives.

Changes in the macroscopic lengths of PureBeta-SiC and CVD-SiC were similar because of the high purity SiC matrix and it is assumed that both of these materials have common responses of neutron irradiation. In addition, those SiC ceramics showed slightly smaller swelling than the SiC ceramics with oxide sintering additives. It is noted that the presence of sintering additives gave difference in swelling which is slightly exceed from the high purity SiC. The group of SiC_f/SiC composites showed less swelling than the group of monolithic SiC ceramics due to smaller swelling of SiC fibers and presence of SiC fibers gives reinforcement to the SiC matrix. Within various SiC_f/SiC composites measured in this study, swelling of the composites fabricated by EPD method was the smallest.

Chapter 3: Recovery behavior of high purity cubic SiC polycrystals by post-irradiation annealing up to 1673 K after low temperature neutron irradiation

In this chapter, changes in macroscopic lengths of PureBeta SiC and CVD-SiC were examined by post-irradiation thermal annealing using a precision dilatometer up to 1673 K with a step-heating method. The specimens were held at each temperature step for 6 h and the change in length of the specimen was recorded continuously during each isothermal annealing step from 373 K to 1673 K with 50 K increments. The recovery curves were analyzed with the first order model, and rate constants at each annealing step were determined. The recovery behaviors were started between 333-363 K, which was similar with irradiation temperature and complete at ~1573 K. Due to medium neutron fluence at a low irradiation temperature, it was assumed that the both specimens contained primarily point defects or point-like small clusters. Therefore, we clarified that the mechanism of defects annihilation is mostly occurred by recombination of vacancies and interstitial atoms. From XRD profile, shifted irradiated peaks were returned to the nearly the same positions as those of the pre-irradiated specimens after the post-irradiation annealing. It is learnt that recovery of defects induced by neutron irradiation in high purity β-SiC have four stages with different activation energies. Below 1223 K the recombination possibly occurred for closely positioned C and Si Frenkel pairs and no long-range migration is essential. Nearly three-fourths of defects induced by neutron irradiation were recovered by this mechanism. In addition, at 1323-1523 K, recombination of slightly separated C Frenkel pairs and more long-range migration of Si interstitials would occur for PureBeta-SiC and CVD-SiC specimens.

Chapter 4: Defect-annihilation behavior of neutron-irradiated SiC ceramics densified by liquid-phase-assisted method after post-irradiation annealing

The recovery behaviors of SiC contained sintering additives either 12 wt% (NITE-A) or 18 wt% (NITE-B) of yttria, silica and alumina were examined using a precision dilatometer by post-irradiation thermal annealing; the specimens were heated at temperatures from RT up to 1673 K using a step-heating method. The experiment technique and analyzing data are precisely similar with previous chapter. It can be seen intelligibly that the recovery commenced at the annealing temperature close to the irradiation temperature (~363 K) for both specimens. The NITE-A specimen recovered completely at ~1573 K; however, it started to shrink at 1673 K, owing to the volatilization of the oxide phases. The NITE-B specimen, on the other hand, did not recover completely, since a secondary phase (YAG) underwent crystallization during the annealing process. The recovery of the NITE-SiC specimens was based mainly on the recombination of C and Si Frenkel pairs, which were very closely sited or slightly separated at temperatures lower than 1323 K as well as the recombination of slightly separated C Frenkel pairs and the migration of C and Si interstitials at temperatures lower than 1573 K; these processes are essentially similar to those responsible for the recovery of pure SiC.

Chapter 5: Radiation damage analysis in SiC by transmission electron microscopy

The crystal lattice of PureBeta, CVD-SiC, NITE-A and NITE-B (unirradiated, irradiated and post-irradiated annealing) were observed under transmission electron microscopy (Hitachi H-9000) with accelerating voltage of 300 kV. Several photos have been taken and the films were developed and scanned, consecutively. High resolution electron microscopy (HREM) was used to obtain atomic configuration of each specimen. Black spot defects or dislocation loops have not been observed for all specimens after moderate neutron irradiation at low irradiation temperature. However, those black spots and/or dislocation loops were found in SiC grains of PureBeta SiC and CVD-SiC after post-irradiation annealing due to the remaining interstitials that were not annealed out tend to agglomerate by themselves rather than recombine with vacancies. Furthermore, HREM images showed that no significant difference of atomic arrangement between unirradiated and irradiated specimen due to intermediated neutron fluence at low irradiation temperature. It is noted that NITE-A and B were swelled mostly due to the presence of point defects and amorphization of YAG phase after the neutron irradiation. No significant effect of sintering additives on atomic orientation of SiC was observed after the neutron irradiation, since they were mostly formed as secondary phase (amorphous YAG) outside SiC grains. Further, anomaly shape of YAG grains were found in NITE-A and B when amorphized YAG phases underwent recrystallization and combined with other crystalline YAG by post-irradiation annealing. At the same time, recombination of interstitials atoms and vacancies occurred and induced volume contraction for both specimens.