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Neutron Irradiation Induced Damage of Silicon Nitride-Related Ceramics and Their Recovery Behavior

Areerak Rueanngoen

Chapter 1: Introduction

The purpose for this chapter is to provide a brief but thorough overview of silicon nitride and SiAlON ceramics, as well as neutron irradiation behavior of crystalline matter. First, the crystal structure and characteristics of silicon nitride and SiAlON ceramics are discussed, highlighting the concept of ideal and imperfect crystal structure. Second, fusion reactor materials, the condition and radiation damage in ceramics materials are discussed. Third, the related researches were reviewed to clarify the problems remained. Finally, the purpose of this study is defined, and contents of the thesis are given.

Purpose of this research

Silicon nitride-related ceramics are one of candidate materials for future fusion applications due to its excellent thermal and mechanical properties at high-temperatures. Up to now, these ceramics have not been applied in any part of fusion applications because their neutron irradiation effects shave been still unclear. Furthermore, current studies were only performed for specimens after severe neutron irradiation. Basically, the defects generation rate depends on neutron flux, and the defects migration depends on irradiation temperature. In addition, defects generation in of silicon nitride by neutron irradiation was reported by Akiyoshi and Yano [38]. Swelling of silicon nitride increased with increasing neutron fluence and decreased with increasing irradiation temperature because high temperature enhances the defects recombination. Most of reports on neutron irradiation effects of silicon nitride-related ceramics have been performed under high neutron fluence. Thus, large amount of defects were generated, and these defects were not recovered completely due to the agglomeration of defects during thermal annealing. Up to now, the basis of thermal annealing behavior of these ceramics has not been still undiscovered. We expected that small amount of point defects will be generated under the low-dose neutron irradiation of silicon nitride-related ceramics. As a result, it is easier to study behaviors of neutron induced defects and the phenomenon of defects recovery of silicon nitride-related ceramics will be discovered. Finally, we will obtain the fundamentals of defects behavior of irradiated silicon nitride-related ceramics at low neutron fluence irradiation. It will be a meaningful to apply silicon nitride-related ceramics for the future fusion applications.

In order to clarify the basic neutron irradiation behavior of silicon nitride-related ceramics, the dimensional stability, thermal stability of as-irradiated materials and microstructural changes of low-dosed neutron irradiated silicon nitride and SiAlON polymorphs were investigated. Next, the recovery behavior of volume expansion was precisely observed to evaluate the thermal stability of induced defects. In addition, microstructural change was investigated. Finally, the insight on the effects of the crystal structure of silicon nitride-related ceramics on their irradiation response will be addressed based on the obtained results.

The concrete purposes of the present research can be defined in each step of experiment separated into 4 Chapters (Chapter 2-5).

Chapter 2: Effects of neutron irradiation on polymorphs of silicon nitride and SiAlON ceramics

In this chapter, macroscopic and lattice parameter changes of low-dose neutron irradiation silicon nitride and SiAlON polymorphs were observed. In addition, microstructural changes were investigated to evaluate the irradiation stability of this kind of ceramics.

Up to present, reports discussing neutron irradiation effects on silicon nitride and SiAlON ceramics are limited, especially at low-dose neutron irradiation. In addition, almost no data is available on effects of their polymorphs. Heavily neutron irradiation induces a large amount and several kinds of defects in materials. So that is difficult to analyze the irradiation behavior. Nowadays, neutron irradiation effects of silicon nitride-related materials are still unclear. In this chapter, α- and β-Si_3N_4 and

SiAlON ceramics were prepared by hot-pressing to evaluate neutron irradiation effects. Si_3N_4 and SiAlON ceramics were neutron-irradiated in the Japan Materials Testing Reactor up to a fluence of 8.5×10^{24} n/m^2 (E > 0.1 MeV) at 563 K. Microstructural changes of irradiated-Si_3N_4 and SiAlON ceramics were investigated using a transmission electron microscope.

2.1 Introduction

Safe, economically and environmental-friendly fusion power reactors have been proposed as a potential solution to the global energy crisis. New materials development is a key issue facing the design and operation of successful fusion reactors. The safe and economical operation of these reactors will rely deeply on the performance of structural materials, specifically their mechanical properties and dimensional stability in harsh irradiation environments and at high temperatures.

Ceramic materials are attractive for fusion applications because of their excellent thermal and mechanical properties, such as high thermal shock resistance and high mechanical strength. From the beginning of the material development for fusion applications, ceramic materials (e.g., Al_2O_3, $MgAl_2O_4$, Si_3N_4, MgO, SiAlONs, and SiC) have been expected to be suitable materials [1]. Ceramics with more complex crystal structures and stoichiometries, such as $MgAl_2O_4$, Si_3N_4, and silicon oxynitride, appear to resist void-induced expansion better than simple oxides [2]. Silicon nitride and related ceramics are excellent engineering ceramics and of interest for nuclear applications because of their excellent mechanical and other properties.

Silicon nitride and related ceramics include a wide range of compounds, which are categorized into two basic crystal structures, α- and β-Si_3N_4. The excellent strength and thermal shock resistance of Si_3N_4 and SiAlONs make them possible candidate materials for fusion applications such as magnet insulators, radio frequency (RF) transmission windows, near-first-wall components, and rotor blades of turbomolecular pumps [1-6]. Up to present, numerous reports have investigated SiC and SiC_f/SiC composites for fusion applications, and not so many researches were conducted for other ceramics. Although silicon nitride-related ceramics are alternatives for this field due to their excellent properties, their irradiation effects have not been thoroughly investigated, and then it should be studied in more details.

One requirement for materials to be used in fusion applications is dimensional stability under irradiation. First, volume swelling of silicon nitride (mostly β-type) and SiAlONs after neutron irradiation up to a fluence of 2.8×10^{25} n/m^2 (E > 0.1 MeV) at 1015 K were reported to be 0.3~0.4 and 0.5 %, respectively [7]. Hurley and Cocks [8] reported that both Si_3N_4 and SiAlON irradiated up to 3×10^{25} n/m^2 by neutrons showed slight line broadening in x-ray diffraction (XRD) profiles and unit cell parameter changes of less than ±0.2%. Next, neutron-induced volume swelling of ~1.0% for the Si_3N_4 irradiated to 2.2×10^{26} n/m^2 (E > 0.1 MeV) at 680 or 815 K was reported [5]. In addition, microstructural analysis of β-Si_3N_4 after heavy neutron irradiation in fluence up to ~2.0×10^{26} n/m^2 at 925 and 1100 K has been reported [9]. Hazelton et al. [3] reported that silicon nitride and SiAlON ceramics, irradiated up to a fluence of 1.0×10^{24} n/m^2 at 323 K, exhibited good thermal shock resistance and low dielectric loss factor. They concluded that silicon nitride and SiAlON ceramics appeared to be excellent options for RF window material.

Basically, radiation effects are influenced by crystal structures of compounds. α-Al_2O_3 and AlN showed larger swelling and degradation of thermal diffusivity than β-Si_3N_4 and β-SiC after the irradiation more than 1×10^{26} n/m^2 [10]. In addition, macroscopic length expansion of Si_3N_4 was roughly one-half of that of SiC after the same irradiation conditions (2.8-4.2 × 10^{26} n/m^2, 753-1003 K) [11]. High-resolution transmission electron microscope (HREM) observation of heavily neutron-irradiated Si_3N_4 revealed the presence of dislocation loops laid parallel to the *c*-axis [12-14]. Furthermore, HREM observation of irradiated β-Si_3N_4 after post-irradiation annealing showed bubbles of He generated by transmutation of ^{14}N[15].

At present, silicon nitride and related ceramics are not primary structural material candidates for fusion reactors, but are still interesting materials in fusion devices. However, reports on neutron irradiation effect on silicon nitride and SiAlON ceramics are still limited, particularly to relatively low neutron fluencies. Furthermore, differences in each polymorph have not been previously investigated. In this chapter, changes in macroscopic length and lattice parameters of silicon nitride and SiAlON ceramics were measured after relatively lower fluence irradiation up to 8.5×10^{24} n/m^2 (E > 0.1 MeV) at 563 K to clarify basic irradiation effects on each polymorph. In addition, microstructural defects in these specimens were observed by HREM.

2.2 Conclusions

Sintered Si_3N_4 and SiAlON ceramics, both α- and β-phases, were examined after concurrent irradiation up to 8.5×10^{24} n/m^2 (E > 0.1 MeV) at 563 K in JMTR. Changes in their macroscopic lengths and lattice parameters caused by the neutron irradiation were investigated along with their microstructural changes. The conclusions are as follows:

1) Changes in macroscopic length expansion of α- and β-SiAlON ceramics and α-Si_3N_4 were similar and almost double those of β-Si_3N_4.
2) Lattice parameter increased on both axes for both α- and β-Si_3N_4. On the other hand, for SiAlON ceramics, the *a*-axis increased while the *c*-axis shrank in both phases. However, the unit cell volume of both SiAlONs slightly expanded.
3) The macroscopic volume changes calculated from the macroscopic length changes were slightly larger than the unit cell volume changes calculated from the lattice parameter changes in the four examined specimens.
4) HREM observations found no voids, dislocation loops, or grain boundary microcracks in all examined ceramics; α- and β-Si_3N_4, and α- and β-SiAlON after the neutron irradiation.

Chapter 3: Recovery behavior of neutron irradiated α and β-SiAlON ceramics by thermal annealing up to 1473 K

In this chapter, thermal annealing behavior of irradiated-SiAlON ceramics was investigated. In the previous chapter, it was clarified that the low dose neutron irradiation on the SiAlON ceramics induced only point defects without formation of dislocation loops or grain boundary microcracks in the as-irradiated specimens. In this chapter, in order to clarify the defects behavior of SiAlON ceramics, the unirradiated and irradiated-SiAlON ceramics, both α- and β-polymorphs, were continuously isochronally and isothermally annealed from 423 to 1473 K in a precision dilatometer. Then recovery behavior of radiation induced defects was investigated. Finally, the activation energy of defects recovery was estimated.

3.1 Introduction

Ceramics are generally well-known as high temperature materials with insulating property. Ceramics can withstand high temperature with high mechanical strength, low thermal expansion, high thermal shock resistance, and corrosion resistance. Due to their excellent properties, ceramics are also expected to be used in new generation fission and fusion reactors. One of the key issues to achieve fusion power reactor is to develop materials that can withstand severe conditions like high temperature and severe neutron damage. The candidate ceramics for fusion applications include Al_2O_3, $MgAl_2O_4$, Si_3N_4, MgO, SiC and SiAlON [1-4].

SiAlON ceramics are one of silicon nitride-related ceramics which have combined good properties of silicon nitride and aluminum oxide. There are two well-known SiAlON phases; α and β. α-SiAlON is a solid solution of α-Si_3N_4 and Al_2O_3, and is formed by the partial replacement of Si-N bond with Al-N and Al-O bonds. The general formula of α-SiAlON, consisting of four "Si_3N_4" units, can be given as $M_xSi_{12-m-n}\,Al_{m+n}O_nN_{16-n}$, where M is one of cations such as Li, Mg, Ca, Y and rare earth elements to compensate charge unbalance and to stabilize the α-SiAlON crytal structure. The "x" is the solubility of the M, while m and n are the numbers of Al-N and Al-O bonds substituting for Si-N bonds, respectively. It has a trigonal crystal structure with the P31c space group. For comparison with the β-phase, hexagonal lattice parameters are used in this study. On the other hand, β-SiAlON is structurally derived from β-Si_3N_4 by the equivalent substitution of Al-O for Si-N and its general formula can be written as $Si_{6-z}Al_zO_zN_{8-z}$, where z represents the number of Si-N bonds replaced by Al-O bonds, and 0<z<4.2 [5, 6]. It has a hexagonal crystal structure of $P6_3$ or $P6_3/m$ space group. β-SiAlON contains the open channels parallel to the c-axis, while α-SiAlON contains the closed channel (large interstices). Bulk α-SiAlON is generally consisted of equi-axed grains, resulting in high hardness, while the β-SiAlON is consisted from elongated grains, and possess good toughness and high strength. These ceramics also have high thermal conductivity and high thermal shock resistance [7]. Therefore, these ceramics are reported to be excellent candidate materials for RF window in fusion reactors [2]. CVD-diamond is used as RF windows of the EC apparatus of JT60 [8], however these ceramics still have potentials for functional or structural applications for future fusion reactors. Up to present, only limited numbers of researches on neutron irradiation effects on SiAlON or Si_3N_4 ceramics have been reported [2, 9-13].

The type and amount of the defects induced by neutron irradiation depend on the neutron flux, energy spectrum of neutrons, irradiation fluence, irradiation temperature and microstructure, and crystal structure. When crystalline materials are irradiated by high energy neutrons, the neutrons will collide with atoms on lattice sites and transfer energy to them. If energy higher than the threshold displacement energy is received by an atom, it will be removed from its lattice site, then move to an interstitial site, and leave a vacancy. Normally, interstitials and vacancies are produced in pairs, as Frenkel pairs. Interstitials and vacancies can migrate to form interstitial-type dislocation loops or voids, respectively. These defects induce property change of materials such as degradation of mechanical and thermal properties, and volume change [14]. Basically all of these point defects could be removed by heat-treatment to such a temperature that individual defects, vacancies and interstitials gain sufficient energy for dissociation and migration, and finally annihilate each other by recombination.

Consider the number of Frenkel pairs present in a crystal after a given irradiation. The collision of neutron to atoms was randomly happened, thus the distribution of energy given to each atom is speeded. So circumference of interstitial atoms should be different in such kind of matter. Basically, the first stage of defects recombination was governed by close Frenkel pairs. They are easy to annihilation in the lattice. Sufficiently close pairs, which have been survived the thermal spike and are thermodynamically meta-stable at the irradiation temperature, could have very low activation energy for recombination. Furthermore, there could be many different activation energies for pair-recombination, varying with the separation of two defects and/or atomic configuration of defects. The later recovery stage was occurred by the separated Frenkel pairs. These defects are displaced far away from their normal positions by collision of high-energy neutrons or primary or secondary or following knock-on atoms.

If the radiation damage were introduced in such a way as to consist of a fairly low concentration of fairly well-isolated interstitials and vacancies, it would seem that the annealing process would correspond closely to a diffusion-limited chemical reaction, in which the reacting species were vacancies, interstitials, and dislocations [15].

Neutron irradiation effect on reaction-sintered silicon nitride (Si_3N_4) was firstly reported by Rover and Hopkins [16], such that the linear swelling was 0.07 % after neutron irradiation of ~3.5 x 10^{24} n/m^2 at 873 K. Volume swelling of ~1.0 % was reported for Si_3N_4 after high-dose neutron irradiation up to a fluence of 2.2 x 10^{26} n/m^2 (E > 0.1 MeV) at 680 and 815 K [17]. It was reported that Si_3N_4 and SiAlON ceramics showed volume swelling of 0.3 and 0.5 %, respectively, due to the neutron irradiation up to a fluence of 2.8 x 10^{25} n/m^2 (E > 0.1 MeV) at 1015 K [9]. Akiyoshi et al. recently reported that linear swelling of Si_3N_4 was about half of that of SiC and much smaller than those of Al_2O_3 and AlN after the irradiation up to 10^{26} n/m^2 [18]. Furthermore, they found that the small recovery of macroscopic length of β-Si_3N_4 started at around irradiation temperature but large part of the swelling did not recover after annealing at 1673 K in the case of heavily irradiated specimens [11]. On the other hand, the macroscopic length recovery of AlN started around 1273 K, which was much higher than the irradiation temperature (563 K). These irradiation and recovery responses should be related to their crystal structures and the type of induced defects (e.g., Frenkel pairs, dislocation loops or voids). High-dose neutron irradiation induced large amount of Frenkel pairs, which migrate easily to form dislocation loops or voids, depending on temperature during irradiation or post-irradiation annealing.

So, the annealing behavior of heavily irradiated specimens should be more complicated.

In this chapter, the recovery phenomenon of low-dose neutron-irradiated SiAlON ceramics, α- and β-polymorphs, following thermal annealing is studied. The interactions of high energy neutrons with atoms induce a variety of crystalline defects, due to the different crystal structures and different dopant or stabilizing elements of each polymorph. Macroscopic length change due to thermal annealing up to 1473 K was measured to clarify the recovery behavior of neutron irradiation induced defects in α- and β-SiAlON, and effects of polymorphs on irradiation response are discussed.

3.2 Conclusions

Recovery behavior of neutron-irradiated SiAlON ceramics after lower fluence and lower temperature (563 K) irradiation was studied in this chapter. The macroscopic length changes of neutron-irradiated α- and β-SiAlON were precisely measured by *in-situ* dilatometry. The recoveries of macroscopic length of α- and β-SiAlON started slightly above the irradiation temperature, and continued up to 1473 K. In addition, for α-SiAlON, recovery rate decreased at temperature ~1123-1273 K, might be related to the presence of the Sr and/or Y interstitials. These interstitial atoms may need higher energy to annihilate in appropriate lattice sites. There were at least two stages of recovery up to 1473 K for both SiAlONs. Activation energies of macroscopic volume recovery of α- and β-SiAlON at lower temperature range (first order estimation) were 0.09 and 0.06 eV, respectively, and those of the higher temperature range (second order estimation) were 0.49 and 0.33 eV, respectively. The activation energies of α-SiAlON were slightly greater than these of β-SiAlON. At thermal annealing temperatures lower than 1073 K, the recombination occurred easily, which may be caused by annihilation of closely-separated Frenkel pairs. On the other hand, at high temperature (>1123 K), the recovery may be governed by the recombination of separated Frenkel pairs along with migration of not only interstitial atoms but also vacancies.

Chapter 4: Analysis of recovery process of low-dose neutron irradiation-induced defects in silicon nitride ceramics by thermal annealing

In this chapter, thermal annealing behavior of neutron-irradiated silicon nitride ceramics was investigated. Base on the results of the previous chapter on SiAlON ceramics, it was clarified that low-dose neutron irradiation on Si_3N_4 and SiAlON ceramics induced only point or point-like defects without formation of dislocation loops or grain boundary microcracks in these specimens. In addition, the macroscopic length recovery behavior of α- and β-SiAlON by isochronal and isothermal annealing clarified that recovery processes were governed by the recombination of different type of Frenkel pairs and depended on its polymorph. Two stages of the recovery process were considered between the irradiation temperature and 1473 K. In this chapter, the macroscopic length of α- and β-Si_3N_4 was observed by continuous isothermal and isochronal annealing up to 1473 K, which is the same condition as Chapter 3. The recovery tendencies of these ceramics were compared to those of the results of SiAlON polymorphs. Finally, the activation energies at each stage of defects recovery were calculated and compared to those of α- and β-SiAlON.

4.1 Introduction

Dimensional stability and stability of mechanical and thermal properties under neutron irradiation are key factors for selecting materials in nuclear applications. In recent studies, it was reported that silicon nitride possessed greater dimensional stability than other ceramics such as SiC, Al_2O_3 and AlN [1, 2]. Silicon nitride-related ceramics are candidates for fusion applications, such as; magnetic insulators, radio frequency transmission windows, near first-wall components and rotor blades of turbomolecular pump (TMP) for vacuum systems [3-8]. At present, these ceramics are not candidates of primary structural materials for fusion reactors. However, they are still interesting materials for fusion devices due to their excellent mechanical and thermal properties. Ioki et al. reported the rotor blades of ceramic TMP were made from silicon nitride has been developed for fusion reactor environments [9]. The ceramic TMP system is subjected to a neutron flux as high $\sim 10^{17} n/m^2 s$ when it is installed in a divertor module near to the core plasma. Up to present, however the data of irradiation effects on these ceramics such as dimensional stability, reduction in physical and mechanical properties, are not sufficient.

High energy neutron irradiation induces several property changes in materials. The distance distribution of interstitials from their appropriate vacancies and the population of defects will depend on irradiation temperature, neutron flux, neutron energy, fluence and materials. The short-range recombination and that of long-range of point defects are important processes affecting the recovery of properties by thermal annealing for low-dose irradiated materials. Annealing can remove some irradiation induced effects, and then physical, thermal, and mechanical properties of irradiated materials are restored. Annealing works on neutron-irradiated ceramics were reported relatively large number of papers [1, 10-15], however it still remained as unclear for silicon nitride-related ceramics.

Akiyoshi and Yano [2, 11] reported swelling of four kinds of ceramics after neutron irradiation up to 2.8-7.3 $\times$ 10^{26} n/m^2 at 775-1039 K. They reported that α-Al_2O_3 and AlN showed larger swelling than β-SiC and β-Si_3N_4. This difference was discussed based on the view point of their crystal structures. In the case of Al-based materials, the closest-packed plane is the (0001) basal plane and interstitial loops are piled up in the basal planes without restriction of number density, and then the anisotropy in the *c*-axis direction and *a*-, *b*-axis directions is progressed. It finally causes intergranular microcracks, and causing large volume swelling. In contrast, for Si-based materials, closest-packed planes are cubic {111} and hexagonal $\{10\bar{1}0\}$ planes of β-SiC and β-Si_3N_4, respectively. Interstitials loops are induced under the restriction of growth or nucleation of new loops, due to the topological interaction of extra planes. This situation restricts the accumulation of individual interstitials, and then forced recombination with vacancies may occur. Therefore, volume swelling of these crystals is limited. However, the tendency of macroscopic length recovery is different, may be due to their different crystal structures. Moreover, atomic bonding nature of the four kinds of compounds is different. That should affect the overall irradiation response. Furthermore, macroscopic length changes of β-Si_3N_4 irradiated up to a fluence of 2.8 $\times$ 10^{26} n/m^2 at 753 K and 4.2 $\times$ 10^{26} n/m^2 at 1003 K were not completely recovered by thermal annealing up to 1773 K [13]. The authors of this paper supposed that, during thermal annealing, formation of voids or difficulty of recovery of point defects/loops should be the reason of incomplete length recovery. This assumption was supported by HREM observation [16], i.e., dislocation loops were frequently revealed in heavily irradiated β-Si_3N_4 specimens. Up to present, neutron irradiation response and recovery behavior of silicon nitride-related ceramics are still remained unclear. In order to study their recovery behavior, exploration of the irradiation response of low-dose neutron-irradiated materials was initiated as it would be easier to clarify the stability of point defects under these conditions.

In previous chapter [17], macroscopic length recovery of α- and β-SiAlON by isochronal and isothermal annealing were measured to clarify defects recovery behavior during thermal annealing. It was reported that recovery processes were governed by the recombination of different type of Frenkel pairs and depended on its polymorph. In this chapter, two polymorphs of silicon nitride ceramics, those are belonging to resemble crystal structures with polymorphs of SiAlON, were selected to study recovery behavior of defects in different polymorphs, and compared to those of α- and β-SiAlON. The specimens were neutron-irradiated up to a fluence of 8.5×10^{24} n/m^2 (E > 0.1 MeV) at 563 K, same as the previous chapters [17, 18]. The macroscopic length recovery was measured in-situ by continuous thermal annealing up to 1473 K in order to clarify the defect recovery process. Furthermore, the differences in length recovery tendencies were discussed from the viewpoints of polymorphs and compounds.

4.2 Conclusions

Neutron irradiated α- and β-Si_3N_4 ceramics were isochronally and isothermally annealed up to 1473 K. Changes in macroscopic length were precisely measured, and compared with those of α- and β-SiAlON ceramics. Macroscopic length of α- and β-Si_3N_4 was mostly recovered to their original length. It suggested that almost all induced defects were recovered. The recovery rate tendencies of α-Si_3N_4 and α-SiAlON resembled each other, as did those of β-Si_3N_4 and β-SiAlON. However, recovery characteristics of α- and β-polymorphs were different in both crystals, maybe due to the difference in crystal structures. There were two stages of recovery processes from 673 K to 1473 K, lower and higher temperature ranges. The activation energies at the higher temperature range of both compounds were almost double of those at lower temperature range. Furthermore, the activation energies of Si_3N_4 were larger than those of SiAlON in both polymorphs. It may be due to the difference in atomic bonding strength, i.e. that of the covalent bonds in Si_3N_4 would be higher than covalent/ionic bonds in SiAlON.

Chapter 5: Microstructure of low-dose neutron irradiated silicon nitride-related ceramics after thermal annealing

In this chapter, microstructural changes of as-irradiated Si_3N_4 and SiAlON polymorphs after low-dose neutron irradiation and those of after thermal annealing up to 1123 K, 1223 K and 1473 K were investigated in order to clarify the neutron irradiation induced defects and their thermal stability of these ceramics. Microstructure was observed with a high-resolution transmission electron microscope (HREM).

In Chapter 2, it was clarified that low dose neutron irradiation on Si_3N_4 and SiAlON ceramics induced only point or point-like defects without dislocation loops or grain boundary microcracks in those specimens. After thermal annealing, the macroscopic lengths were mostly recovered to their original length. The recovery tendencies of α-Si_3N_4 and α-SiAlON were resemble each other, and those of β-Si_3N_4 and β-SiAlON also resemble each other. However, the recovery tendencies of α- and β-phases were different, as described in Chapters 3 and 4. In order to clarify this phenomenon of the irradiated materials, it is necessary to investigate their microstructural change. In this chapter, the results of volume recovery after thermal annealing were further discussed based on the microstructural observation. HREM microstructures of the as-irradiated specimens revealed that the atomic configuration projected onto the basal plane was similar with a perfect crystalline arrangement without lattice distortion. It was confirmed that only point defects or point-like defects were generated during the neutron irradiation of the present condition. In addition, microstructural analysis of thermally annealed specimens mention in this chapter did not reveal any voids along grain boundaries and triple junctions. Furthermore, formations of dislocation loops or voids were not confirmed after thermal annealing up to 1473 K in all Si_3N_4 and SiAlON polymorphs.

5.1 Introduction

Nuclear fusion energy is a safe, clean, and cost-effective sustainable energy resource. It is interested for solving the energy crisis of the world in mid 21th century. However, materials' research and development will play a key role to improve economics and long-term stability of any advanced nuclear systems. Ceramic materials are expected to be used in nuclear fusion application due to their excellent mechanical and thermal properties [1-4]. When ceramic materials are applied in nuclear fusion reactors, the most important issue is stability of materials under high-energy neutron irradiation and other hazardous conditions such as high temperature and corrosive environment. High-energy neutron-irradiation induces several types of defects in materials. These defects lead to the property change in materials such as volume expansion, degradation of thermal conductivity and mechanical properties. Therefore, neutron irradiation responses of materials should be clarified to apply materials in neutron environment. Silicon nitride (Si_3N_4) ceramics and silicon-aluminuium-oxynytride (SiAlON) ceramics are one of the promising candidates for fusion applications because of excellent high temperature mechanical properties and good thermal properties [4-6]. Up to present, there are still limited numbers of research on neutron irradiation effects on Si_3N_4 and SiAlON. In recent reports, Si_3N_4 exhibited higher-dimensional stability than SiC after severe neutron irradiation up to 2.8-4.2 $\times$ 10^{26} n/m^2 [7, 8].

In order to clarify the stability of ceramics, it is necessary to investigate the microstructural changes of the ceramics after neutron irradiation. Microstructure observation of irradiated materials can show presence of extended defects. Transmission electron microscopy (TEM) is a powerful technique for the characterization of radiation damage microstructures [9]. High densities of defects were clearly observed in heavily neutron irradiated β-Si_3N_4 [10, 11]. Youngman and Mitchell [10] analyzed microstructural of defects aggregates formed in β-Si_3N_4 after neutron irradiation up to 2.0×10^{26} n/m^2 at 925 K and 1100 K. They reported that the faulted dislocation loops lying on the $\{10\bar{1}0\}$ planes which correspond to the insertion of an extra layer of SiN_4 tetrahedra on the $\{10\bar{1}0\}$ planes. These loops formation depended on the irradiation temperature. In addition, a structural model of defects in β-Si_3N_4 produced by heavily neutron irradiation was reported by Akiyoshi et. al. [11, 12]. They found that the extra layer of SiN_4 tetrahedra was inserted into the $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ planes. This report was further confirmed by Yano et. al. [13]. The microstructure of neutron irradiated β-Si_3N_4 up to a fluence of 0.4-3.7 $\times 10^{26}$ n/m^2 at temperature range of 650-900 K was observed, and several kinds of tiny interstitial dislocation loops on the $\{10\bar{1}0\}$ or $\{11\bar{2}0\}$ plane were revealed by HREM observation, and size distribution change due to thermal annealing was clarified. In addition, formation of voids/bubbles along grain boundaries was observed after annealing at 1773 K. In the case of AlN, it has hexagonal crystal structure as same as β-polymorph of Si_3N_4 and SiAlON, and structure of AlN is consisted from alternative stacking of AlN_4 tetrahedral sheets along the [0001] direction. So that the crystallographic feature of AlN is closely related with those of Si_3N_4 or SiAlON. The microstructure observation of neutron-irradiated AlN up to 9.1×10^{25} n/m^2 [14] revealed the formation of high density interstitial-type dislocation loops lay on the (0001) basal plane in grains and microcracks along grain boundaries. It was suggested that the expansion of the *c*-axis should be related to formation of the interstitial loop on the basal plane. Large anisotropy of lattice expansion along the *c*-axis and the *a*-axis induced grain boundary microcracking.

As shown in Chapter 3 and 4 on thermal annealing behavior of irradiated-Si_3N_4 and SiAlON ceramics [15-17], the length recovery tendencies of α-Si_3N_4 and α-SiAlON resemble each other, and those of β-Si_3N_4 and β-SiAlON also resemble each other. However, the tendencies of length recovery of α- and β-polymorphs were different in both crystals. It suggested that the different in the length recovery rate of these irradiated-ceramics was related to their crystal structures. Recovery rate of the α-phases stopped during annealing at 1123 K-1223 K. Therefore, it was expected that the microstructure observation on the specimens annealed at those temperatures could reveal the difference in their recovery process. In this Chapter, the microstructure of the as-irradiated silicon nitride-based ceramics, which were evaluated in Chapter 3 and 4, and those of after thermal annealing up to 1123, 1223 and 1473 K was observed with a high-resolution transmission electron microscope (HREM) in order to clarify the feature of defects and their thermal stability.

5.2 Conclusions

In this chapter, TEM was used to evaluate microstructural change of the as-neutron irradiated and after thermal annealed Si_3N_4 and SiAlON polymorphs. HREM micrographs of the as-irradiated specimen revealed that the atomic configuration projected onto the basal plane was similar with a perfect crystalline arrangement without lattice distortion. It confirmed that only point defects or point-like defects were generated during the neutron irradiation of the present condition. HREM micrographs of the irradiated Si_3N_4 and SiAlON polymorphs after thermal annealing up to 1473 K did not show any dislocation loops or voids/bubbles formation in grains or along grain boundaries, respectively. It suggested that without defects agglomeration in grain or at grain boundaries, neutron irradiation induced defects were mostly annihilated by thermal annealing up to 1473 K, in any materials observed in this study. It was still not clear that the reason for the difference in macroscopic length recovery during thermal annealing between α-polymorphs and β-polymorphs of silicon nitride-related compounds. It should be related to the kind of point or point-like defects.

Chapter 6: Conclusions

The overall conclusion of the present research consisted of 4 parts.