

Ion Irradiation Studies for the Development of Novel Nuclear Fuels

A Dissertation Presented for the
Doctor of Philosophy
Degree

The University of Tennessee, Knoxville

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December 2021

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À mes parents, Bernadette et François

À ma sœur, Anaïs

Acknowledgments

I would like to thank first and foremost Dr. Steven Zinkle, my academic advisor at the University of Tennessee. It was an honor to work with him on this research, and I will always be grateful for his knowledge, help, and support throughout these years.

I would also like to recognize the thoughtful conversations, help, and feedback that I've received from the other members of my committee: Dr. William Weber, Dr. Andrew Nelson, and Dr. Tyler Gerczak.

This research allowed me to collaborate with brilliant individuals, and their help and expertise was essential in the completion of the work presented here. Special thanks to Jim Kiggans and Dr. Caen Ang for their help with the sintering of the high thermal conductivity samples at ORNL; Dr. Miguel Crespillo and Dr. Haizhou Xue for performing the ion irradiations at IBML; Dr. Ling Wang for her help conducting TEM and STEM imaging on the irradiated samples; Alicia Raftery for her help using SPS to sinter ZrN samples; Benjamin Dacus and Dr. Michael Short at MIT for conducting TGS testing on the irradiated samples, and Joshua Ferrigno and Dr. Marat Khafizov at OSU for their help with thermoreflectance measurements on the studied samples.

I also would like to thank Dr. John Dunlap and Dr. Michael Koehler at JIAM whom helped selflessly, and day after day, every student that walked through their doors.

Thank you to past and present members of Dr. Zinkle's research group, including Dr. Shradha Agarwal, Dr. Congyi Li, Dr. Kelsa Benensky, Dr. Caleb Massey, Dr. Peter Doyle, Dr. Tyler Smith, Ty Austin, Yan-Ru Lin, Yajie Zhao, Pengcheng Zhu, Taylor Duffin, Yao

Li, Ishtiaque Robin, and Emily Proehl. I've enjoyed discussing, learning, and collaborating with all of you as well as the rest of the group.

I would have not been able to be here today without the constant support, understanding, and encouragement that I've received from my parents and my sister, and for that I want to dedicate this dissertation to them.

Finally, I would like to thank my partner, Hannah, who was there for me when I needed it the most during these arduous times, and for her daily encouragements.

Abstract

Following the Fukushima Daiichi accident, important efforts were made to improve the materials used in nuclear reactors, from the fuel/clad combination to structural materials, in order to provide greater tolerance towards accidents. This study discusses the fundamental stability of two types of ceramic materials after irradiation: uranium oxide surrogates with 10 vol. % high thermal conductivity additives (aluminum oxide and silicon carbide) and nitride ceramics (silicon nitride and zirconium nitride). Ion irradiations were performed using 20 MeV Ni^{6+} ions for the fuel surrogate samples and 15 MeV Ni^{5+} ions for the nitrides ceramics. Midrange (around 3 μm) doses varied from 1 to 50 dpa and temperatures from 300 to 700 °C. Thermal conductivity was measured using laser flash analysis and thermoreflectance. Volumetric lattice swelling of the ceramics was determined by grazing incidence X-ray diffraction. Defect production and evolution were tracked using Transmission Electron Microscopy, while nanoindentation was performed to quantify the ceramics' mechanical properties evolution.

The thermal conductivity of the fuel surrogates showed significant enhancement following sintering as measured by laser flash while novel measurement techniques such as transient grating spectroscopy presented some limitations. Differences in sintering behavior compared to traditional UO_2 were observed and chemical compatibility issues occurred as low as 1150 °C for SiC. Both ceramics presented a decrease of their mechanical properties above 15 dpa. Microcracks due to anisotropic swelling were not observed, but parallel clustered dislocation lines were found adjacent to the second phase grains, suggesting high stresses in the matrix.

Irradiation studies in nitride ceramics helped fill the current gap present in the literature. Coherent behavior with past work was observed on thermal conductivity evolution as well as mechanical properties and defect formation up to 15 dpa and 500 °C. Failure of the sintering

aid in Si_3N_4 was observed above these conditions. Different behavior was observed in both nitrides at 50 dpa and 700 °C, where lattice swelling increased past potential saturation values. Unreported cavity formation was witnessed, in both materials, under all irradiation conditions, with stable number density and slight size increase above 15 dpa and their origin remains to be determined.

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Chapter 1

Introduction

1.1 Introduction

Nuclear energy is a no emission clean energy source, the second largest source of low-carbon electricity in the world behind hydro-power. It produces electricity occupying less land than all other clean energy sources. To produce the same typical power as a nuclear reactor, around 1,000 megawatts, we would need more than 430 wind turbines or more than 3 million solar panels. Finally, due to its extreme density compared to traditional sources of energy, where a uranium pellet is equivalent to 1 ton of coal, 17,000 cubic feet of natural gas or 120 gallons of oil, the amount of waste produced is quite small. Taking into account the entirety of the used nuclear combustible used by the United States in the last 60 years, all of this waste could fit inside a football field within a 10-yard depth. Moreover, this waste can also be recycled and reprocessed, even though this option is currently not being followed by the United States. Despite all of these advantages, it has been quite challenging for the nuclear industry to evolve, build, and use more modern reactor design and materials selection, which would further increase its reliability, safety, sustainability and overall cost.

While advanced reactor concepts have been developed over the years, they never managed to replace the light water reactor fleet existing around the world, one of the reasons being the fear of the unknown coming from industries. With growing concerns around energy security, availability, and climate change, countries around the world as well as global research groups decided in the early 2000's to dedicate time, money and effort in their upcoming research

towards developing the next generation of nuclear systems: Generation IV. The six main reactor concepts selected by the Generation IV International Forum (GIF) were: the molten salt reactor (MSR), the sodium-cooled fast reactor (SFR), the lead-cooled fast reactor (LFR), the gas-cooled fast reactor (GFR), the supercritical water-cooled reactor (SCWR) and the very high temperature reactor (VHTR).

As observed in Figure 1.1, the operating environment of these advanced reactors is much more aggressive, where both higher temperatures (300 °C to 1000 °C) and increased irradiation damage (up to 200 dpa) can be found as opposed to current traditional light water reactor systems (Generation II – III reactors). The use of alternative coolants such as sodium, molten salt or high temperature water will also increase the chemical attacks on the systems. Since these novel reactors would be designed and built with a longer life expectancy, up to 100 years, both structural materials and fuel elements will need to sustain this environment over time.

Shortly after the severe accident at the Fukushima Daiichi power plant on March 11th 2011, researchers multiplied their efforts in order to find a better usable fuel system than the traditional UO_2 /Zircaloy fuel/clad combination with their main goal being to have a final combination that would provide a greater tolerance towards accidents. These accident tolerant fuels systems should be usable in light water reactors while displaying better properties than UO_2 /Zircaloy and being able to have a better response towards both reactivity-initiated accidents and loss of coolant accident.

Improving accident tolerance can be achieved by [159]:

- Enhancing the retention of fission products, both solid and gaseous.
- Improving the reaction kinetics with steam to reduce the hydrogen embrittlement of the cladding, reduce the combustible gases production as well as decrease the oxidation rate.
- Improving the cladding properties (better fracture and shock resistance, reduced fuel-cladding interaction, higher melting temperature).
- Improving the fuel properties such as having a higher melting temperature, reducing the fuel dispersion and internal cladding oxidation, and lowering the overall fuel operating temperature via thermal conductivity/heat capacity increase.

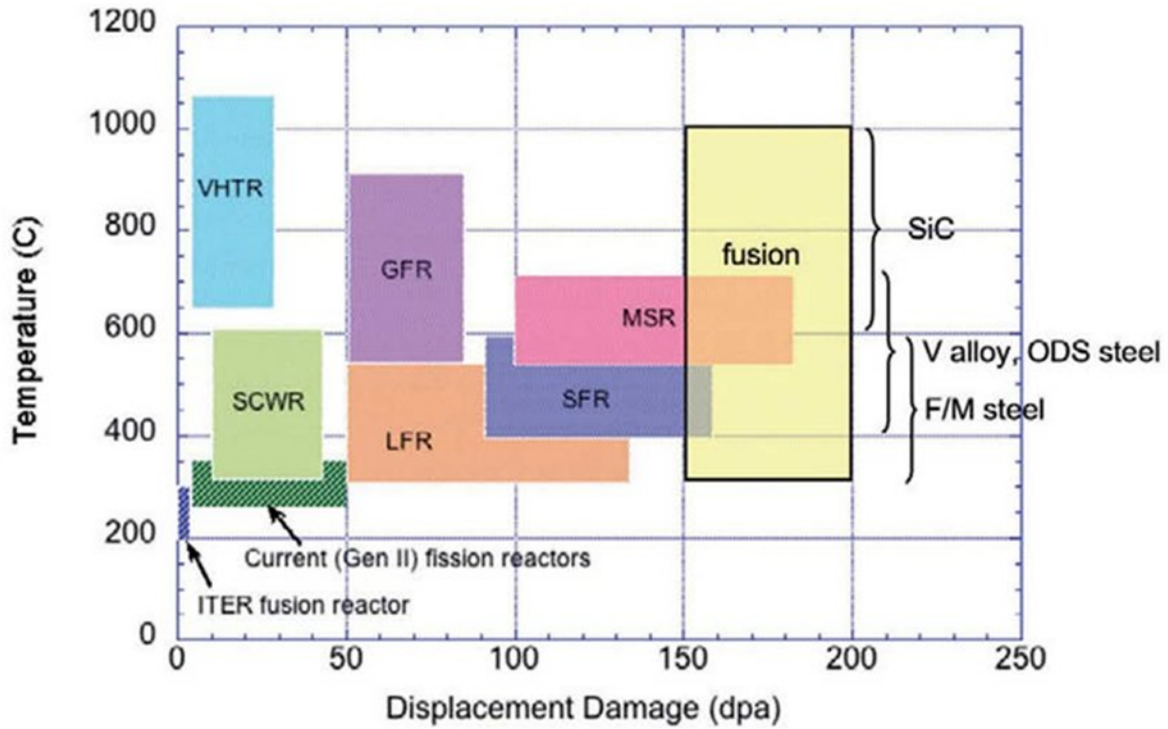


Figure 1.1: Operating temperature and displacement damage dose for current and future gen IV fission and fusion reactors. Presented here are the Very High Temperature Reactor (VHTR), Super Critical Water Reactor (SCWR), Gas-cooled Fast Reactor (GFR), Lead-cooled Fast Reactor (LFR), Molten Salt Reactor (MSR) and the Sodium-cooled Fast Reactor (SFR). From Zinkle et al. [187].

To accelerate this process in order to have solutions within the next 10-15 years, two of the major accident tolerant fuels concepts currently being looked at are the use of different fuels (TRISO particles inside a matrix, FCM fuel, U_3Si_2 , UN) and the modification of traditional UO_2 using additives to improve its overall properties, with the most interesting one being the thermal conductivity. Its important impact on the overall reactor safety and performance has become one of the major talking points in reactor design. Thermal conductivity controls the heat conversion process, from fission events to electricity. It also is one of the crucial properties associated with phenomena such as fission gas release, fission product migration, swelling, and grain growth. Due to the important temperature gradient being formed in the fuel, a low thermal conductivity will increase the thermal stress and can induce cracking of the fuel which could result in a release of radioactivity in the environment. Fully Ceramic Microencapsulated (FCM) fuel brings unique accident-tolerant capabilities and dramatically reduce the potential for radioactivity release in the case of an accident. Usable in multiple fuel assembly designs, FCM fuel can match or surpass conventional fuel on overall performance specifications in reactor while having an increased safety margin [178].

As a result of the inclusion of additives, through coatings in TRISO or second phases within UO_2 , the current challenges are to determine the overall stability of these coatings/additives after irradiation. How stable are they under irradiation? Do they react at certain temperatures with the matrix and undergo phase transformation? How mechanically stable these components are? Do they tend to swell up to an unacceptable level? What sort of thermal conductivity evolution can we expect? These are some of the questions that fueled the work presented below where the main goal was to improve the fundamental understanding of the irradiation effects on components for advanced nuclear fuels. While these concepts have been pushed forward in the recent years, more work needs to be accomplished. Initial testing has been conducted and some appear to be quite promising, but data focused on the second phase's compatibility and interface behavior are still lacking. Particularly, post irradiation information such as fuel swelling, grain growth, neutronic behavior and fission product retention are still quite unknown. Further economic research has to also be done to determine the cost related to these modifications (different fabrication processes, higher

uranium enrichment due to non-fissile second phase...) and if it can be competitive with the current system in place [178].

The second chapter of this dissertation will present a review of the literature on both high thermal conductivity fuels and coated particle fuels with a focus on silicon and zirconium nitride. The third chapter will present the materials used in this research as well as the characterization techniques that helped provide our results. The fourth chapter will be focused on the results obtained on the high thermal conductivity work and will critically discuss them. Results and discussion from the nitride ceramics work will be presented in chapter five. Finally, the sixth chapter will conclude on this research and will present possible future work to further develop areas of interest surrounding these materials.

1.2 Research goals

In this study, the potential impact of displacement damage irradiation effects will be investigated for two important categories of high performance and/or accident tolerant fuels: high conductivity fuels incorporating a nonfissile high conductivity additive, and nitride ceramics as an alternative to SiC for TRISO fuel particles and/or inert fuel matrices.

The effects of irradiation on the feasibility of adding nonfissile high thermal conductivity second phase to nuclear fuels was investigated. Focus was oriented towards cases where the nonfissile material is noncubic and may exhibit grain boundary cracking or other enhanced radiation degradation effects due to anisotropic swelling. Of particular importance is the investigation of the stability of the nonfissile ceramic and fuel surrogate phases under irradiation, including the interface between the nonfissile and fuel surrogate materials. CeO₂ and yttria-stabilized ZrO₂ were selected as surrogate materials for UO₂ due to their similar cubic fluorite crystal structure. SiC and Al₂O₃ were selected as additives due to their high conductivity and good compatibility with UO₂ as well as being available in a wide range of product form including platelets, fibers and powder. BeO was excluded from this study due to the health restrictions and cost surrounding the use of the material. Instead, Al₂O₃ was selected as model hcp system with its similar anisotropic swelling which would provide useful insight on the possible behavior of BeO after irradiation.

Coated particle fuels and particularly the high temperature ceramic structural layer present within TRISO particle fuel was then studied using nitride ceramics ($\text{Si}_3\text{N}_4/\text{ZrN}$) as possible replacement for the traditional SiC layer in order to alleviate the shortcomings of SiC. Fundamental data on silicon nitride and zirconium nitride are also necessary to learn behavioral information that can be applied to other applications such as ceramic matrix surrounding ceramic fuel particles (UN, etc.) or waste form burn-up pellets in ceramic/ceramic composite (CERCER) fuel systems [88]. These are being examined for their potential to achieve transmutation of long-lived actinide isotopes in so-called inert matrix fuel concepts (thereby reducing waste repository requirements) or to achieve ultra-high burn-ups (variations of the SiC or ZrC based “fully ceramic micro-encapsulated” fuel system) in Gen IV reactor concepts such as VHTR or GCR [24]. They are also of potential interest for space nuclear reactor systems such as the ceramic matrix in UN-containing CERCER fuel system for nuclear thermal propulsion.

In order to examine potential irradiation effects on these two advanced fuel forms, ion irradiations were conducted throughout a wide range of temperatures as well as different doses. Following irradiation, the microstructure and some mechanical properties of the samples were observed using an array of characterization technique including but not limited to GIXRD, SEM, TEM, and nanoindentation. Finally, as introduced earlier, one of the key properties for accident tolerant fuels systems is the thermal conductivity. The potential applicability of transient grating spectroscopy and modulated thermorefectance towards ion irradiated ceramics and composite materials was investigated.

Chapter 2

Literature Review

2.1 High thermal conductivity fuels

Improvement in the performance of traditional UO_2 nuclear fuel is of importance to further evolve the safety and power output of nuclear reactors. Throughout the years, UO_2 has become the fuel of choice for commercial applications due to its very well studied behavior as well as several key advantages [16]: it has an acceptably high fissile atom density, good chemical compatibility with Zr alloy cladding and water coolant, a high melting point, and most importantly it exhibits acceptably low volumetric swelling and fission gas release up to high burnups (significantly lower than alternatives such as metallic U, UN or UC) [95]. The main disadvantage of UO_2 is its low thermal conductivity which degrades even further during irradiation [127]. In order to select better possible fuel candidates, the key criteria taken in consideration are uranium enrichment, thermal conductivity and melting point. These properties are considered a priority over others due to their behavior during loss of coolant accident (LOCA) and in beyond design basis accidents (BDBA). Several fuel candidates have been investigated and they all come with their benefits and drawbacks. Uranium carbide for example (UC) has a high melting point and a good thermal conductivity, but its extreme reactivity with water makes it unviable for LWR use. Uranium nitride (UN) is quite attractive, with a high melting point, low neutron cross section and high thermal conductivity but requires ^{15}N enriched nitrogen and has a high reaction rate with coolants used in LWR at operating temperatures. UO_2 -doped fuel with a non-fissile high

conductivity second phase would allow to use the beneficial properties of UO_2 while its thermal conductivity. Unfortunately, it is not clear at the moment if this modification (which reduces the amount of U present in the fuel) and its benefits are maintained post irradiation. The behavior of the second phase, sintering parameters, and form aspect (platelets, powder, fibers...) also needs to be studied further as their impact are not completely clear at the moment [7].

Using a nuclear fuel with a higher thermal conductivity would have several benefits towards traditional behavior encountered in reactor [12]. The temperature gradient between the center and the edge of the fuel pellet would be less steep, allowing a lower fuel centerline temperature. Lower temperatures would reduce thermal stresses and thereby reduce the creation of cracks and deformation within the fuel pellet. Moreover, it would enhance the overall safety of the reactor (higher temperature margin to fuel melting) and reduce fuel swelling and fission gas release, thereby enabling higher burnup levels (better utilization of the nuclear fuel) [127, 97]. Prior published scoping studies have examined the sintering capabilities and evolution of the thermal conductivity of UO_2 with 5 to 20 % of a high conductivity non-fissile second phase such as SiC , BeO , or Al_2O_3 and are discussed below. Due to the non-fissile aspect of these second phases, the overall amount added to the matrix should be limited (around 10 %) in order to produce similar levels of energy.

2.1.1 $\text{UO}_2\text{-BeO}$

More than fifty years ago, work was already being conducted on this topic. Nishihgaki et al. studied the thermal conductivity evolution of $\text{UO}_2\text{-BeO}$ hot pressed pellets as well as the effect of Be addition. A 10-20 times increase was reported with 20 wt.% BeO content compared to undoped UO_2 , and additional Be did not affect the overall thermal conductivity [105].

In order to maximize the very high thermal conductivity of BeO , improved sintering techniques were then developed. Ishimoto et al. fabricated $\text{UO}_2\text{-BeO}$ pellets with varying dopant volume fraction (between 1.1 and 36.4 %) two ways: spherical BeO particles were dispersed in the UO_2 matrix and a continuous BeO precipitated along UO_2 grain boundaries. The dispersed phase pellets were obtained via sintering below the eutectic temperature at

1800 °C for 2 hours while the continuous type pellets were sintered above, at 2150 °C for 1 hour. At comparable additive content, they shown that the continuous type pellets displayed a larger grain size and higher density than the dispersed pellets. Modeling of the thermal conductivity for the dispersed pellets showed a good agreement with the experimental results (within 5 % error) but the continuous type model overestimated the thermal conductivity measured by 20 %. The measured thermal conductivity increased with increasing volume fraction of BeO, and the continuous pellets constantly had higher values than the dispersed pellets (at 830 °C and with 4.2 vol.% BeO, a 25 % increase was observed for the continuous pellets vs 10 % for the dispersed ones when compared to pure UO_2). One main issue with these results is the very high temperature needed during sintering (higher than 2150 °C) in order to achieve such thermal conductivity improvement [64].

Sarma et al., used a “co-sintering” method to sinter dense pellets with 5-10 % of continuous BeO phase. The BeO powder was uniformly distributed in UO_2 after a “self-milling” step to render the UO_2 granules more spherical. High density was achieved using undisclosed filler particles. Dissolution of the UO_2 allowed to demonstrate the continuity of the BeO phase, forming a robust skeleton even with only 5 vol.% of BeO. The intergranular BeO phase was contaminated during sintering by finely dispersed UO_2 particles, which was reduced by using harder bisque granules creating less dense pellets. The main benefit from this contamination would be the BeO grain size reduction. Under irradiation, BeO possess an anisotropic swelling behavior, causing microcracking within the specimen. A smaller grain size would allow to delay this cracking behavior [131].

Using green granules and slug-bisque processes, Latta et al. produced UO_2 -BeO pellets with 10 vol.% of additives in order to study the thermal conductivity evolution via the two different processing routes. An average thermal conductivity increase of 45 % over pure UO_2 was measured (56 % at 200 °C and 33 % at 1000 °C) using Laser Flash technique, and no differences were found between the two different fabrication methods [87].

Camarano et al. investigated the compaction pressure and volume fraction effects on UO_2 -BeO pellets. Pellets were sintered with 7, 10, 16, and 21.5 vol.% BeO powder and the green pellets were pressed at 400, 500, and 600 MPa before being sintered at 1750 °C for 3 h in a horizontal furnace. The compaction pressure did not allow any significant differences

in the sample's properties aside from a very slight thermal diffusivity enhancement at low BeO volume fraction. It was then suggested that manufacturing of BeO pellets should be done at 400 MPa, pressure commercially used in the fabrication of UO_2 pellets in order to prevent any cost increase. Thermal diffusivity was taken at room temperature and showed an increase with increasing BeO content, from 18 to 48 % for (7 to 21.5 vol.%) compared to UO_2 [22].

Lastly, Li et al. used SPS (Spark Plasma Sintering) to fabricate 10 vol.% BeO/ UO_2 pellets and reported the thermal conductivity evolution and coefficient of thermal expansion for temperatures up to 1600 °C. The sintering was done at 100 °C/min up to 1300 °C and slowed to 50 °C/min to reach the final sintering temperature of 1400 °C for 10 min. 25 MPa of pressure was applied on the punches during the whole process. The average UO_2 grain diameter was observed to be around 5 μm and the BeO grains were around 2 μm . Smaller BeO grains can reduce cracking during irradiation, but it was not conducted during this work. The coefficient of thermal expansion slowly increased with increasing temperature up to 1500 °C, where it rapidly dropped possibly due to inner stress release or further sintering. Reported thermal conductivity was well improved, showing a 45.3 % increase at room temperature up to 60 % at 1600 °C [91]. Such thermal conductivity values would greatly decrease the temperature gradient present in the fuel pellets, reducing pellet failure and increasing the overall safety of the reactors.

2.1.2 UO_2 -SiC

Silicon carbide (SiC) possess great advantages compared to UO_2 . While having a good chemical and irradiation stability, it also has a high melting point, a low thermal neutron absorption cross section and its thermal conductivity is sixty to thirty times higher than UO_2 's (room temperature vs 800 °C). As a very attractive material for the nuclear energy sector, numerous studies have been done on SiC [140]. Several techniques can be used to fabricate SiC such as sintering, polymer pyrolysis, gas phase reaction and direct conversion. Due to differences in stacking possibilities, SiC has a multitude of polytypes (most common ones being 3C, 4H, 6H and 15R). 3C-SiC is the only one displaying a cubic symmetry and is often referred to as β -SiC. While its lattice parameter tends to increase with increasing

temperature for all polytypes, the value remains quite small (≈ 0.5 % at 1000 °C) which results in a low thermal expansion coefficient (given by the change of lattice parameter at elevated temperatures).

In the early 2000's, Sarma et al. developed the PIP method (Polymer Impregnation and Pyrolysis) and tried to use commercially available SiC precursor to impregnate UO_2 fuels and to consolidate particle fuels such as TRISO particles in order to increase their thermal conductivity. These fuels were called ECO fuels (Enhanced Conductivity Oxide fuels). A novel "slug/bisque" method was developed, where UO_2 was sintered with an open pore structure, allowing a subsequent SiC impregnation. The PIP process was convenient for the consolidation of particle fuels, as it allows the formation of a continuous β -SiC phase at 1300 °C. Despite their effort, they were not able to obtain high density samples (maximum density of the SiC phase around 75 % TD) due to the low crystallization temperature and the blockage of the porosity by the SiC. In order to get a high thermal conductivity silicon carbide using the PIP process, multiple impregnation cycles as well as high crystallization temperatures are required. This experiment concluded with a lack of improvement of the overall thermal conductivity of the UO_2 composite, possibly due to the limited infiltration of the precursor. While a good contact was observed between the matrix and the additive, transgranular cracks were present due to the shrinkage occurring during the pyrolysis step [131].

In 2008, Singh et al. published their research also using the Polymer Infiltration and Pyrolysis process but following a different approach. UO_2 was directly incorporated into the preceramic polymer and then converted to SiC during the pyrolysis step. A uniform distribution of the uranium and a low amount of open porosity was observed. Due to the limitation of the pyrolysis temperature to 900 °C, the α -SiC formed during the PIP process was not crystallized. A higher pyrolysis temperature between 1150 to 1650 °C would have formed crystalline β -SiC, which also would be more practical for nuclear applications [138].

Yeo et al. looked with more details into the effects of particle size and volume fraction of the additive. Using both UO_2 and SiC as starting materials, multiple particle size (0.6 μm to 55 μm), different volume fraction (5 – 20 %) and different sintering techniques (oxidative sintering and Spark Plasma Sintering) were used to sinter composite samples.

While smaller particle size (up to 10 μm) and higher volume fraction appeared to enhance the thermal conductivity of the pellets, larger particle size (17 μm and 55 μm) induced the formation of cracking and additive debonding, which reduced the thermal conductivity below UO_2 literature values. Spark Plasma Sintering was also revealed to be a better sintering alternative, allowing smaller grain size, a reduction in chemical products formation, higher final density, and a better interfacial contact as opposed to oxidative sintering. To prevent the need to have a much higher uranium enrichment due to the reduced amount present in the pellet because of the higher SiC volume fraction, it would also be necessary to limit the volume percent of second phase added. Up to 62 % increase in thermal conductivity (at 900 $^{\circ}\text{C}$; 55 % was reported at 100 $^{\circ}\text{C}$) was measured on SPS sintered samples at 1600 $^{\circ}\text{C}$ with 10 % of silicon carbide present within the UO_2 matrix. Oxidative sintering failed to deliver high density samples (none of them were above 90 % dense), and the poor interfacial contact were the main reasons while the overall thermal conductivity measured on these samples ended up lower than pure UO_2 values [175, 176].

Roleček et al. aimed to present a methodology to sinter CeO_2 , a surrogate to UO_2 , with added silicon carbide to further study the thermal conductivity enhancement of this system. Samples were sintered using conventional and spark plasma sintering, with varying volume fraction of SiC (0 – 18 %). Thermal diffusivity measurements were taken of green body pellets, and the results indicated a decrease with increasing SiC volume fraction. This behavior is entirely opposite to what should be expected, and it was explained by the increase in interphase boundaries, which act as phonon scattering centers, reducing the overall thermal conductivity. Furthermore, their SPS sintered samples showed the same trend, where a reduction in thermal conductivity was noted with increasing SiC volume fraction. Conventionally sintered pure CeO_2 also had a worse thermal conductivity compared to SPS sintered material. SEM observations revealed microcracks in the microstructure of the pure sample and a bad interfacial binding in the composite samples. Additionally, they observed oxidation of the SiC into SiO_2 under traditional sintering and reduction during SPS sintering into Ce_2O_3 . They were not able to increase the cerium thermal conductivity, and SPS sintering concluded in worse results than traditional sintering [126]. While Yeo et al. seemed to display benefits of sintering UO_2 using SPS, Roleček, showcased some limitations

of this technique while using CeO_2 as matrix and further work should be conducted on it to look at this phenomenon in more details.

Li et al. focused their work on the SPS technique and investigated which sintering temperature is more beneficial to the enhancement of the thermal conductivity of UO_2 -SiC pellets. The critical temperature above which SiC additive in UO_2 improves its thermal conductivity was observed to be 1300°C . The thermal conductivity increased with increasing volume fraction of SiC (measured using 4 to 10 % of SiC) and decreased with decreasing sintering temperature (work done between 620 and 1500°C) [90].

2.1.3 UO_2 -Others

While BeO and SiC additives lead the work done to date on high thermal conductivity fuels, some research has also been done on less traditional materials, such as diamond and carbon nanotubes. Chen et al. used 5 vol.% of synthetic diamond combined with Spark Plasma Sintering in order to increase the thermal conductivity of UO_2 . Multiple particle sizes were studied (0.25 , 3 , 12 , $25\ \mu\text{m}$) and SPS sintering was conducted between 1300°C and 1600°C . While small particle size ($0.25\ \mu\text{m}$) resulted in poor powder mixing and low pellet densification, composite with particles larger than $12\ \mu\text{m}$ showcased microcracks, reducing both thermal and mechanical properties of the samples. A thermal conductivity increase was noted for the UO_2 - $3\ \mu\text{m}$ diamond composite pellet, from 41.6 % at 100°C to 34.2 % at 900°C [25].

Economically, synthetic diamond would be more affordable than CNT or graphene, at around $\$2.5/\text{g}$ vs $\$270/\text{g}$ and $\$125/\text{g}$, an important factor to keep in mind in case of future wide scale commercialization. Kim et al. studied thermal properties and fabrication issues of metallic micro-cell UO_2 -Mo pellets. Various UO_2 granules density were used (30 – 65 %) during the pellet fabrication as well as different Mo powder size (300 nm, 10 – 20 μm). The volume fraction of the additive was also changed between 2, 5, and 10 %. The pellet density decreased with increasing UO_2 granule density, and a maximum granule density of 43 % allowed for pellets higher than 95 % TD. Further experiments were conducted using the 33 % granule density as it delivered the highest final pellet density. Thermal conductivity measurements were done on micro-cell UO_2 -Mo pellets, UO_2 -Mo dispersed particles pellets

and pure UO_2 . It was shown that continuous Mo channels greatly increased the thermal conductivity of the pellets as opposed to dispersed Mo particles (80 % increase above 800 °C for micro-cell UO_2 -Mo pellets vs 30 % increase for UO_2 -Mo dispersed powders), and the thermal conductivity was proportionate to the volume fraction while not being affected much by the wall thickness and cell size. Mo micro-cell acted as heat conducting channels within the pellets [78].

Cartas et al. proposed to combine UO_2 and carbon nanotubes (CNT) to create a nuclear fuel with enhanced thermal conductivity. CNT's main reason for being chosen was its very high directional thermal conductivity, which is better than diamond / graphite. Ethanol and ortho-dichlorobenzene (ODCB) were used as possible solvents during the mixing process with UO_2 and SPS was conducted at 1300 °C to sinter the pellets. Only ODCB allowed for an effective and homogeneous CNT dispersion in the matrix. Ethanol allowed for large CNT clusters to form, which did not allow the thermal conductivity to be better than the one of pure UO_2 . A combination of 5 % single walled carbon nanotubes (SWNT) with ODCB increased the UO_2 thermal conductivity by 29.7 %. The thermal conductivity increase is highly dependent of the second phase dispersion in the matrix. Moreover, the ideal volume fraction of CNT still appears to be uncertain, as higher than 5 vol.% did not further increase the thermal conductivity, and possible CNT-CNT interaction was mentioned as the possible issue [23].

2.1.4 Radiation damage in $\text{BeO}/\text{Al}_2\text{O}_3$

Microstructural evolution due to radiation induced defects have been shown to heavily influence mechanical and physical properties of irradiated materials. These changes have taken an important place during novel fuel form consideration and selection. Irradiation temperature have often impacted materials' microstructure in major ways, and the several temperature regimes are presented in Figure 2.1 and discussed below.

Five recovery stages have been identified and the extent of the defect recovery in all of them is based on PKA spectrum, irradiation dose, purity and the irradiated material itself. Stage I represents the onset of long-range self-interstitial atom (SIA) migration. Migration of small self-interstitial atom clusters (with or without impurity atoms) occurs during Stage

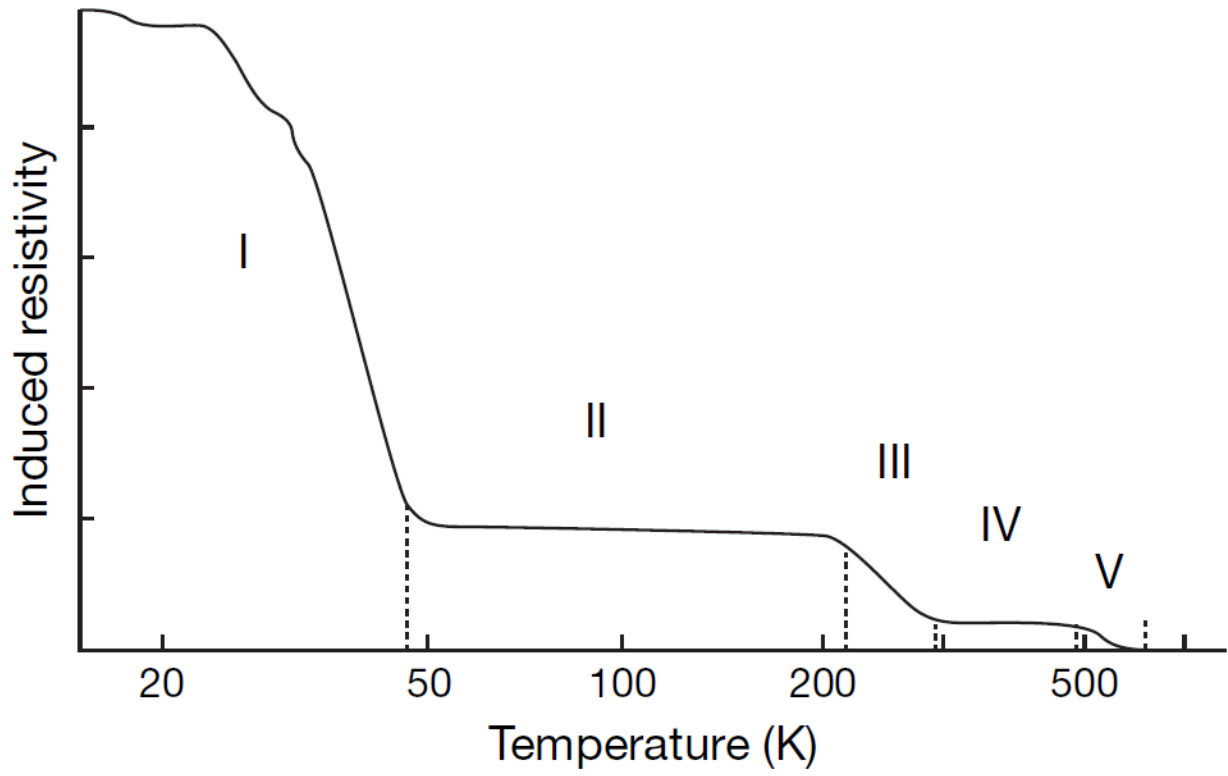


Figure 2.1: The different electrical resistivity defect recovery stages for copper after electron irradiation at 4 K from Zinkle [185]

II while the onset of vacancy migration begins with Stage III. Migration of vacancy/impurity clusters occurs during Stage IV while thermal dissociation of sessile vacancy clusters is observed during Stage V. At temperatures below Stage I, defect migration is not observed, and defect saturation is often observed by ≈ 0.1 dpa and amorphization is often observed in ceramics and ordered metallic alloys within this temperature range. Between Stage I and Stage III, point defects and self-interstitial atoms become mobile can form dislocation loops or recombine with sessile monovacancies and vacancy clusters. Immobile vacancies limit the size of defect clusters and SIA loops above ≈ 0.1 dpa. A decrease in the irradiated lattice parameter swelling with increasing temperature has been reported in this temperature regime. Between recovery Stage III and Stage V, both self-interstitial atoms and vacancies are going to be mobile, and the most common observable features are interstitial loops, voids and vacancies. Loop can unfault and become network dislocations during prolonged irradiation. Void formation in this temperature range is also associated with large macroscopic swelling. At temperatures above recovery Stage V, dislocation loops, network dislocations and cavities are visible. Important cavity swelling is present and cavity density monotonically decrease with increasing temperature [185].

Several of the possible high conductivity nonfissile second phase materials possess anisotropic crystal structures (such as hexagonal close packed (hcp) BeO, Al₂O₃, α -SiC and AlN) and are prone to grain boundary cracking during neutron irradiation at temperatures between 300 and ≈ 600 -800 °C due to anisotropic lattice swelling pictured in Figure 2.2 [141, 171, 72, 169].

This radiation-induced volumetric swelling from point defect clusters in ceramics is generally most pronounced at low to intermediate temperatures of around 100 to 600 °C (below the onset for vacancy migration), depending on the specific material. Volumetric swelling in ceramics due to cavity formation generally occurs at much higher temperatures of around 600 °C to 1400 °C, above the onset for vacancy migration [185, 140]. The anisotropic lattice swelling at low to intermediate temperatures can cause a reduction in strength of the anisotropic materials as well as a degradation of its thermal conductivity due to anisotropic stress-induced cracking. Furthermore, the use of multiple materials within one fuel concept

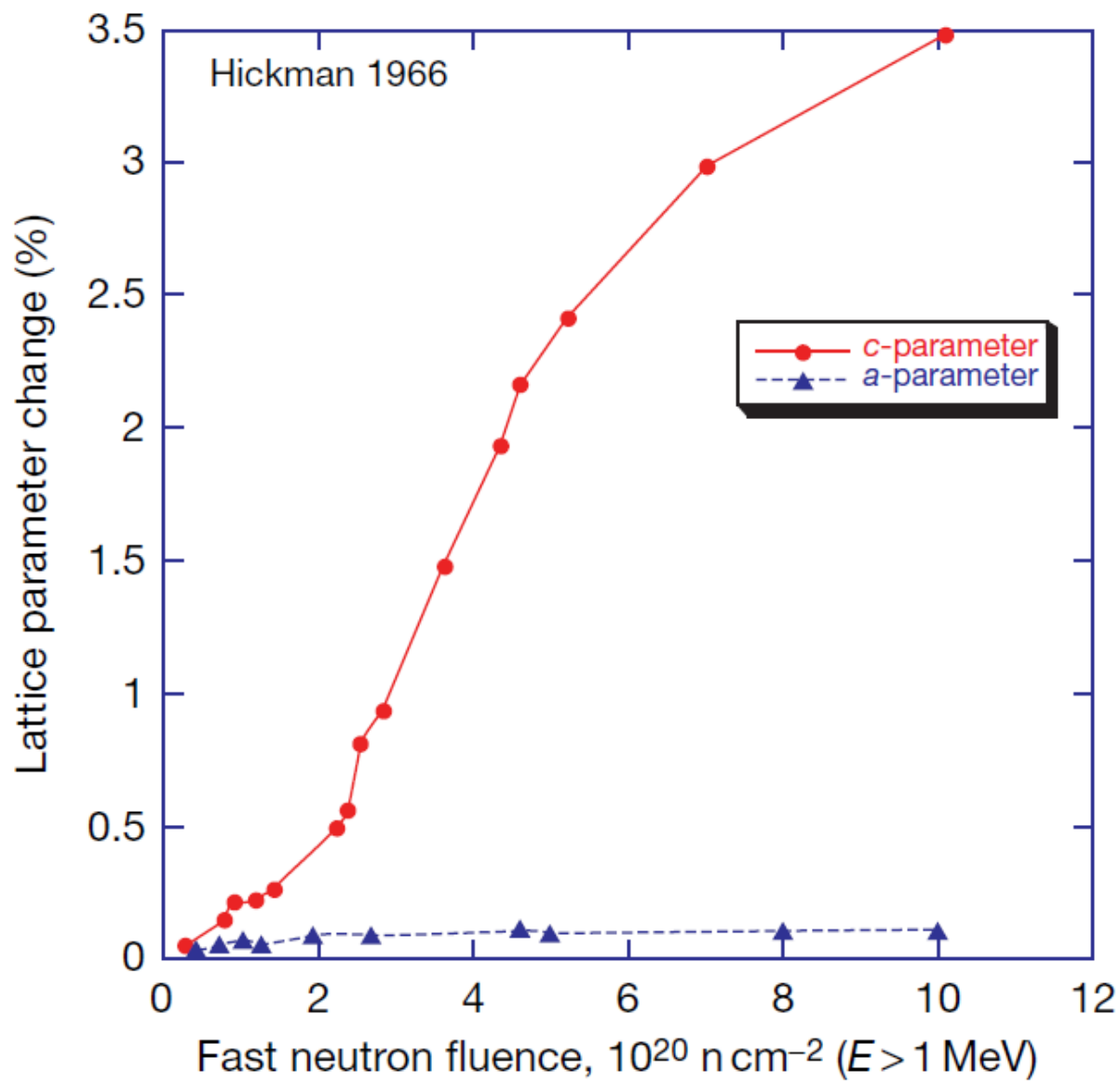


Figure 2.2: Lattice parameter change for BeO after neutron irradiation at 75 °C from Zinkle [185] based from Hickman et al. [56]

such as high thermal conductivity additives could create different swelling behavior (itself being multiplied severalfold when anisotropic materials are being used), potentially allowing for delamination at the interfaces between the two materials and reducing heat transfer capabilities. Historical work and results are described below.

Wilks reviewed several irradiations conducted from 1962 to 1967 and presented the nature of the radiation damage as well as macroscopic changes found in the properties of Al_2O_3 [161]. This review paper included the works of Hickman and Walker [58], Wilks et al. [162], Stevanovic and Elston [144] and Thorne and Howard [150]. X-ray diffraction in polycrystalline Al_2O_3 reported no peak broadening at 80 °C and doses below 5×10^{20} nvt [58, 144] and a slight broadening at 5×10^{20} nvt [58]. At 8×10^{20} nvt, an asymmetrical broadening was observed at 250 °C while a symmetrical broadening was observed at 700 °C [150]. Lattice parameter evolution has been conducted in multiple studies. Hickman and Walker [58] reported an isotropic swelling up to 3×10^{20} nvt and a small anisotropy at higher doses. The a parameter swelling was found to be saturating around 5×10^{20} nvt and the expansion decreased with increasing temperature (phenomenon also observed by Thorne and Howard [150]). Lattice parameter recovery was observed by Hickman and Walker [58] and was found to be independent from the irradiation dose up to 5×10^{20} nvt. Complete recovery was reached by 1400 °C. Macroscopic growth measurements done by density or linear dimensions measurements showed a slight anisotropy for irradiations at 150 °C and a large anisotropy at 650 °C, increasing with increased dose. Recovery following annealing was found to be independent of dose (between 4×10^{19} and 5×10^{20} [58]. Thorne and Howard [150] observed a greater macroscopic growth compared to the lattice parameter evolution for doses higher than 6×10^{20} nvt, which they assumed to be due to interstitial defects clustering. TEM observations by Wilks et al. [162] showed the presence of interstitial loops in irradiated Al_2O_3 at 10^{20} nvt and 650 °C. Microcracking in polycrystalline Al_2O_3 was not reported after irradiations conducted at $5 \times 10^{19} - 10^{20}$ nvt and 80 °C but observations were only done using optical microscopy [58, 144]. As opposed to these results, Higgins [59] reported microcracking (observed via X-ray microscopy) in polycrystalline materials with 50 μm grain size and 7.5 % porosity but no microcracking in single crystals with 37 μm

grains and 0.5 % porosity (3.2×10^{19} to 1.3×10^{20} nvt irradiation at 150 °C). High porosity was presented to be the reason for microcracking and that cracks would nucleate from pores within grains. A 25 % thermal conductivity reduction was reported by Stevanovic and Elston [144] (measured at 300 °C) after irradiation at 10^{20} nvt and 70 °C but a 24 hours anneal at 1000 °C restored it to its pre -irradiation value. Young’s modulus evolution was reported to decrease by 3 % after 1.5×10^{20} nvt irradiation at 70 °C [144] and by 5 to 10 % around 5×10^{20} nvt at temperatures between 250 to 700 °C [150].

Clinard et al. conducted neutron irradiation on single crystal and polycrystal Al_2O_3 using fast neutron fluences up to 2.3×10^{26} n/m² ($E > 0.1$ MeV). Irradiation temperatures were 652 °C and 827 °C, representing 0.39 and 0.44 T/T_m respectively at doses from 3 to 23 dpa. Higher irradiation temperature in this dose range caused the formation of larger voids but reduced the overall void density while higher fluence mostly increased the overall swelling. At the highest irradiation temperature, 827 °C, a larger swelling was found compared to the one at 652 °C (6.0 % vs 3.5 % in polycrystalline Al_2O_3) as well as extreme grain boundary cracking. This important swelling was attributed to the unfaulting of dislocation loops and formation of dislocation network, serving as sinks for interstitial point defects conversion to lattice atoms [30].

Rohde et al. measured the thermal conductivity evolution of Al_2O_3 after different irradiations using laser flash technique. Neutron irradiations were conducted at fluences between 5×10^{20} and 2.1×10^{21} part./cm² (0.5 to 5 dpa) and temperatures from 200 to 550 °C. An alpha particle irradiation was also conducted (1×10^{17} part./cm², 0.001 dpa at 427 °C). Thermal conductivity was measured up to 1427 °C while avoiding annealing effects. Annealing studies (90 min hold at temperature followed by thermal conductivity testing at room temperature) were also done on the samples from 27 to 1727 °C in vacuum. Thermal conductivity decrease due to irradiation induced defect was shown to be mostly dependent on irradiation temperature and not only dependent on damage dose. The irradiation performed at the lowest temperature showed a 100 % thermal conductivity at the lowest annealing temperature. This was associated with the different defect structure in the samples. Small defect clusters or single point defect are assumed to be created during low temperature irradiation while large defects accumulation acting as sinks for point defects would be

formed at higher temperature. 100 % recovery would then be reached at higher annealing temperature for samples irradiated at high temperature [124, 125].

Dienst studied the mechanical strength evolution of Al_2O_3 following neutron irradiation between 400-600 °C and fluences from 5×10^{24} to 3.7×10^{26} n/m² (0.5 – 37 dpa equivalent). While no changes were observed at a fluence up to 5×10^{24} n/m², a 50-60 % reduction of the mean ultimate bending strength was observed at 1×10^{26} n/m². Strength decrease and volume swelling appeared to correlate for Al_2O_3 . It was assumed that the strength decrease observed in Al_2O_3 was mainly due to irradiation defects which do not interact in a significant manner with microstructure flaws allowing for crack formation [43]. Other work has shown contradictory results using indentation methods and further work need to be conducted on this.

A study by Konings et al. was carried out on the impact of neutron irradiation at 437 °C and 4.6×10^{25} n/m² neutron fluence (equivalent to 4.6 dpa) on Al_2O_3 using the Petten High Flux Reactor. Swelling values were measured on five samples using dimensional measurements and averaged 1.9 %, which correlates with other literature values published in the past around the same temperature [82].

The larger swelling data found by Keilholtz et al. [71] (circles on Figure 2.3) may be explained from grain separation at the grain boundaries. Temperature effect remains quite unclear, where some literature work indicates a strong correlation and reaching a maximum around 677 °C [60] while other work showed swelling increase up to 600 °C and no effect above [71]. Moreover, Clinard et al. [29] found similar swelling at 600 °C and 752 °C, higher than that at 327 °C. Later work by Clinard et al. [30] reported swelling at 827 °C to be double than the one at 652 °C at higher neutron fluence. TEM observation showed a large density of dislocation loops, matching with other literature results showing that swelling in Al_2O_3 comes with aligned voids and dense dislocation networks.

Zinkle et al. measured the volumetric swelling and observed the microstructure evolution of polycrystalline Al_2O_3 irradiated using 4 MeV Ar^+ ions at -73 °C and room temperature and doses from 0.1 to 10 dpa. Step height and lattice parameter were used to measure the volumetric swelling. No important anisotropic swelling was observed in a vs c axis. Step height measurements reported larger swelling than lattice parameter measurements

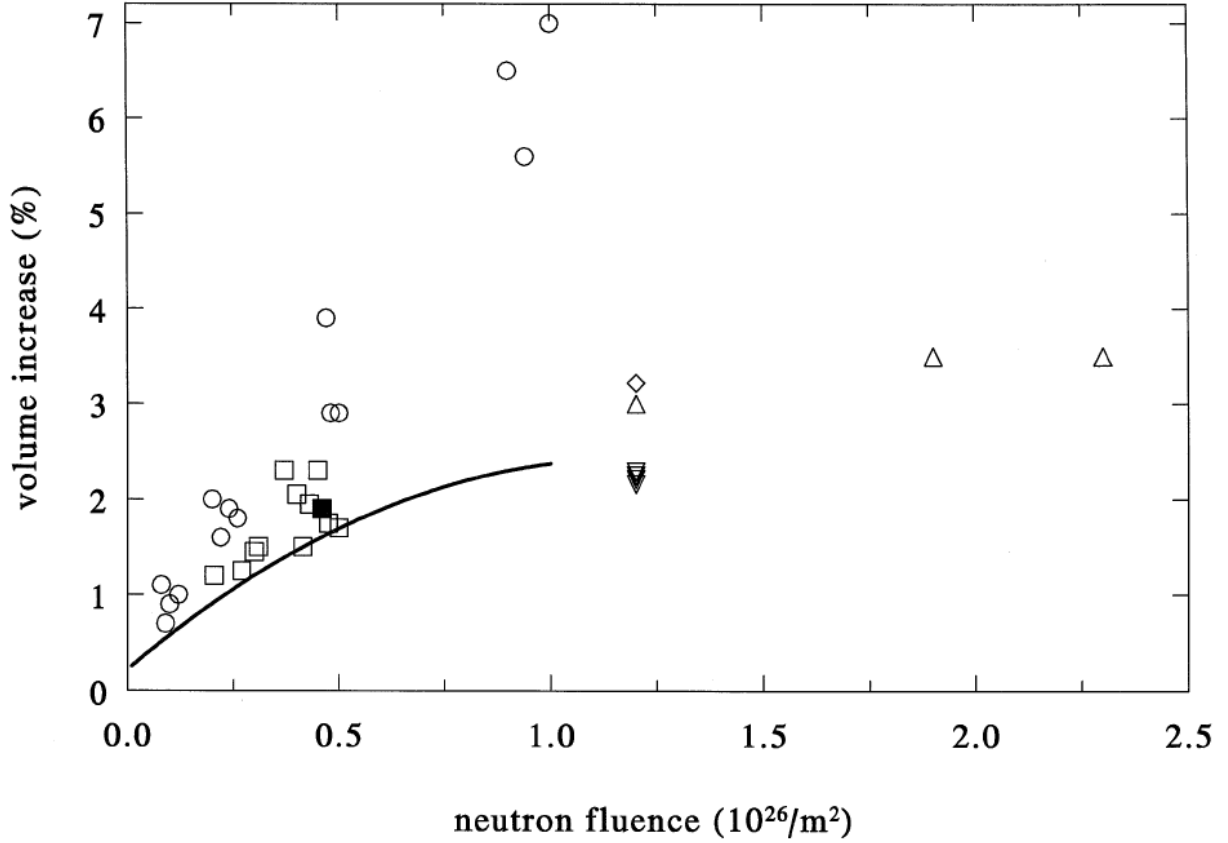


Figure 2.3: Swelling of polycrystalline Al_2O_3 as a function of neutron fluence ($E > 0.1$ MeV): $\diamond$, $T = 660$ K, Tucker et al. [153]; $\triangle$, $T = 925$ K, Clinard et al. [30]; solid line, $T = 673\text{--}823$ K, Dienst [43]; $\circ$, $T = 673\text{--}853$ K, Keilholtz et al. [44]; ∇ , $T = 658$ K, Pells et al. [116]; $\square$, $T = 650\text{--}875$ K, Clinard et al. [?]; $\blacksquare$, $T = 710$ K, Konings et al. [42]. From Konings et al. [82]

calculated from electron diffraction pattern (3.5 vs 1 % at room temperature, 10 dpa). Past work has shown a good correlation between lattice parameter swelling and macroscopic up to 0.5 dpa while showing a much lower value for lattice parameter swelling at doses above 1 dpa [71, 161, 69]. This phenomenon has been associated with the swelling contribution from large defects (voids, dislocation loops), producing macroscopic swelling while not affecting the lattice parameter. Loop formation was not observed in this work at -73 °C and no point defect swelling was measured using lattice parameter values. One assumption given by the authors is the possibility of step height expansion being associated with plastic flow due to ion implantation stress. Macroscopic swelling was reported to decrease with increasing temperature, similar to SiC behavior. This was attributed to the decrease of the thermal stability in point defect aggregates. No amorphization was found at either dose/temperature. High density of dislocation loops and network dislocation was observed at room temperature. Cavity formation was not observed at either temperature [189].

Yano et al. irradiated Al_2O_3 samples in the JOYO experimental fast reactor at fluences up to 0.4 to 4.2×10^{26} n/m² ($E > 0.1$ MeV), equivalent to 4 to 42 dpa, and temperatures from 377 to 735 °C. The macroscopic length change varied from 1.2 % to 2.3 % and increased with increasing temperature. It is worth noting that two trends can be observed as shown in Figure 2.4, higher than 850 K (577 °C) and lower than 650 K (377 °C) [169].

The higher temperature group represents the start of the void formation regime while the lower one represents the low defect mobility regime. TEM observations indicated the presence of small voids in all samples above 527 °C and 28 dpa as well as the presence of dense and tangled dislocations. Grain boundary microcracking was also observed. No irradiation temperature dependency was observed on the lattice parameter change compared to previous literature values [161, 30] and while anisotropy in the lattice expansion was observed, it was much lower than earlier results. Almost no changes were observed in the a-axis parameter and 0.17 % expansion in the c-axis parameter. A reduction of 65 % of the thermal diffusivity was observed after 4 dpa irradiation at 542 °C and 74 % reduction was noted after 14 dpa irradiation at 394 °C.

Akiyoshi conducted high dose neutron irradiation on Al_2O_3 . Samples were irradiated in the JOYO reactor between 500 – 765 °C at doses between 2.8 – 7.3×10^{26} n/m² (28 – 73

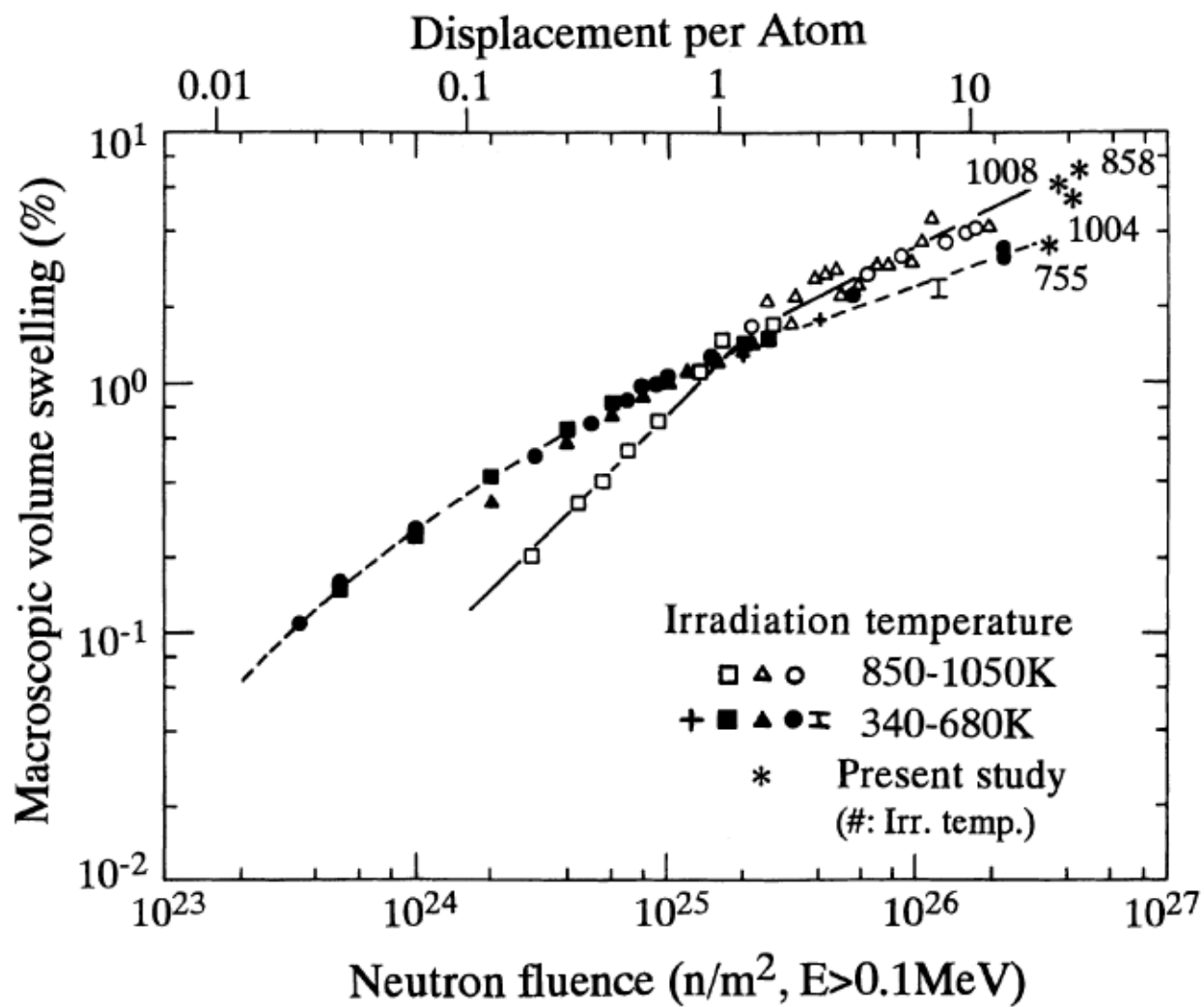


Figure 2.4: Macroscopic volume swelling of Al_2O_3 vs neutron fluence. From Yano et al. [169] based from Pells' review [115].

dpa equivalent). Macroscopic length change showed a large increase between 1.11 and 2.6 % for Al_2O_3 , increasing with increased temperature. Interstitial dislocation lines were observed via TEM, inserted mainly on the (0001) hexagonal basal plane and not interfering with each other. This allowed the formation of new loops without restrictions and the anisotropic lattice swelling consequently induced in the c-axis allowed for intergranular cracking [2].

Snead et al. observed the thermal conductivity evolution of several commercial ceramics, including BeO , Al_2O_3 , and SiC after neutron irradiation. Samples were irradiated at HFIR (ORNL) using thermal neutron flux of $7.8 \times 10^{18} \text{ n/m}^2\text{s}$ and $2.2 \times 10^{19} \text{ n/m}^2\text{s}$ ($E > 0.1 \text{ MeV}$). The irradiation doses were equivalent to 0.001 and 0.01 dpa at 60 °C and 0.01 and 0.1 dpa at 300 °C. All ceramics showed an important thermal conductivity degradation aside for BeO after the 60 °C irradiation at doses as low as 0.001 dpa. This deterioration was similar or greater than other reported at higher temperatures and higher damage levels and was more important at 60 °C than 300 °C. The thermal conductivity degradation due to neutron irradiation at low temperature was mainly correlated with the critical interstitial mobility temperature: materials with higher interstitial mobility (lower critical temperature) have a lower radiation-induced thermal defect resistance [142].

Akiyoshi et al. studied the degradation of the thermal diffusivity in Al_2O_3 and SiC after neutron irradiation in the JOYO fast reactor at fluences between $0.4 - 8 \times 10^{26} \text{ n/m}^2$ ($E > 0.1 \text{ MeV}$) at 373 – 766 °C. For both materials, the dose dependence of thermal diffusivity saturated around $3 \times 10^{26} \text{ n/m}^2$ (saturation value being different for each material). Above this value, the thermal diffusivity is only determined by the irradiation temperature, and it was shown that the thermal diffusivity slightly increased with increasing temperatures [11].

2.1.5 Radiation damage in SiC

The work of Snead et al. covered a vast range of irradiated properties of silicon carbide by reviewing existing literature and presenting new data at high temperature [140]. A lot of work has been published on irradiated SiC due to its wide range of application in the nuclear industry, from structural composites to fuel coating and the microstructure evolution is shown in Figure 2.5.

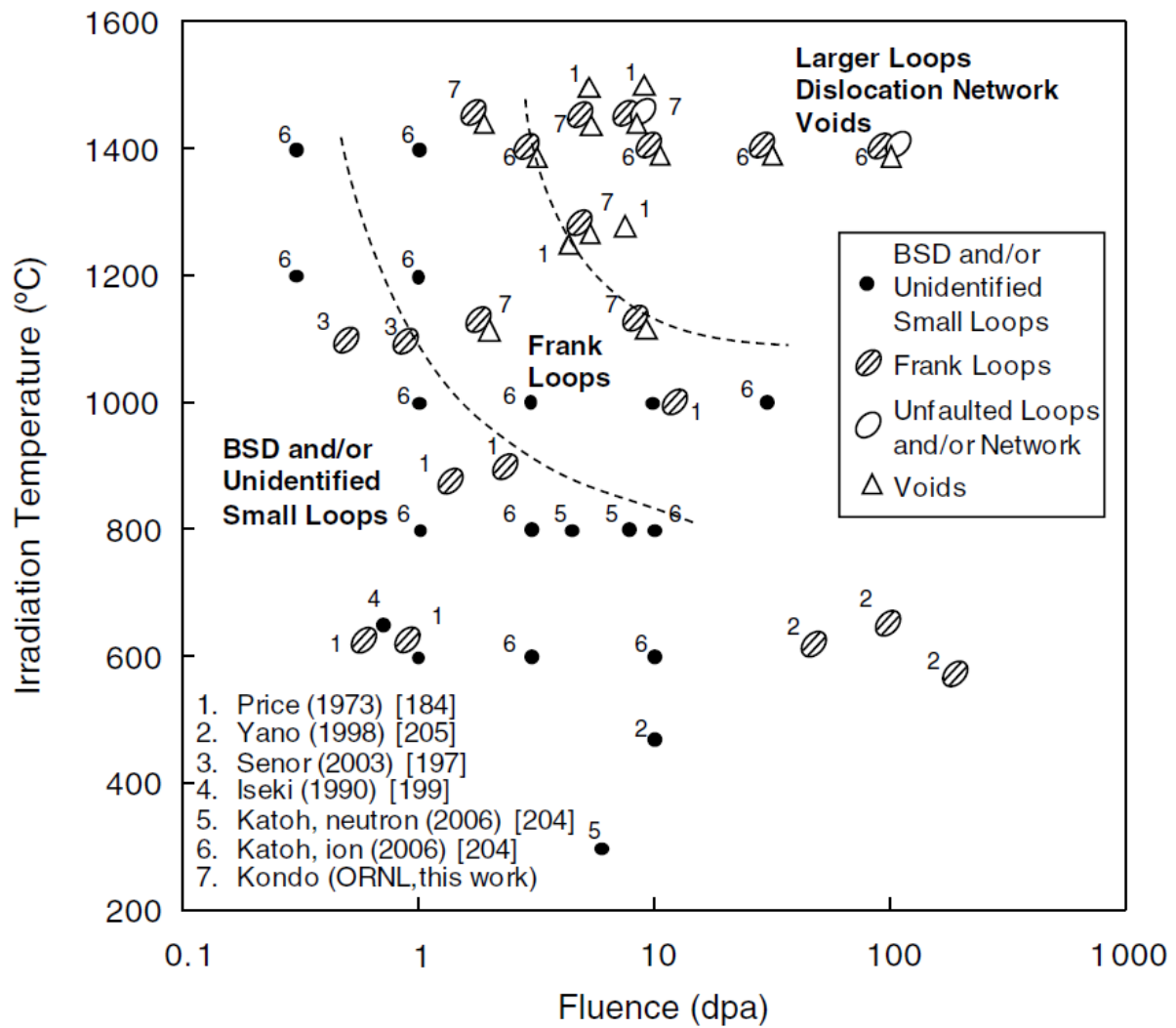


Figure 2.5: Microstructure evolution summary for neutron and self-ion irradiation in cubic SiC from Snead et al. [140]

For low to intermediate temperatures (up to ≈ 1373 K), the microstructure of irradiated SiC has been mostly studied and understood. Black spot defects have been observed at cryogenic temperatures. Below 423 K, also called the critical amorphization temperature, SiC was shown to be amorphous due to strain accumulation generated by defects formed during irradiation. Above 423 K, swelling has been shown to increase with increasing dose up to saturation and increasing temperature was shown to decrease the swelling saturation level. This intermediate temperature range from 423 K to 1273 K has also been referred to the point-defect swelling regime. Black dots defects within this range do coarsen with increasing temperature. Finally, the swelling reduction observed at higher temperature has been linked with the enhanced recombination of defects due to lower interstitial clustering density. It also saturates at low dose in the point-defect recombination range, after damage levels of a few dpa. At high temperatures (above 1173 K), interstitial type Frank loops were observed as the dominant defect type in the microstructure. When vacancies are becoming mobile (reported to be 1523 K under neutron irradiation for SiC), void formation was reported. The thermal conductivity of irradiated SiC was reported in the different temperature regimes. At lower temperature, rapid decrease in thermal conductivity has been directly correlated with high swelling. Meanwhile, even if the swelling is increasing in the high temperature regime due to the presence of voids, the thermal conductivity degradation is less dramatic. Most of the published data have been limited to room temperature measurements and direct measurements at higher temperature are still needed to better understand the effects of irradiation-induced defects. A reduction in Young's modulus was also reported, more important at lower temperatures and negligible once reaching 1273 K.

2.2 Non-fissile nitride ceramics

Coated particle fuels built around uranium oxycarbide or uranium nitride kernels are of interest for several reactor applications given their ability to retain fission products under a range of conditions. The most common modern coated particle fuels (e.g. TRISO) consist of a SiC layer between inner and outer pyrolytic carbon layers. These coatings are supposed to retain fission products within. More precisely, the silicon carbide layer behaves as protection

layer preventing the release of metallic fission products as well as increasing the overall mechanical strength of the particle. Despite its very good properties, prior studies on TRISO particle fuel performance have found that several mechanisms can affect the integrity of the SiC layer. In particular, SiC loses its mechanical strength via thermal dissociation above 1700 °C. It also can be rapidly consumed in a very short amount of time forming SiO_(g) if the IPyC layer fails, and it is vulnerable to localized chemical attacks by fission products such as palladium. In order to raise the possible operating temperature and avoid these issues, alternative coatings such as ZrC, TiC, and TiN have been examined since the 1970's. While the performance of ZrC under irradiation has received previous research, there is generally a lack of information surrounding nitride-based coatings and their behavior under irradiation. Furthermore, data on nitride ceramics are also important due to their relevance for inert matrix fuels, CERCER fuels, as well as space nuclear power [88, 24]. To this day, Si₃N₄ and AlN have been the most studied nitrides, followed by BN while limited studies have been conducted around ZrN and HfN [172, 164, 193, 185, 154, 151, 111, 109, 79, 8].

2.2.1 Silicon nitride

Often used in the industry as abrasive, β -Si₃N₄ is both hard and brittle while remaining quite cheap to produce. Its common β -Si₃N₄ phase mostly used in the industry possess a hexagonal crystal structure (hcp) with space group P6₃ and melts around 1850 °C (see Figure 2.6 and 2.7). Reported lattice parameter varies between 7.595 – 7.608 Å (a) and 2.9023-2.9107 Å (c) [93]. Si₃N₄/SiC composites (or other mixtures) can also be designed, combining thermal shock resistance, strength and fracture toughness of the nitride with the hardness and high temperature creep resistance of the carbide producing ceramics usable at high temperatures (around 1400 °C). The creation of structural parts tailored to specific ceramic properties is a step forward towards novel materials research designed for advanced reactor concepts [46].

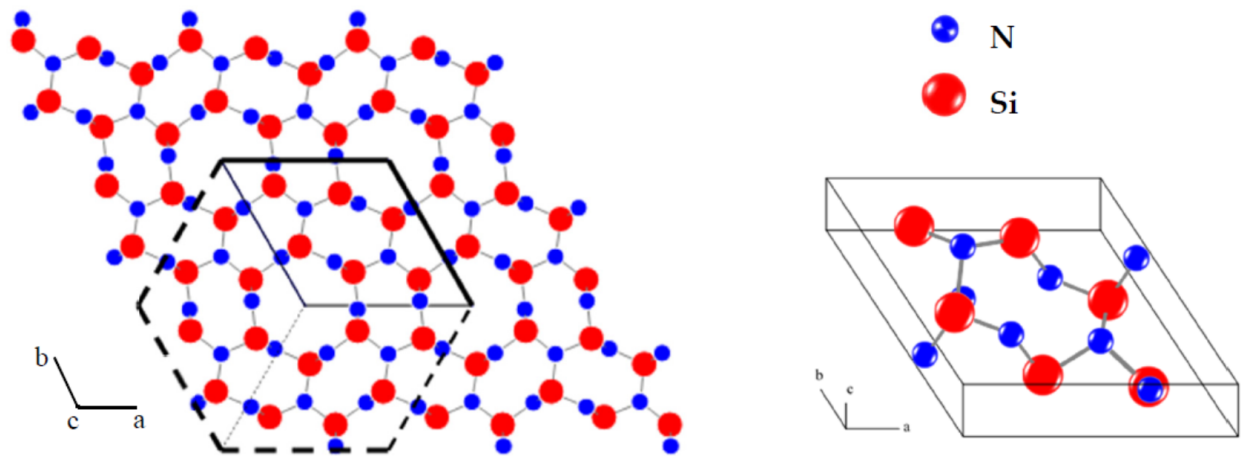


Figure 2.6: Crystal structure and unit cell of β -Si₃N₄ from Mostafa et al. [103]

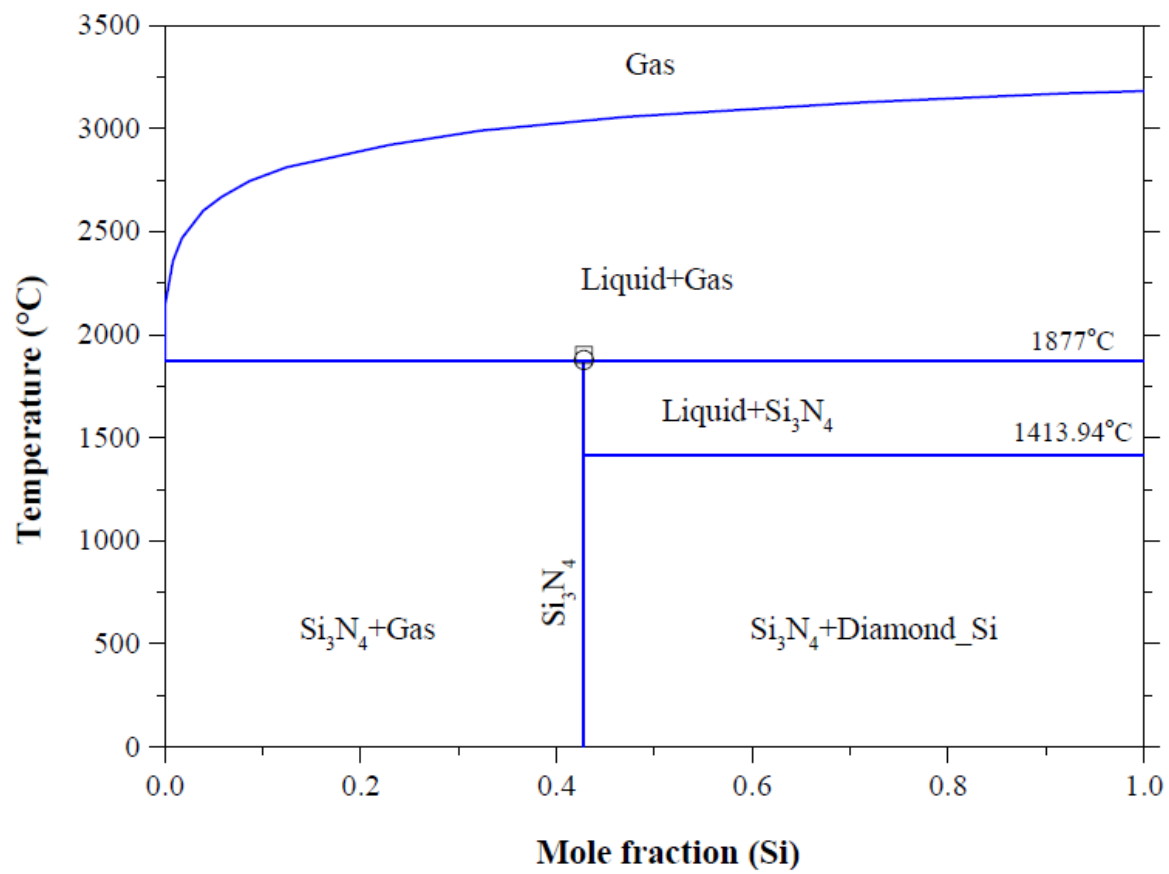


Figure 2.7: Phase Diagram for the N-Si system from Mostafa et al. [103] calculated from Ma et al. [93]

2.2.2 Zirconium nitride

Cubic B1 stoichiometric zirconium nitride possess the rock salt (NaCl) crystal structure, a face-centered-cubic (fcc) Zr lattice where the nitrogen sits in the octahedral interstitial sites as shown in Figure 2.8. Carbides and nitrides assume this structure when the ratio of carbon or nitrogen to metal falls below 0.59. General lattice parameter was measured around 4.57 Å [143].

Variation between reported literature values of lattice parameter was heavily correlated with the stoichiometry of the studied compound (reduction in nitrogen content and leftover oxygen and carbon from the carbothermic reaction process) as shown in Figure 2.9. Zr-N phase diagram is shown in Figure 2.10. The upper limit of the 1:1 stoichiometric ZrN phase at 3410 °C is of particular interest for ultrahigh temperature applications. Not a lot of data has been reported on the behavior of ZrN after irradiation, but recent research seemed to have regained interest.

On the topic of Palladium interaction mentioned above, Tan et al. looked into the high temperature interaction between palladium and four different ceramics with potential to be used in nuclear particle fuels: titanium carbide (TiC), zirconium carbide (ZrC), titanium nitride (TiN), and zirconium nitride (ZrN). Diffusion couples were annealed for 10 hours at 1400 °C and were subsequently characterized using SEM, EDS and EBSD. Both nitrides ceramics (TiN and ZrN) showed the best resistance to palladium attack with only ZrN showing a small amount of ZrPd_3 and C (amorphous) formation within the diffusion couple. Both carbides (TiC and ZrC) had better resistance than SiC but showed a large reaction zone including TiPd_3 and ZrPd_3 formation as well as amorphous carbon. Palladium attack was also noted along the grain boundaries. Overall, all discussed ceramics had a better palladium resistance compared to silicon carbide, where Si_xPd_y , SiPd_2 ; and C (amorphous) formation are observed with the complete crumbling of the SiC layer [147].

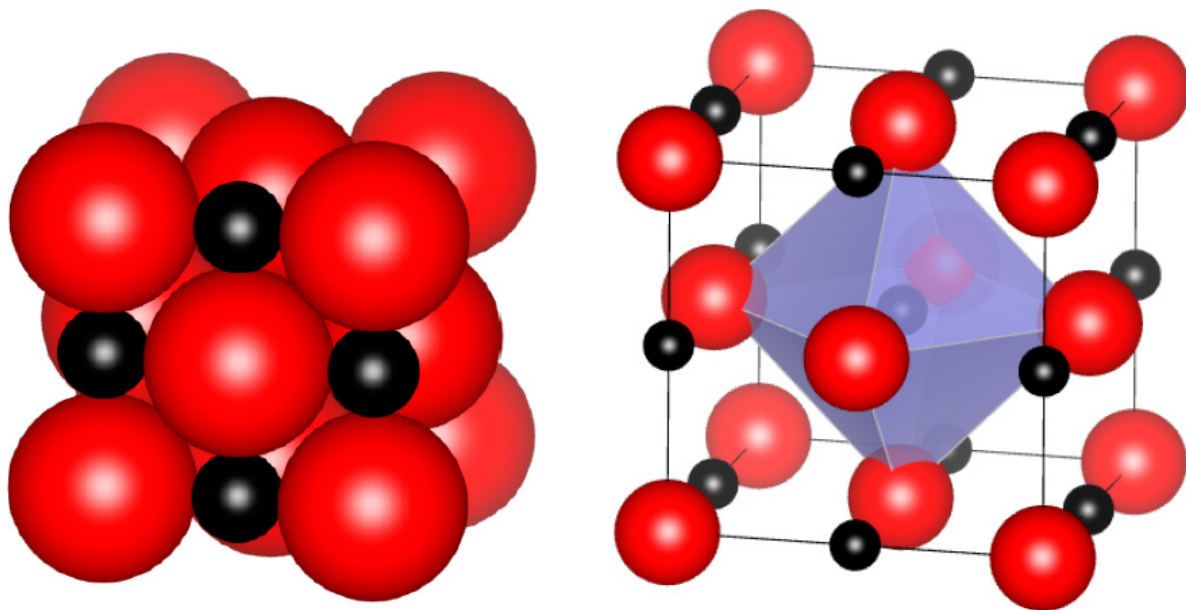


Figure 2.8: Rock salt crystal structure of zirconium nitride. Red spheres representing Zr atoms while black spheres are the nitrogen atoms in the octahedral voids from Ushakov et al. [154].

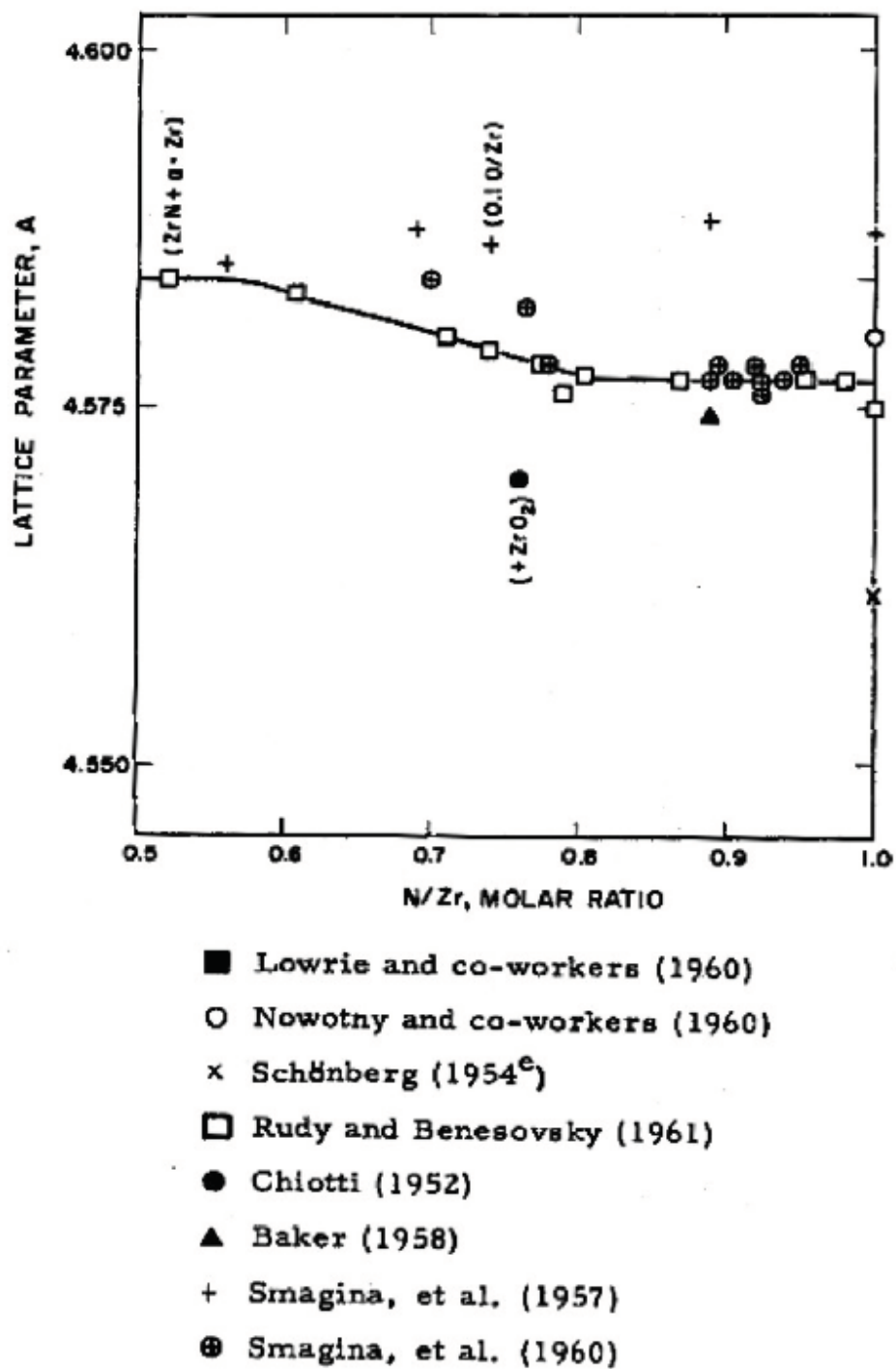


Figure 2.9: Lattice parameter variation with different nitrogen content from Toth [151]

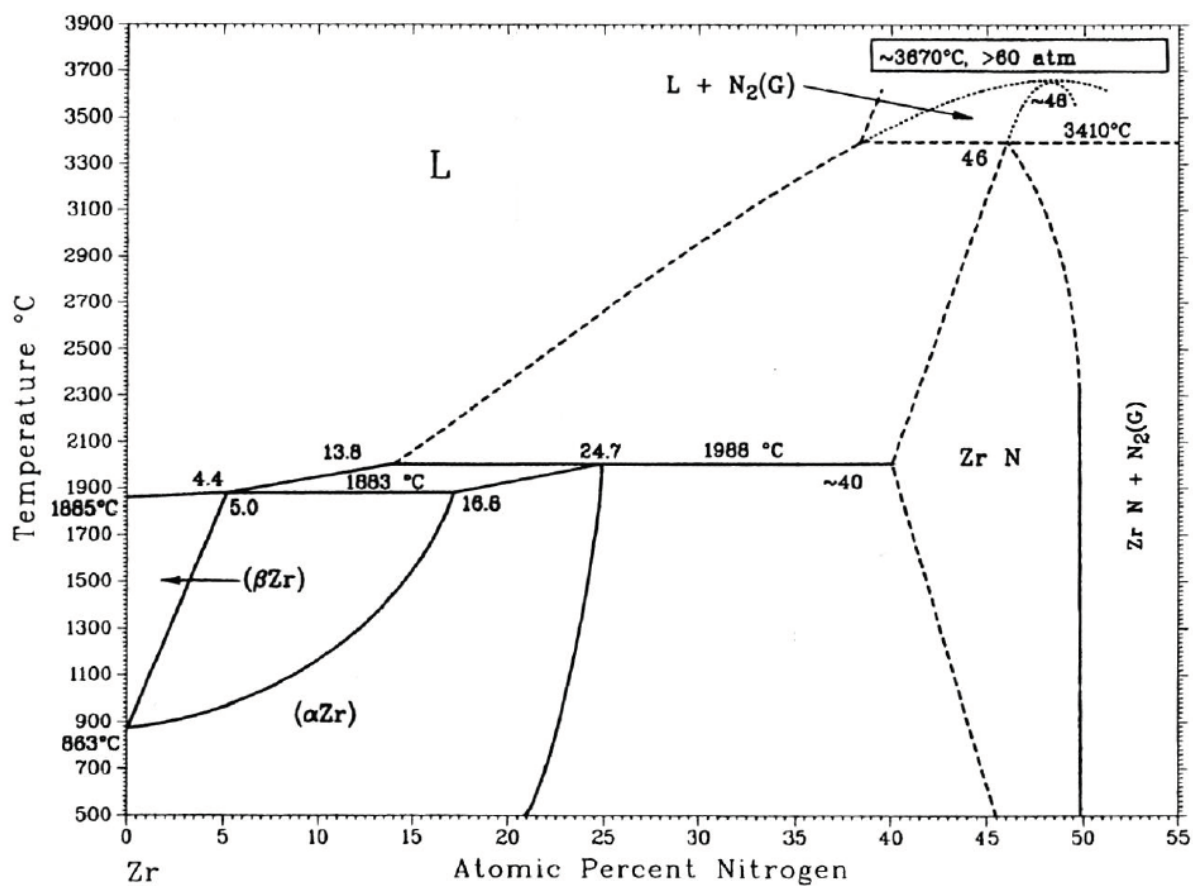


Figure 2.10: Phase Diagram for the Zr-N system from Gribaudo et al. [53]

2.2.3 Radiation damage in silicon nitride

Historical data on irradiated Si_3N_4 by Hurley et al. first reported a volumetric swelling around 0.35 % and a reduction in thermal diffusivity around 52 % after neutron irradiation at 3 dpa ($3 \times 10^{25} \text{ n/m}^2$) at 740 °C [62].

Billy et al. investigated the structural modifications in Si_3N_4 after fast neutron irradiation between 2×10^{19} and $3 \times 10^{20} \text{ n/cm}^2$ at temperatures below 660 °C [18]. A high irradiation resistance was reported after lattice parameter measurements, with reported volumetric swelling of 0.25 % for the $\alpha\text{-Si}_3\text{N}_4$ and 0.27 % for $\beta\text{-Si}_3\text{N}_4$ (values at the highest irradiation dose).

A more important volumetric swelling up to 1 % was later reported by Clinard et al [32, 31] at 22 dpa ($2.2 \times 10^{26} \text{ n/m}^2$) and temperatures varying between 410 °C to 825 °C. The lattice parameter evolution was very sparsely reported Hurley et al. [63], indicating a reduction in the a-axis and no change in the c-axis on Ceradyne Si_3N_4 while a slight increase was reported on both a and c-axis using Norton NC-132 Si_3N_4 (MgO doped) after a 3 dpa neutron irradiation ($3 \times 10^{25} \text{ n/m}^2$) at 740 °C.

Zinkle et al. observed the microstructure evolution of silicon nitride after ion irradiation using a variety of ions at temperatures between 200 and 450 K [191]. The microstructure response varied based on the ions used during irradiation. Amorphization was observed using low fluence, 3.6 MeV Fe ions ($2.2 \times 10^{19} \text{ ions/m}^2$), corresponding to a peak damage of ≈ 1.3 dpa. At higher dose (up to 7 dpa peak damage), the microstructure outside the Fe implanted region did not show any amorphization. Contrastingly, 0.8 MeV He irradiation using a fluence of $1.5 \times 10^{19} \text{ ions/m}^2$ (equivalent to ≈ 2.6 dpa) produced no amorphous region. Dual beam irradiation using both Fe and He ions showed no amorphization, indicating that the He beam annealed the amorphous region. The amorphization resistance of silicon nitride was directly correlated with the chemical species implanted during irradiation.

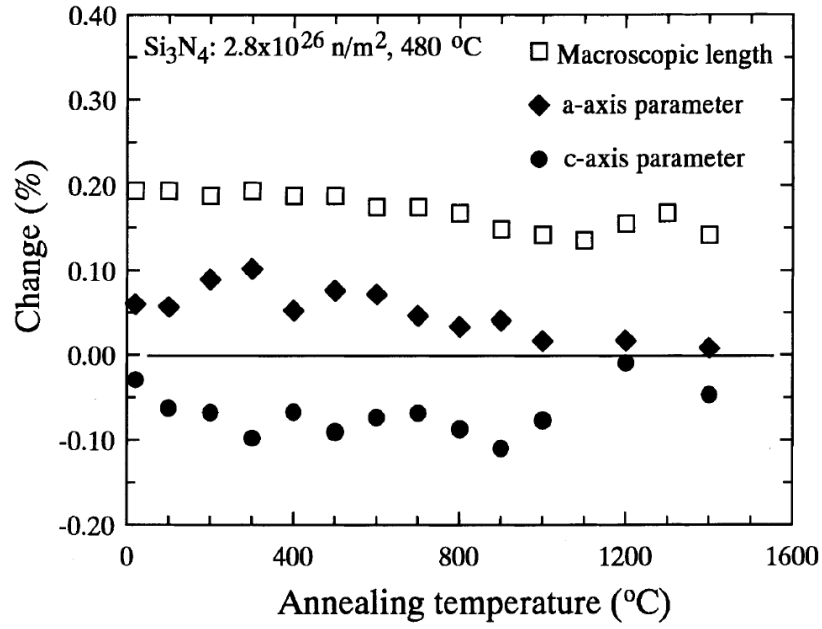
Hazelton et al. used fast neutron irradiation to 0.1 dpa at 150 °C to investigate the thermal and mechanical properties of Si_3N_4 after irradiation. Compared to other ceramics such as AlN, SiAlON and spinel, they showed Si_3N_4 have the best retention of flexural

strength and thermal diffusivity, a low dielectric loss factor and exhibited generally good radiation resistance [55].

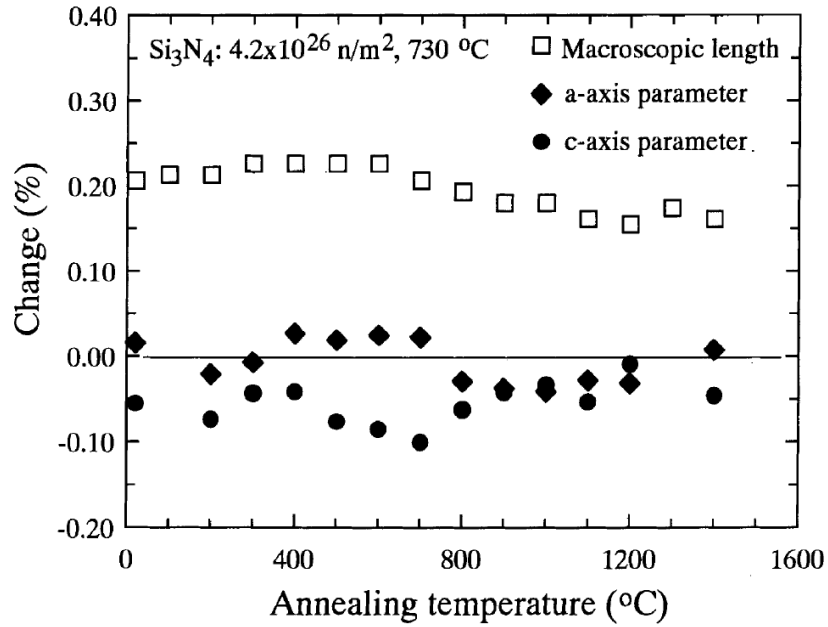
Zinkle et al. studied the microstructure evolution of silicon nitride after 2 MeV Si ion irradiation up to 4×10^{20} ions/m² and temperatures of 80 and 400 K [193]. They observed a buried amorphous band at both temperatures in the peak damage region. Amorphization was not reported in regions away from the implanted ions yet irradiated to doses up to 3 dpa (80 K) while it was observed in the ion implanted region for damage as low as 0.6 dpa. This behavior was reported as primarily controlled by the implanted ions and not the damage level. Small defect clusters (< 3 nm) were observed in the non-amorphous irradiated region. Finally, swelling associated with amorphization was reported as being less than 10 %.

Yano et al. investigated the physical properties changes of Si₃N₄ and their recovery after thermal annealing up to 1400 °C. Neutron irradiation was conducted at 4 dpa at 540 °C, 14 dpa at 390 °C, 28 dpa at 480 °C and 42 dpa at 730 °C. Lattice parameter and macroscopic length change was only conducted at the two highest dose. Similar results were found for the length change (≈ 0.43 % increase). The lattice parameter change was smaller, showing a small increase in the a-axis and small decrease in the c-axis as seen in Figure 2.11. Illustrated in Figure 2.12, the thermal diffusivity was reduced by 71 % at 4 dpa and by 81 % at 14 dpa (not measured at higher doses). Most of the unirradiated thermal diffusivity was recovered after annealing at 1400 °C while not affecting much the macroscopic length change [168].

Akiyoshi et al. investigated the macroscopic properties evolution for silicon nitride irradiated at fluences between 2.8 and 4.2×10^{26} n/m² and temperatures from 482 °C to 735 °C [4]. Swelling and thermal diffusivity data were reported after isochronal annealing up to 1500 °C. Macroscopic length change up to 0.36 % was measured and gradually decreased during annealing up to 1100 °C. Large shrinkage was observed above 1300 °C and samples became shorter than unirradiated ones at 1500 °C. This was associated with the pyrolysis of silicon nitride in vacuum. Thermal diffusivity was seen to be mostly influenced by the irradiation temperature. Thermal diffusivity recovery followed two unique stages, where the first one began around the irradiation temperature and the second one began around 1100 °C. Combining this with TEM observation, it was shown that these temperatures correspond with the mobility of interstitial atoms and vacancies respectively.



(a)



(b)

Figure 2.11: Evolution in macroscopic length and a/c axes lattice parameter at room temperature for Si_3N_4 irradiated to (a): $2.8 \times 10^{26} \text{ n/m}^2$ at 480°C and (b): $4.2 \times 10^{26} \text{ n/m}^2$ at 730°C during annealing up to 1400°C . From Yano et al. [168].

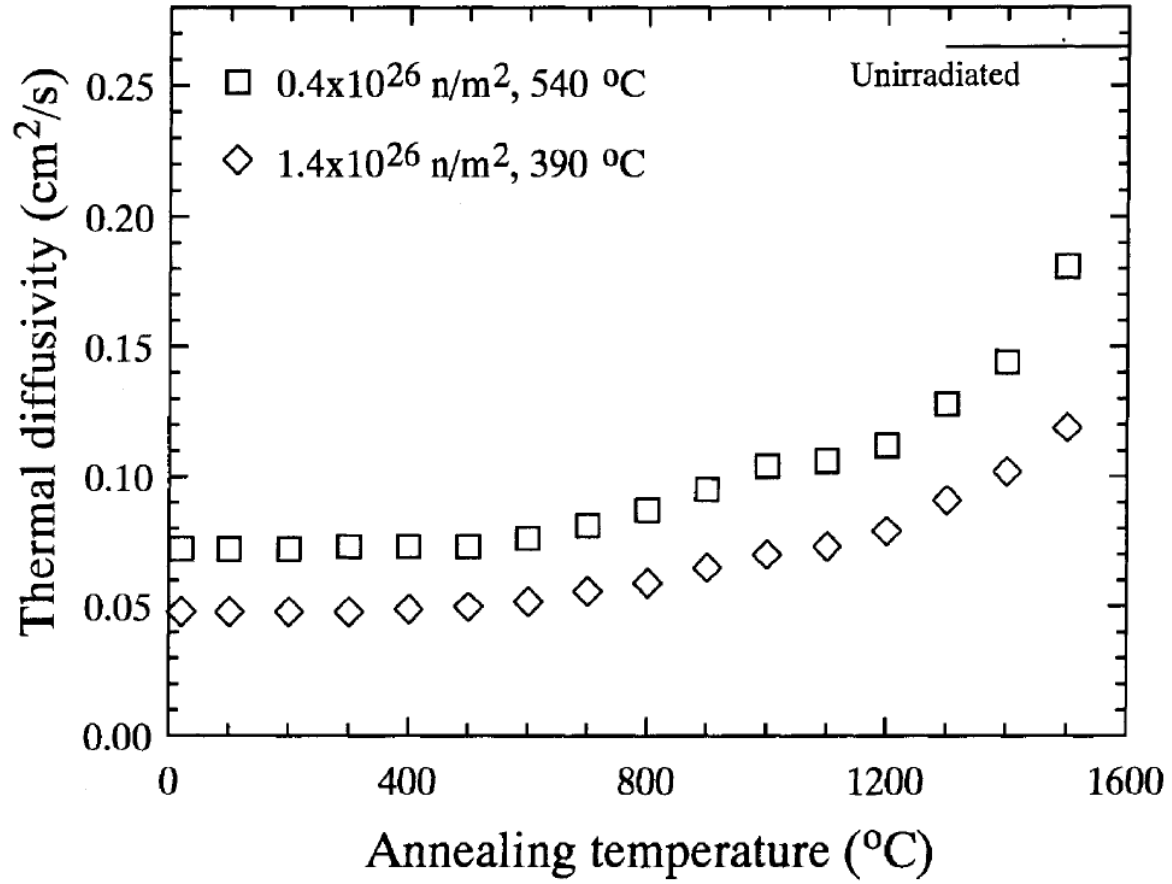


Figure 2.12: Room temperature thermal diffusivity for Si₃N₄ irradiated to 0.4 x 10²⁶ n/m² at 540 °C and 1.4 x 10²⁶ n/m² at 390 °C (Unirradiated value = 0.266 cm²/s). From Yano et al. [168].

Snead et al. measured the thermal conductivity evolution of several commercial ceramics including Si_3N_4 as previously introduced in section 1.4. Si_3N_4 thermal conductivity value decreased by about 23 W/m.K after 0.01 dpa at 60 °C (36 W/m.K unirradiated value). Complete recovery of defect resistance after irradiation to a dose of 0.001 dpa required annealing at 1050 °C [142].

Akiyoshi et al. presented thermal diffusivity and macroscopic swelling results after neutron irradiation between 2.8 and 8×10^{26} n/m² and temperatures between 502 and 766 °C for silicon nitride and other ceramics [10]. A maximum macroscopic length change of 0.4 % was reported showing saturation with neutron dose around 4×10^{26} n/m² and showed little change afterwards. Thermal diffusivity results discussed showed recovery for all samples between 673 and 773 K, threshold where interstitial atoms would become mobile and recombine with vacancies.

Akiyoshi et al. presented in a book chapter the impact of neutron irradiation on the thermal diffusivity of Si_3N_4 . The post irradiation measurements were taken at room temperature. Results from 11 neutron irradiation done at the JOYO fast reactor are presented in this document, ranging from 4 to 80 dpa and 373 °C to 766 °C as shown in Table 2.1.

Si_3N_4 maintained a good thermal diffusivity post irradiation compared to Al_2O_3 , AlN and SiC. The dose dependence of thermal diffusivity saturated around 3×10^{26} n/m² as shown in Figure 2.13. After saturation, the thermal diffusivity was determined solely by the irradiation temperature.

Further verification of this statement can be found in Figure 2.14: higher thermal diffusivity can be found in the samples irradiated below 30 dpa. These T7X samples were not saturated by neutron fluence as opposed to the T5X samples, where the thermal diffusivity was only determined by the irradiation temperature.

Thermal diffusivity was measured using laser flash techniques on neutron irradiated samples since no reliable apparatus existed at that time to measure the thermal diffusivity of an ion irradiated sample due to the small irradiated depth [8]. Yano et al. used neutron irradiated samples at 4 – 37 dpa and 377 – 727 °C and used HRTEM to study the evolution of their microstructure before and after annealing. The size and density of defects were

Table 2.1: Neutron irradiation conditions and samples ID

ID	T51	T52	T53	T54	T55	T56	T57	T58	T71	T72	T73
Neutron fluence (10^{26} n/m ²)	2.8	5.3	3.9	7.3	4.2	8.0	3.7	6.9	0.5	1.4	0.4
Irradiation temperature (K)	775	775	864	835	1004	950	1011	1039	646	668	853

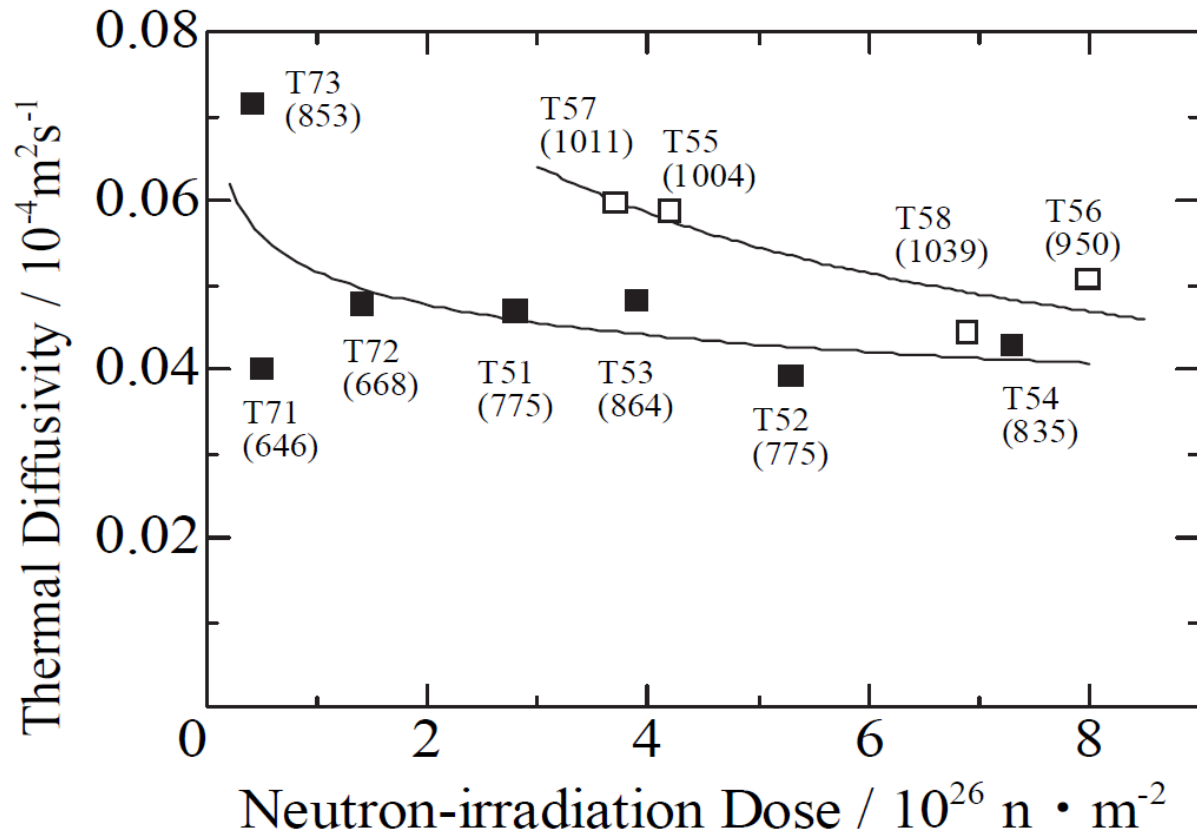


Figure 2.13: Dose dependence vs thermal diffusivity of Si_3N_4 , high temperature irradiation shown by open symbols and lower temperature irradiation shown by solid symbols.

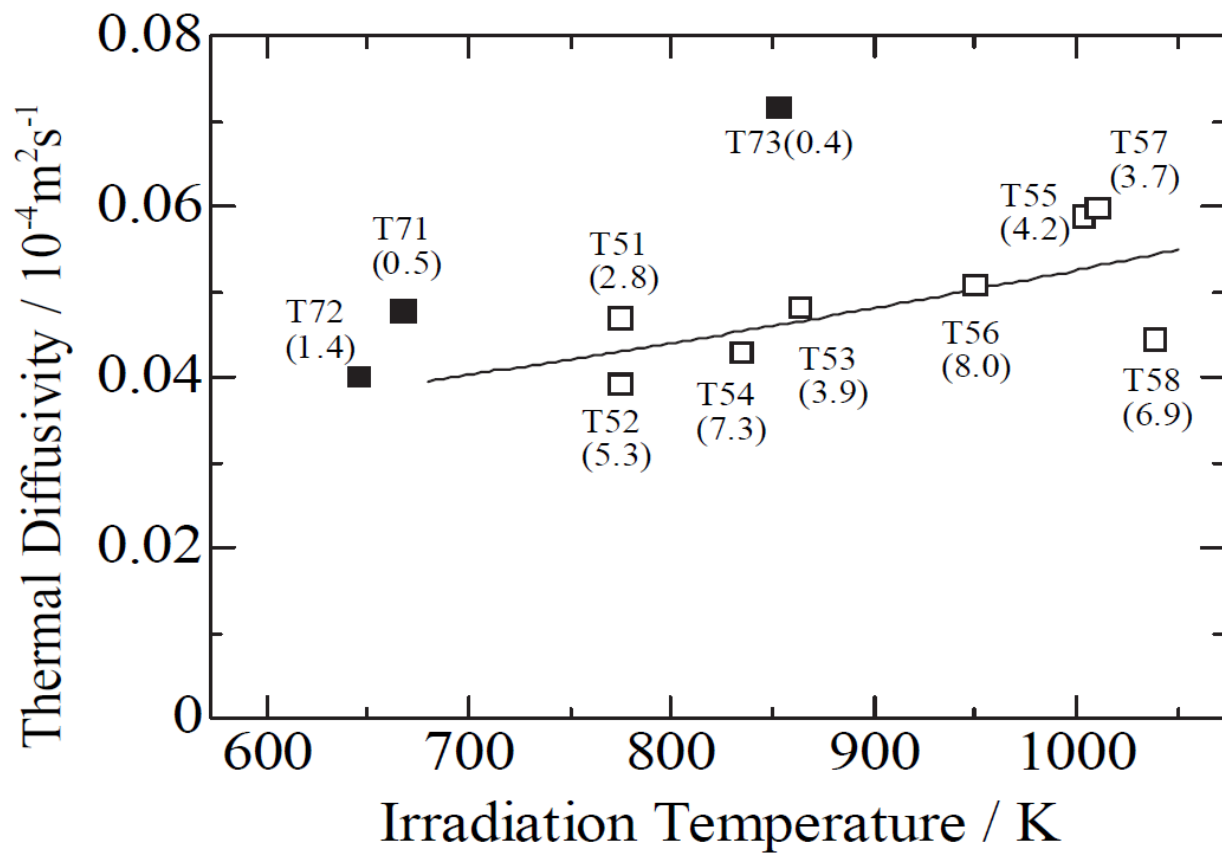


Figure 2.14: Irradiation temperature dependence on thermal diffusivity for Si_3N_4 . High neutron fluences shown in open symbols while lower fluences are shown with solid symbols. Neutron fluences in parentheses given in $\times 10^{26} \text{ n/m}^2$.

characterized. Due to the lower fluence and irradiation temperature, most defects were small nuclei of planar defects (less than 4 nm). Increase in temperature did not modify the defect size and remained stable up to high temperature. An increase in dose resulted in the increase of the density and size of induced defects on both the $(10\bar{1}0)$ and $(11\bar{2}0)$ planes and showed clear interstitial dislocation loops aspects. The remained stable with increasing temperature and did not show any significant growth. Defects were overall more numerous on the $(10\bar{1}0)$ planes than on the $(11\bar{2}0)$ planes, no matter the irradiation condition [173].

Rueanngoen et al. studied the macroscopic length change and lattice parameter evolution of Si_3N_4 after neutron irradiation at $8.5 \times 10^{25} \text{ n/m}^2$ ($\approx 0.85 \text{ dpa}$) at 290°C . Macroscopic length change for $\alpha\text{-Si}_3\text{N}_4$ was reported as 0.11 % and $\beta\text{-Si}_3\text{N}_4$ as 0.06 %. A small lattice parameter increase was observed on both a and c axis direction and the reported macroscopic volume change was slightly larger than the unit cell volume change (0.18 % vs 0.11 % respectively) [129].

Follow-up publication by Rueanngoen et al. discussed the recovery process of neutron irradiated α and $\beta\text{-Si}_3\text{N}_4$ at $8.5 \times 10^{25} \text{ n/m}^2$ ($\approx 0.85 \text{ dpa}$) at 290°C after annealing up to 1200°C . Macroscopic length change for $\alpha\text{-Si}_3\text{N}_4$ was reported as 0.11 % and $\beta\text{-Si}_3\text{N}_4$ as 0.06 %, recovering most of their original length (most defects were removed). This indicates that Si_3N_4 , and especially $\beta\text{-Si}_3\text{N}_4$ would showcase great properties at high temperature use, where this recovery process would prevent defect accumulation. The difference between α and β was suggested to be due to the different crystal structure. Two recovery stages were observed, at lower temperature between 450 and 800°C and at higher temperature between 1000 and 1200°C . The activation energies at higher temperature was found to be close to double as opposed to the one at lower temperature ($0.39 - 0.70 \text{ eV}$) [130].

Akiyoshi et al. carried out a study focusing on the effect of annealing on the thermal diffusivity of Si_3N_4 after electron and neutron irradiation. While electron irradiation was conducted using a 30 MeV beam up to 0.01 dpa at 80°C , the neutron irradiations were conducted at 28 dpa ($2.8 \times 10^{26} \text{ n/m}^2$) at 502°C and 37 dpa ($3.7 \times 10^{26} \text{ n/m}^2$) at 738°C . Isochronal anneal was conducted up to 1100°C for electron irradiated samples and 1400°C for the neutron irradiated ones. Recovery of the thermal diffusivity of the electron irradiated samples started around 300°C . Neutron irradiated samples recovery started around 400°C ,

and the recovery rate increased above 1000 °C as shown in Figure 2.15. It was unexpected to observe the recovery starting that low, as it usually starts above the irradiation temperature [6].

Rueanngoen et al. irradiated Si_3N_4 using low dose neutron irradiation (0.85 dpa at 290 °C) and studied the microstructure evolution via TEM post irradiation. Annealed samples at 850, 950, and 1200 °C were also investigated. No damage agglomeration or grain growth was observed. Only point defects were generated during the neutron irradiation. Thermally annealed samples up to 1200 °C did not show any dislocation loops or bubble/void formation, suggesting that neutron induced defects were mainly annihilated by the annealing process [128].

Tada et al. used neutron irradiation at 3.9 and 55 dpa at 700 °C to observe the impact of fast reactor irradiation on the fracture toughness of Si_3N_4 . This focused study was designed to observe the behavior of a possible candidate for inert matrix design towards minor actinide burning in fast reactor systems. A degradation of the fracture toughness was observed at both 3.9 and 55 dpa, attributed to the high density and smaller size of induced defects (interstitial dislocation loops, no voids was found under TEM). Radiation hardening was also observed at both doses as shown in Figure 2.16. Black dot defects were primarily observed at 3.9 dpa while larger interstitial dislocation loops appeared at 55 dpa [146].

2.2.4 Radiation damage in zirconium nitride

Less work has historically been done on zirconium nitride and it is reflected in the literature data presented below, where all the research done date back 20 years at best.

Chauvin et al. discussed several inert-matrix fuels concepts for americium transmutation where both TiN and ZrN are looked into as possible candidates for nitride fuel inert matrix [24]. This nitride selection was made based on several factors such as: thermal conductivity, coolant/cladding compatibility, melting point, price and availability. Most interestingly, they talked about the optimum microstructure for such materials. Spherical particles were introduced as the best choice for this application due to their lowest surface area, leading to the least amount of damage within the matrix. The size of the particles themselves was displayed as a case by case basis question, varying between 50 and 300 μm , where the lower

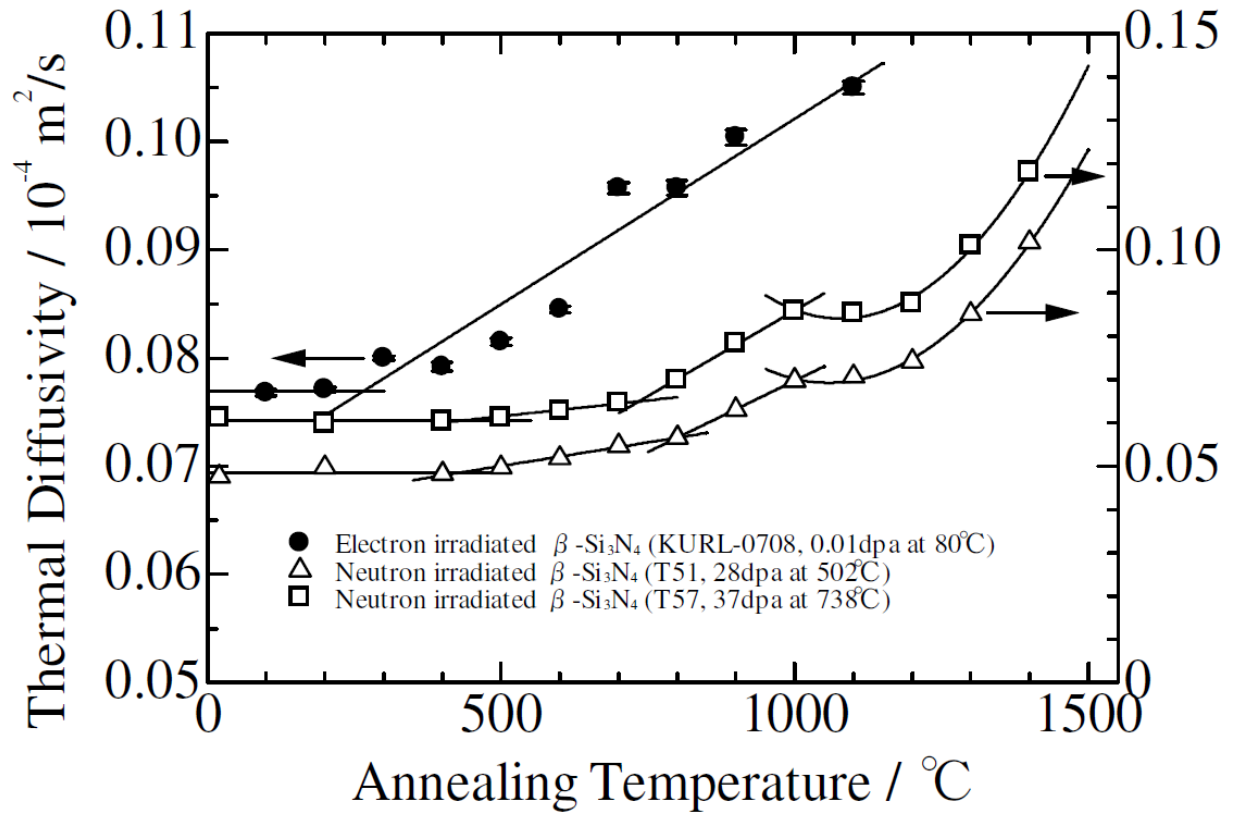
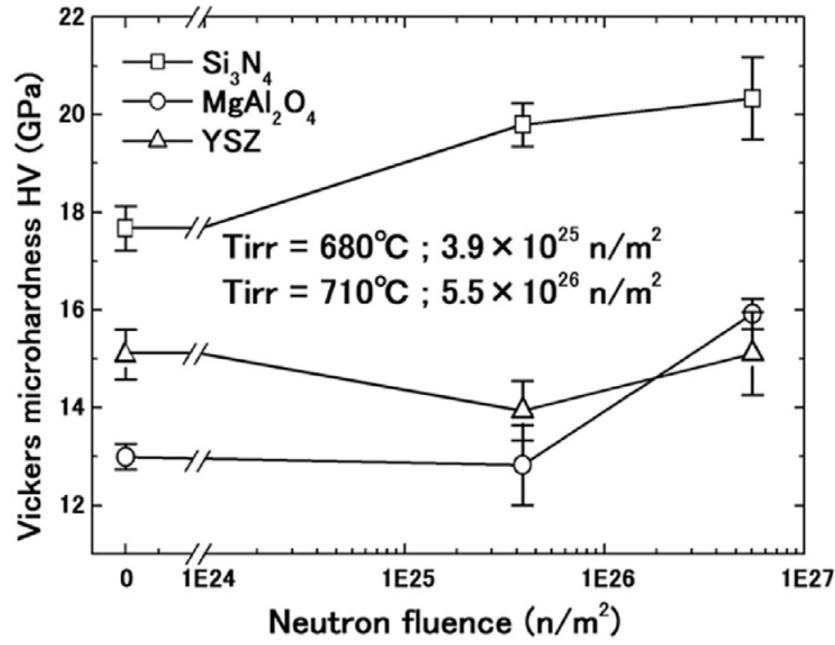
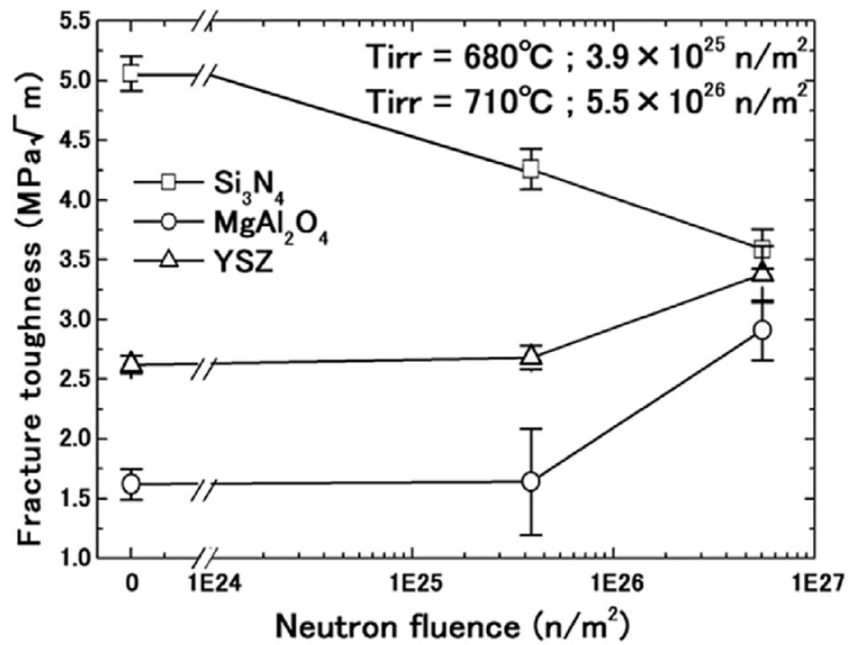


Figure 2.15: Recovery of thermal diffusivity of Si_3N_4 after electron irradiation (filled symbols) and neutron irradiation (open symbols).



(a)



(b)

Figure 2.16: Effects of neutron irradiation on (a): Vickers microhardness and (b): Fracture toughness for Si₃N₄.

limit was determined by the increase of the damaged fraction of the matrix and the upper limit by the temperature gradient in the particle. Since these numbers were predicted for a perfect interfacial contact between the inert matrix and particles, it was reminded that a poorer contact will cause a larger temperature gradient but could also help will particle swelling (due to fission gases release for example), avoiding stress propagation to the inert matrix.

Nosek et al. used finite element models to evaluate possible fuel/coating candidates for a possible coated particle fuel usable in a gas-cooled fast reactor (GFR). ZrN was one of the materials studied (as well as other carbide and nitride such as TiC, SiC, ZrC and TiN). The thermomechanical performance of these BISO fuels was compared, including thermal expansion, fission gas release, swelling and creep during both fuel fabrication and operation in reactor. While UN/ZrC was awarded the best combination in the case that all coatings had the same failure stress, UN/ZrN was labeled as good and a strong candidate if its creep rate was sufficiently large (creep rate was not known at the time of the study and TiC values were assumed for ease of calculation) [109]. An in-depth fracture analysis would be needed to study the resistance of crack propagation of these ceramics, as it was not done in this work. Gan et al. observed the behavior of ZrN microstructure after 2.6 MeV proton irradiation at 1.8 dpa and 800 °C. No dislocation loops were found in the irradiated sample, whereas faulted loops were found in ZrC, suggesting that their microstructure behaves differently under irradiation. No amorphization or precipitation was found either. No evolution in lattice parameter was observed using the HOLZ line patterns. ZrN overall showed less microstructural changes compared to ZrC and SiC, the other two materials compared in this study [52].

Yang et al. studied the stability of ZrN under 2.6 MeV proton irradiation at 800 °C at 0.35 and 0.75 dpa. No radiation induced bubbles or voids were produced as well as no radiation induced amorphization or precipitates. Using TEM to observe the evolution of the microstructure, a high density of point defects and dislocation loops were mainly observed. The defects size remained constant with increased dose, but the density increased. A very small lattice expansion was measured at 0.75 dpa but no differences were seen at 0.35 dpa. Finally, Knoop microhardness testing showed a 9.5 % hardening at 0.35 dpa and 14.6 % at

0.75 dpa. It was concluded that point defects as well as small defect clusters are the main cause of this hardening while large dislocation loops were not playing an important role in it [167].

Egeland et al. focused their work on the radiation damage tolerance of ZrN using heavy ion implantation (300 KeV Xe/Kr) to implant gaseous atoms and simulate fission induced radiation damage. TEM, and GIXRD were used at 0.4, 0.9, 4, 9, 40, 90, 160, and 200 dpa at cryogenic temperatures (-173 °C) with nanoindentation testing added at 0.9, 9, and 90 dpa. Only TEM and GIXRD were conducted at 80 dpa at 350 °C, 40 dpa at 580 °C, and 70 dpa at 800 °C. GIXRD conducted at cryogenic temperatures did not show any sign of amorphization at doses up to 200 dpa. Close to no change was observed using nanoindentation on the Young's modulus values. Hardness increased with increasing dose and was attributed to the increase in radiation induced defects present in the samples. TEM observations showed no sign of displacement defects evolution up to 580 °C. At 800 °C, the implanted layer depth doubled from 120 nm to 260 nm, indicating the mobility of some defects at this temperature. No distinct dislocation loops or bubbles were found in this study using He, Xe, or Kr gases [48].

Van Vuuren et al. studied the radiation tolerance of nanostructured ZrN coatings using 167 MeV Xe, 250 MeV Kr, and 695 MeV Bi ions to fluences from 3×10^{12} to 1.3×10^{15} /cm² for Xe, 10^{13} to 7.06×10^{13} /cm² for Kr and 10^{12} to 10^{13} /cm² for Bi ions at room temperature. No shift in the diffraction peaks was found using XRD and no phase composition changes was seen. The nanocrystalline microstructure remained intact, indicating a good radiation tolerance. All changes in hardness observed using nanoindentation remained within the standard deviation even at the highest fluence (equivalent to ≈ 0.2 dpa). Nanostructured ZrN and other materials in general tend to showcase a higher radiation resistance compared to microstructured ones. This study seems to indicate a good radiation resistance to swift heavy ions of fission fragment energies (higher than 100 MeV) [155].

Kuznetsov et al. irradiated compact ZrN samples using 136 MeV Xe ions at a fluence of 5.3×10^{14} /cm² at room temperature. No changes were found in the lattice parameter and phase composition of the sample. TEM data did not show any changes in the grain

microstructure. Some local distortion of the ZrN lattice may have been found in some region, in the order of the lattice parameter in size [86].

Ogarkov et al. observed the evolution of ZrN after 167 MeV Xe ion irradiation at a fluence of 5.3×10^{14} /cm² at 25 °C. No changes in lattice parameter or phase composition was observed post irradiation. Pores present in the ZrN surface layer appeared to increase in size as opposed to the unirradiated condition (dimensions not quantified) [111].

Olive et al. irradiated ZrN samples at the Advanced Test Reactor using neutrons up to a dose of 1 dpa at 800 °C. Using TEM, they measured an average dislocation loop size of 7.1 nm and a dislocation loops density of 5.2×10^{22} /m³. The distance between loops was around 20 nm, which suggested that ZrN was less prone to accumulation of dislocation loops (more radiation tolerant) as opposed to ZrC (6.5 nm), the other ceramic looked at in this study [112].

Bao et al. studied the microstructure evolution of hot pressed Zr after 4 MeV Au irradiation at a fluence of 5×10^{16} /cm² (equivalent to ≈ 250 dpa at midrange) at room temperature. Using BSE and EBSD imaging, they were able to observe no crystal structure change and the structural integrity of the polycrystalline ZrN without amorphization, helping the idea that it can be used as a material in advanced nuclear reactor design. ZrN lattice was found to be heavily distorted by both dislocation loops and elastic strains. Long dislocation lines were also found in the top layer of the irradiated region followed by a zone including easily resolvable dislocation lines and loops. Finally, a saturated dislocation zone can be found where no single dislocation can be resolved [14].

Nanostructured coatings evolution was studied by Wu et al. after 600 KeV Kr irradiation at fluences varying from 0 to 1×10^{17} /cm² at room temperature. Columnar grains varied between 30 – 50 nm in size. No reaction or phase transformation was observed using GIXRD. As the fluence increases, surface etching can be observed inducing recrystallisation and grain coarsening as well as microcracks on the surface grains. This also causes the hardness (24 to 15 GPa) and modulus (380 to 215 GPa) to decrease at the highest fluence [164].

Chapter 3

Experimental Materials and Methods

3.1 Materials

The cerium oxide powder obtained from Aldrich Chemistry was 99.9 % pure and had a powder diameter $d < 5 \mu\text{m}$. Natural (TZ-0) and 8 mol % yttria-stabilized cubic (TZ-8YS) zirconia powders were obtained from Tosoh with a 99.7 % purity. Alumina powder from Nanoproducts Corporation was used (> 99 % purity, $d < 10 \mu\text{m}$) as well as alumina nanofibers from Aldrich Chemistry ($d < 20 \text{ nm}$, fiber length $L = 100 \mu\text{m}$). Superfine grade high aspect ratio silicon carbide platelets were obtained from C-Axis Technology (α -SiC, hcp crystal structure), > 99 % purity, $d \approx 11 \mu\text{m}$, average aspect ratio ≈ 10). Silicon carbide nanofibers were obtained from Aldrich Chemistry (98 % purity, $d < \approx 2.5 \mu\text{m}$, $L/D \geq 20$). SEM images of the various forms of Al_2O_3 and SiC high conductivity additives can be seen in Figure 3.1.

Hot pressed silicon nitride was obtained from Kyocera (SN733). Zirconium nitride powder was purchased from MilliporeSigma and sintered at ORNL.

3.2 Sintering and sample preparation

The four sets of investigated high thermal conductivity surrogates composites (CeO_2 and 10 vol. % Al_2O_3 , CeO_2 and 10 vol. % SiC, TZ-0 and 10 vol. % SiC, and TZ-8YS and 10 vol. % SiC) were moistened with ethanol until half wet and thoroughly mixed using a planetary

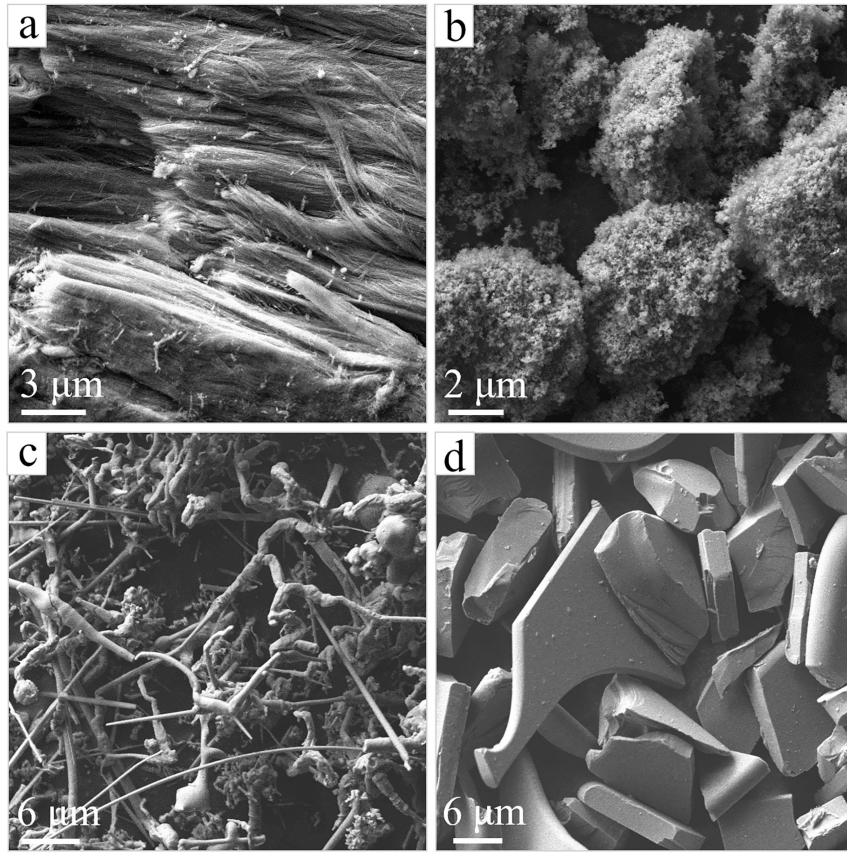


Figure 3.1: SEM images of non-fissile high conductivity additives used in this research: Al_2O_3 (a) nanofibers, (b) powder and SiC (c) nanofiber, (d) platelets.

centrifugal mixer for one hour. The mixture was then dried using an autoclave until full evaporation of the ethanol. This process allowed us to obtain uniformly mixed composite powders.

Green body pellets were cold pressed at 193 MPa for the cerium oxide-based composite and at 69 MPa for the zirconium oxide-based composite in a stainless-steel die and held at pressure for 1 minute. Close to 5 g of powder was used to make each pellet. The inner die wall as well as the punches were coated with stearic acid to prevent cracking of the green body when pushed out of the die. A 12.7 mm diameter die was used for this process. Cold isostatic pressing following cold uniaxial pressing was conducted on some cerium oxide pellets at 200 MPa. The green body pellets were sintered for 4 hours at 1650 °C for the CeO₂ pellets and at 1600 °C for the ZrO₂ pellets. They were placed within the furnace on zirconium oxide microspheres (milling media) to prevent any reaction at the base of the pellets. The sintering occurred under traditional air atmosphere for Al₂O₃-containing samples and under high purity argon atmosphere for the SiC-containing samples. After cleaning, sample thickness was around 50 mm. As discussed in more detail in the results section, due to a reaction occurring during sintering between CeO₂ and SiC, this specific composite was not studied further and ZrO₂ was selected as the matrix of choice for SiC-containing samples [149].

Sintering via Spark Plasma Sintering (SPS) was also attempted using a SPS Model 25-10 (Thermal Technology, Santa Rosa, CA). Pre-mixed powders were inserted inside a 15 mm diameter graphite die. Grafoil graphite paper was used to cover the inner wall of the die to prevent unwanted interaction between the powders and the die itself. Grafoil discs were placed between the punches and the powder at both ends of the die. Once loaded inside the chamber, a constant pressure of 40 MPa was applied at the start of the run to prevent any loss of contact during the pulsed electric current. Vacuum was maintained at less than 10 Pa in the chamber during sintering. Heating and cooling rate were set at 100 °C/min with a hold time of 5 min. Temperature was monitored using a pyrometer focused on a small hole at the center of the graphite die. Pressure during ramp down was lowered to 10 MPa. CeO₂/Al₂O₃ pellets were sintered at 1600 °C while CeO₂/SiC pellets were sintered at 1150 °C.

Pre-mixed zirconium nitride powder was inserted inside a 20 mm diameter graphite die. Grafoil graphite paper was also used to cover the inner wall of the die. Grafoil discs were placed between the punch and the powder at both ends of the die. Once loaded inside the chamber, a constant pressure of 60 MPa was applied at the start of the run to prevent any loss of contact during the pulsed electric current. Vacuum was maintained at less than 10 Pa in the chamber during sintering. Heating and cooling rate were set at 100 °C/min with a hold time of 10 min. Temperature was monitored using a pyrometer focused on a small hole at the center of the graphite die. Pressure during ramp down was lowered to 10 MPa. ZrN pellets were sintered at 1700 °C.

The density of the sintered materials was measured at room temperature following the Archimedes method using ethanol as the working liquid. The sintered high thermal conductivity surrogate samples were machined down to 3 mm diameter by 0.5 mm thickness disks by Bomas Machine Specialties (Somerville, MA). The surface of each specimen was then mechanically polished with an Allied Multiprep Polishing System using diamond lapping films and a final polishing step with colloidal silica down to 0.02 microns.

3.3 Ion irradiations

Ion irradiations were performed at the Ion Beam Material Laboratory (IBML) at the University of Tennessee, Knoxville using the 3MV tandem accelerator. 3 mm diameter disk samples with a thickness of 0.5 mm were irradiated using 20 MeV Ni⁶⁺ ions at 300, 500, and 700 °C to midrange irradiation doses of 1 and 5 displacements per atom (dpa) and at 500 °C to 15 dpa (with corresponding fluences equal to 8.25×10^{14} , 5.50×10^{15} and 1.65×10^{16} ions/cm²) for the high thermal conductivity surrogate project. This irradiation matrix was chosen to investigate relatively low dose behavior where pronounced point defect swelling effects are known to occur in ceramics and correlates with only the neutron-type damage observed in reactor (around 20 dpa). The chamber vacuum during the irradiation was below 10^{-7} torr. The ion beam was defocused and rastered over a 7 x 7 mm² area to cover the entirety of the samples in a homogeneous manner. A midrange depth of ≈ 3.5 μ m was selected in order to minimize potential issues associated with surface effects and diffusional broadening. The

SRIM 2008 computer code was used to determine the fluence needed to reach the desired damage, and to calculate the depth dependent implanted ion distribution and damage level. The calculation was done using the quick Kinchin-Pease method with a 40 eV displacement threshold energy as shown in Figure 3.2 [179].

During the irradiation, the temperature was continuously monitored by a thermocouple wire attached next to the samples. PELCO high performance silver paste was used to glue the samples to the stage to ensure good thermal contact with the substrate. One disk specimen each for the three compounds ($\text{CeO}_2\text{-Al}_2\text{O}_3$; TZ0 $\text{ZrO}_2\text{-SiC}$; TZ8YS $\text{ZrO}_2\text{-SiC}$) were simultaneously irradiated for each irradiation condition.

For the nitride coatings project, 4 x 4 mm samples were irradiated using 15 MeV Ni^{5+} ions at 300, 500, and 700 °C to midrange irradiation doses of 1 and 15 displacements per atom (dpa) and at 700 °C to 50 dpa (with corresponding fluences equal to 8.0×10^{14} , 1.2×10^{16} and 3.8×10^{16} ions/cm²). The chamber vacuum during the irradiation was below 10^{-7} torr. The ion beam was defocused and rastered over a 9 x 5 mm² area to cover the entirety of the samples in a homogeneous manner. A midrange depth of ≈ 3.5 μm for Si_3N_4 and ≈ 2 μm for ZrN was selected in order to minimize potential issues associated with surface effects and diffusional broadening. The SRIM 2008 computer code was used to determine the fluence needed to reach the desired damage, and to calculate the depth dependent implanted ion distribution and damage level. The calculation was done using the quick Kinchin-Pease method with a 35 eV (Zr) / 25 eV (N) / 15 eV (Si) displacement threshold energy as shown in Figure 3.3, 3.4. The temperature was continuously monitored by a thermocouple wire attached on a dummy sample outside of the irradiation area. PELCO high performance silver paste was used to glue the samples to the stage to ensure good thermal contact with the substrate. One sample of each composition was simultaneously irradiated for each irradiation condition aside for the 50 dpa irradiations, where two separate irradiations occurred.

3.4 Microstructure characterization

Microstructural characterization was performed on the surfaces and interior regions of the samples before and after ion irradiation. Scanning Electron Microscopy was used to conduct

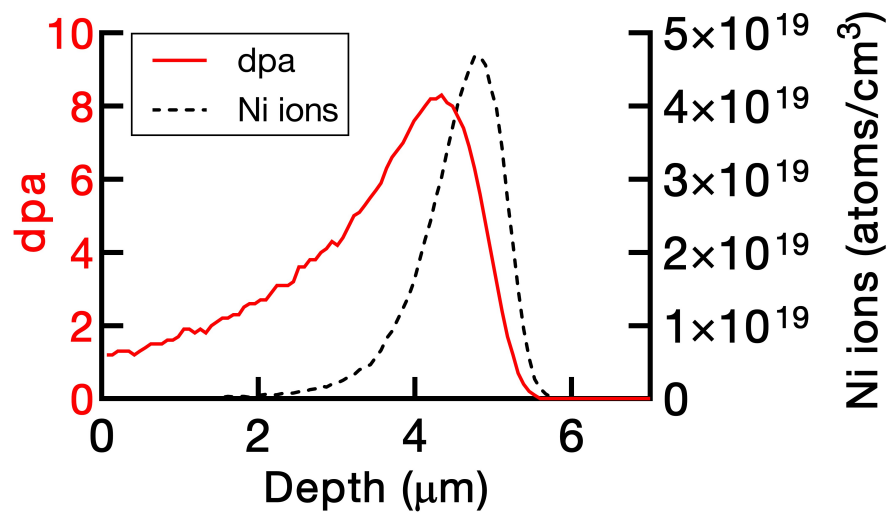


Figure 3.2: SRIM plot of the 5 dpa midrange dose irradiation of $\text{CeO}_2\text{-Al}_2\text{O}_3$ target by 20 MeV Ni^{6+} ions and implanted Ni ion distribution.

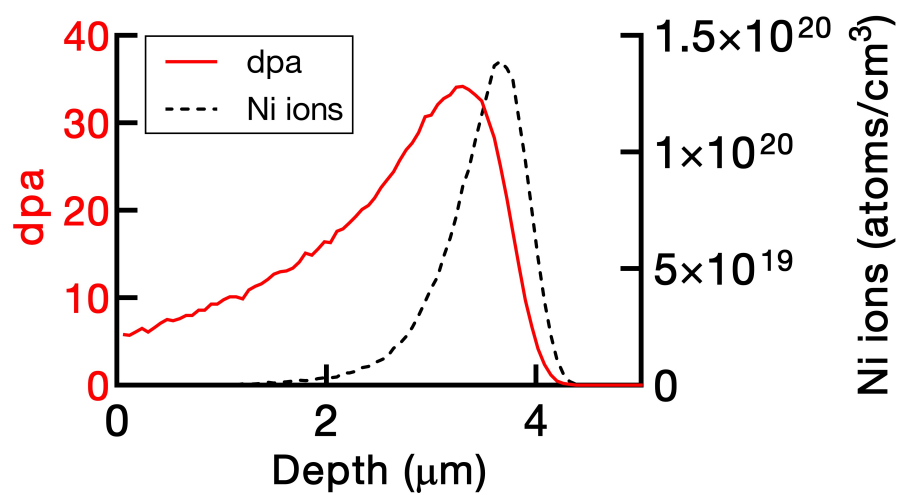


Figure 3.3: SRIM plot of the 15 dpa midrange dose irradiation of ZrN target by 15 MeV Ni^{5+} ions and implanted Ni ion distribution.

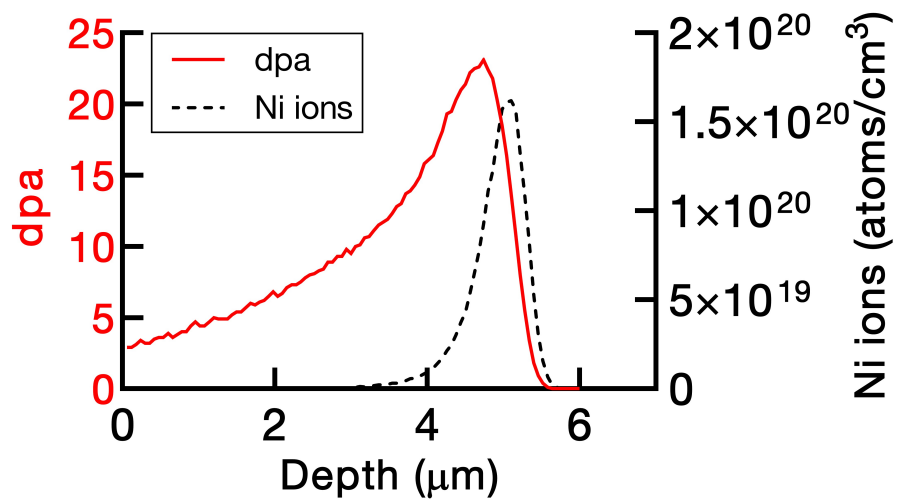


Figure 3.4: SRIM plot of the 15 dpa midrange dose irradiation of Si_3N_4 target by 15 MeV Ni^{5+} ions and implanted Ni ion distribution.

microstructural analysis of the surface of the polished surrogate fuel pellets before and after irradiation. Micrographs were taken using the secondary electron mode in a ZEISS Auriga crossbeam FIB/SEM at 5 kV (to further minimize surface charging) for characterization of general microstructural features, grain size and grain boundary evolution. More detailed elemental chemistry information was obtained using Energy Dispersive X-Ray Spectroscopy (EDS) on a ZEISS EVO SEM. This provided independent semiquantitative information on potential new chemical phases and to ensure that no secondary element was locally concentrated at the surface of the samples. Surface feature evolution (grain boundary, second phase, new phase formation) following ion irradiation and topographic mapping was performed using a Jupiter XR (Asylum Research) Atomic Force Microscope.

3.5 Grazing Incidence X-Ray Diffraction

Grazing Incidence X-Ray Diffraction (GIXRD) was conducted at room temperature before and after ion irradiation in order to observe the possible chemical reactions that may have happened during the sintering and irradiation. Due to the detection limit for second phases (around 5 wt.%) of the GIXRD technique and the small size of the samples, the lattice parameter of the second phase was separately determined using Transmission Electron Microscopy. GIXRD was also used to quantify the evolution of the lattice parameter of the matrix after sintering and irradiation. Several grazing angles were used to cover different irradiation depths in order to ensure the quality of our results and to investigate possible dose (depth) dependent processes. The X'Pert HighScore Plus software was used for phase identification as well as lattice parameter determination using Rietveld refinement.

3.6 Nanoindentation

Nanoindentation mechanical property measurements were obtained at room temperature using an Agilent Technologies (Keysight) G200 system on the polished surfaces of both unirradiated and irradiated fuel surrogate samples. A Berkovich diamond indenter tip and the Continuous Stiffness Mode were used at a constant load rate of 400 $\mu\text{N/s}$ and maximum

indentation depth of 2000 nm in order to obtain detailed information on the hardness and elastic modulus vs. indent depth. A minimum of 20 valid indents were performed on each sample. Room temperature nanomechanical testing was conducted using a KLA uNano system equipped with a Berkovich diamond tip for the nitride samples. Continuous stiffness measurements were done using 0.05 1/s for indent strain rate, 2 nm for target dynamic displacement, and 45 Hz for target frequency. Arrays of 6 x 5 indents were done with a maximum indent depth of 2000 nm.

3.7 FIB/TEM

A JEOL 2100F Transmission Electron Microscope (TEM) operated at 200 kV and located at the Low Activation Materials Development and Analysis (LAMDA) laboratory at Oak Ridge National Laboratory was used to conduct microstructure characterization. Cross-sectional TEM samples were prepared by the focused-ion beam (FIB) lift-out method using a FEI (now Thermo Fisher Scientific) Versa 3D FIB instrument located at LAMDA and a ZEISS Auriga crossbeam FIB/SEM instrument located at the Joint Institute of Advanced Materials (JIAM) in Knoxville, TN. To increase the conductivity and to prevent charging on the surface of the ceramic samples, their surface was sputter-coated with ≈ 7 nm layer of gold. The final thinning step was conducted using 2 keV Ga^+ with a $\approx \pm 5^\circ$ incidence angle between the Ga^+ beam and the sample surface for 10 min to remove most of the FIB-induced damage and further reduce the sample thickness. Scanning TEM (STEM) mode was utilized to quantify the microstructural changes associated with ion irradiation.

The microstructure of the unirradiated and irradiated areas of the Si_3N_4 and ZrN samples were observed and characterized using TEM-BF, STEM-BF, and enhanced energy dispersive X-ray mapping (EDS) using the ChemiSTEM technique. TEM images were taken using under and over focused conditions with a defocus value of 1200 nm for Si_3N_4 and 1500 nm for ZrN. To quantify the voids present in the samples, under-focused images (dark Fresnel fringe around a white center) were used to measure both void size and number density. The void diameter is represented by the inner diameter of the dark Fresnel fringe surrounding the white dot. A minimum of 200 voids were quantified in every image.

3.8 Thermal conductivity

3.8.1 Laser Flash Analysis

The standard approach for thermal conductivity measurements in materials for nuclear applications have been the use of laser flash technique (LFA) [114]. Using disks specimens with parallel surfaces, a short laser pulse is emitted on one side while the infrared emission is measured on the other. The heat conductivity of the tested material is quantified using the time it took for the opposite side to be heated by the laser pulse. While the laser flash measurement provides thermal diffusivity data, both specific heat and density values are also needed to convert it to thermal conductivity values. Results obtained through laser flash analysis correspond to an average value across the entirety of the sample thickness. Despite being extensively used, this technique has some limitations. Several nuclear fuel concepts for advanced reactors are based on multi-layer/composite materials and modeling studies may require spatially resolved thermal conductivity measurements. Moreover, this technique cannot be applied to ion irradiated materials, where a thin surface layer has been damaged while the deeper region remained unirradiated.

The thermal conductivity of the unirradiated sintered pellets was determined through measurement of their thermal diffusivity using 6 mm diameter x 2 mm thickness samples. A NETZSCH LFA 457 Laser Flash setup was used and measurements were performed three times for each sample at 50 °C and every 100 °C between 100 °C to 900 °C in vacuum before the start of the experiment, then in flowing Argon [100]. Graphite coating spray was applied on both sides of the pellets to minimize reflection for the laser. The thermal conductivity was obtained using equation 3.1:

$$K = a \times C_p \times \rho. \quad (3.1)$$

Where K is the thermal conductivity of the pellet, a is the experimentally measured thermal diffusivity, C_p is the specific heat capacity and ρ is the density of the pellet. Specific heat capacities of the pellets were found using the Neumann-Kopp law as shown in equation 3.2:

$$Cp = Cp_{additive} \times f_{additive} + Cp_{matrix}(1 - f_{additive}). \quad (3.2)$$

Where $Cp_{additive}$ and Cp_{matrix} are the specific heat capacities of the additive and matrix, and $f_{additive}$ is the mass fraction of the second phase. Specific heat capacity values were obtained using the HSC Chemistry software. The pellet density was obtained from the Archimedes method measurements mentioned previously.

3.8.2 Modulated Thermoreflectance

Modulated thermoreflectance techniques are based on the use of two laser beams incident to the sample surface [37, 74, 75, 73]. One beam act as a heater with a modulated intensity (square or sine wave function) while the other beam behaves as a sensor, where its intensity change correlates with the temperature change at the surface of the sample. A transducer metal layer such as aluminum is deposited at the surface of the polished sample to ensure the optical absorption of the pump beam while also behaving as a temperature sensor (the deposited metal layer is chosen depending on the laser wavelength). Minute changes in the temperature of the deposited metal layer induces reflectivity change. Various thermoreflectance-based techniques exist including time domain thermoreflectance (TDTR), frequency domain thermoreflectance (FDTR) and spatial domain thermoreflectance (SDTR). Time domain thermoreflectance uses an ultrashort pulse to excite a thermal pulse while a probe beam is used to trace the temperature evolution on a nanosecond timescale. TDTR tends to only be sensitive to thermal transport in the depth direction. FDTR is based on continuous wave lasers examining phase lags between excitation pulse and temperature based on a modulation frequency. Finally, SDTR measures the temperature profile around the beam excitation spot. This technique can be applied to irradiated materials, included hot cell applications for neutron irradiated samples since the exact values of some of the experimental parameters (deposited metal layer thickness, thermal interface resistance, beam spot sizes) are not required [73, 160, 122, 121, 76].

Ion irradiated samples were characterized using spatial domain thermoreflectance in collaboration with Dr. Marat Khafizov at the Ohio State University. Figure 3.5 shows

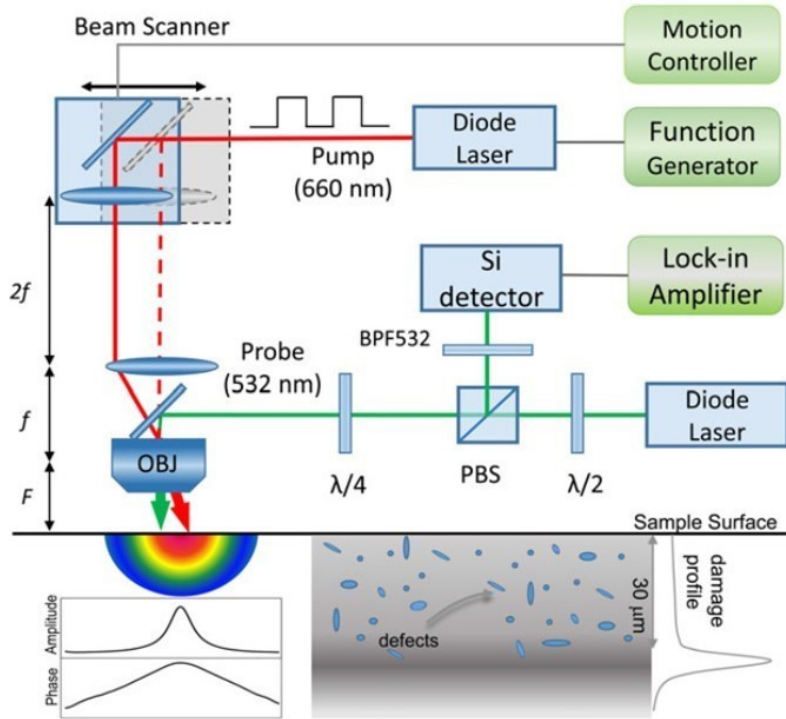


Figure 3.5: Spatial domain thermoreflectance (SDTR) experimental apparatus. The pump beam is oscillated and scanned on the sample surface using an optical two-lens lever. The probe beam remains fixed and its reflectivity change is recorded. (From Khafizov et al. [73]).

a diagram of the SDTR system. The pump and probe beams were emitted from continuous wave diode lasers at 660 nm and 532 nm respectively. The pump signal was modulated using direct modulation of the laser with an electronic trigger. Both beams were focused on the sample surface using a 50X optical microscope allowing for a $\approx 1 \mu\text{m}$ spot size. Lateral scanning was achieved using an optical two-lens lever. The minute reflectivity changes of the probe beam (10^{-5} to 10^{-3}) were measured using lock-in amplification of the photodiode voltage signal.

3.8.3 Transient Grating Spectroscopy

The thermal conductivity of the ion irradiated region as well as the unirradiated region and unirradiated samples will also be measured using Transient Grating Spectroscopy (TGS) in collaboration with Dr. Short's research group at the Massachusetts Institute of Technology. Transient Grating Spectroscopy is a non-destructive, non-contact spectroscopy technique capable of revealing a materials' elastic, acoustic and thermal properties in one measurement. It uses pulsed laser beams (pump) to create a standing acoustic wave (SAW) on the surface of the sample and a continuous laser beam (probe) to study the SAW [40, 135]. The laser pulses generate an interference pattern on the sample surface, resulting in thermal expansion proportional to the intensity of the interference pattern. This non uniform thermal expansion causes the propagation of acoustic waves in the sample. When interacting with each other, these waves will create the standing acoustic wave (SAW) which will be probed by the continuous laser beam. This signal will then be diffracted from the SAW and allow for property analysis. The probe spot diameter used for data collection is around 100-150 μm . Thermal diffusivity accuracy was tested using Ge single crystals and the results varied from 1.7 to 7.2 % compared to modeled data [41]. A typical TGS signal is presented in Figure 3.6. The thermal spike decay can be directly correlated with the thermal diffusivity of the sample. The signal frequency can be correlated to the elastic properties of the sample using an FFT. Finally, the oscillation decay rate can be correlated to the acoustic damping [51].

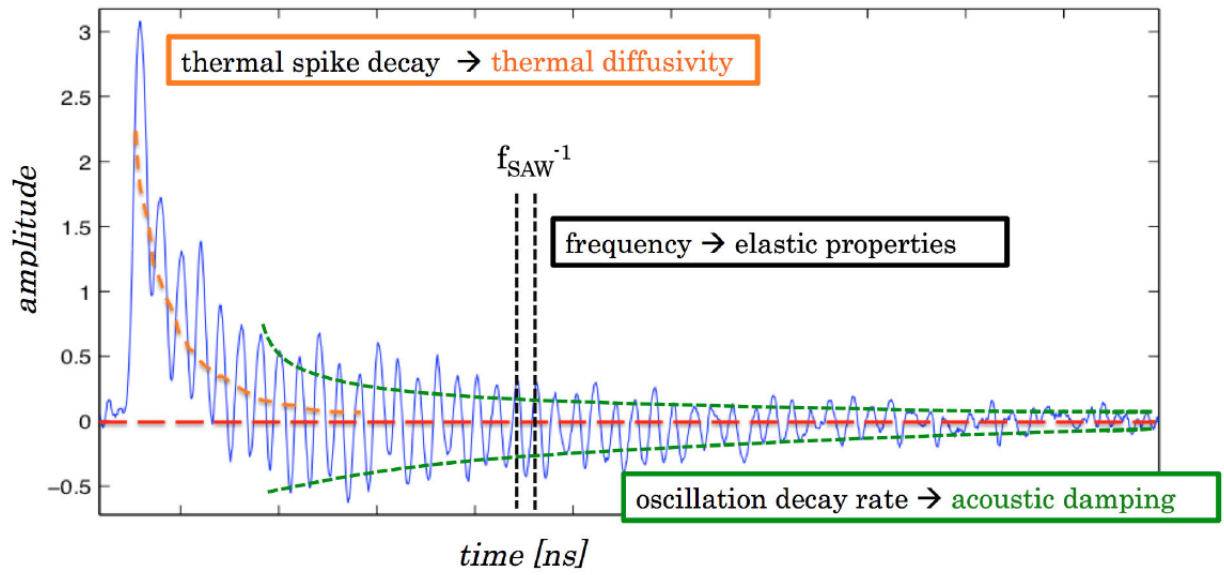


Figure 3.6: Thermal, elastic and acoustic properties represented on a TGS signal from Ferry [51]

Chapter 4

High Thermal Conductivity Fuel Surrogate

4.1 Sintering

The thermal conductivity of a sintered material decreases rapidly with increased porosity. Therefore, one of the primary goals for the sintered sample was to achieve a sufficiently high density compared to the ideal theoretical density. Multiple sintering parameters were used, both with conventional sintering and SPS. The incorporation of Al_2O_3 nanofibers was initially considered to be a convenient pathway to introduce a high thermal conductivity second phase while also causing reduced/suppressed grain boundary cracking during irradiation compared to micron-grain size powders (due to the fine grain size in the fibers). Unfortunately, the sintering of the Al_2O_3 fibers with the CeO_2 matrix caused imperfect interfacial contact with the matrix as well as generation of transgranular cracking with conventional sintering methods. The Al_2O_3 nanofibers also tended to agglomerate and form heterogeneous macroparticles, cancelling the first reason for using this high aspect ratio additive. In order to alleviate this issue, samples containing Al_2O_3 powder were selected for the consolidated $\text{CeO}_2/\text{Al}_2\text{O}_3$ composites due to their high density and lack of imperfection in the sintered product. SPS sintering and consolidation using Al_2O_3 nanofibers produced undesirable results including relatively low-density pellets (65 % - 85 %), a non-uniform distribution of the Al_2O_3 second phase, and most of the matrix was reduced to Ce_2O_3 . It is possible that

CeO₂ reacted with the surrounding die/graphite foil, causing CO(g) release which further reduced the CeO₂ matrix into Ce₂O₃ [102, 118]. CeO₂/powdered Al₂O₃ pellets for this study were sintered at 1650 °C using conventional sintering and reached a final 95.3 % theoretical density. The Al₂O₃ particle second phase was dispersed uniformly within the CeO₂ matrix.

Despite reports of successful sintering between UO₂ and SiC presented in recent literature [175, 176], we observed severe chemical compatibility problems during the sintering of this high conductivity SiC second phase with CeO₂. Throughout our work, it was found that CeO₂ is more reactive than UO₂ and tends to decompose at a relatively low temperature when sintered with SiC additives. The initial 4 hours conventional sintering experiments revealed both total melting at 1650 °C (air atmosphere) and partial melting at 1600 °C (Argon atmosphere) of our composite samples. After several modifications in sintering conditions, a pellet was sintered at 1450 °C for 1 hour under Argon atmosphere with the appropriate dimensions and no apparent melting, but its density was quite poor (75 %) so further work was not conducted on it. All of these samples exhibited a reduction of the CeO₂ matrix into Ce₂O₃ which might be attributed to the hydrogen present in the atmosphere (Ar + 4% H₂). The obtained density values were similar to a recent CeO₂/SiC study reported in the literature [126]. Recent work by Yeo et al. [175, 176] introduced SPS as a practical technique allowing to sinter high density UO₂-SiC samples while preventing oxidation of the SiC second phase. However, unsatisfactory results were obtained during our research attempts to sinter CeO₂ and SiC using SPS. Our sample was sintered at 1300 °C under Argon atmosphere, using a 100 °C/min ramp up/down and 5 min hold time. According to visual observations, SEM and XRD, the final sintered sample was divided into two distinct zones as shown in Figure 4.1.

The top part of the sample, with a gold coloration, contained most of the SiC platelets, as well as some CeO₂, but most of the Ce-containing material in this region was reduced to Ce₂O₃. The bottom part of the sample, with a grey coloration, seemed to be lacking in the presence of SiC platelets, and instead showcased a new phase, a Ce₂Si₂O₇ compound. Large transgranular fractures were present throughout the pellet, rendering it quite brittle. While Roleček et al. [126] also reported CeO₂ reduction into Ce₂O₃ and formation of Ce₂Si₂O₇ in their SPS sintered work, the separation of the sample in two distinct phases apparently wasn't

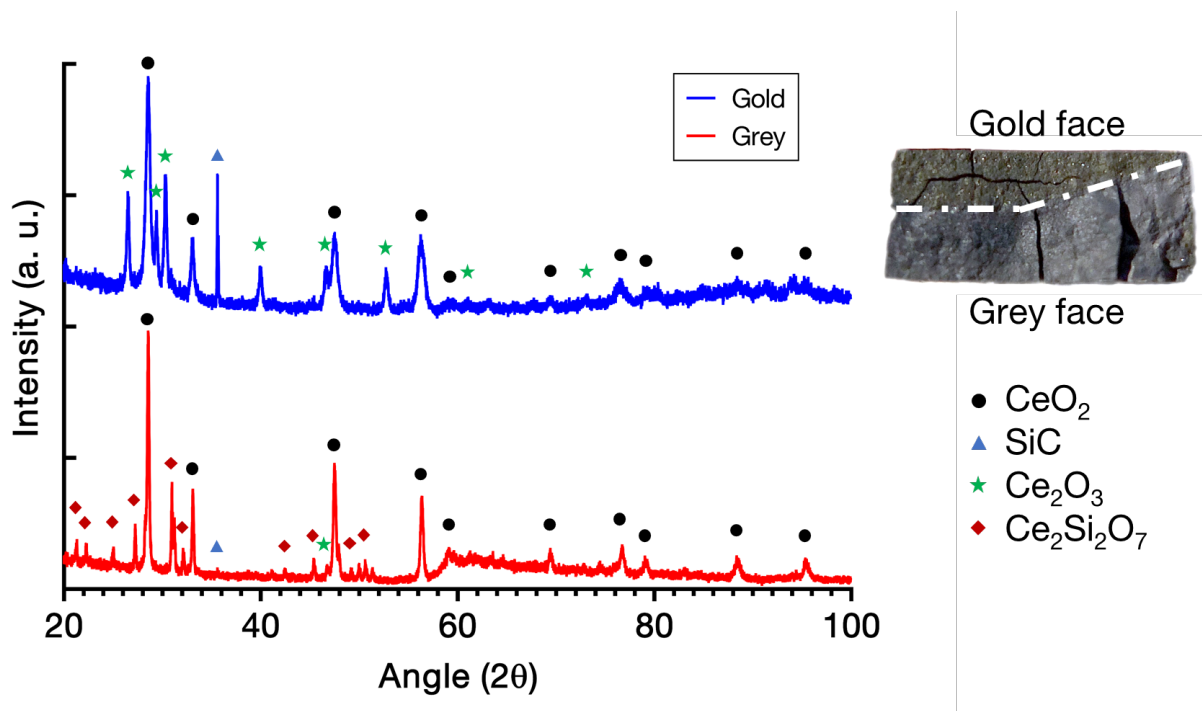


Figure 4.1: XRD diffraction patterns comparison between the top and the bottom faces of the SPS sintered CeO_2 -10 vol. % SiC sample at 1300 °C.

present in their research. While the SPS process apparently works quite well for some cases using UO_2/SiC composites [175, 176], Roleček et al. encountered issues trying to sinter high conductivity phases with CeO_2 using SPS, such as lower final thermal conductivity than the same samples sintered with conventional sintering and poor interfacial contact [126]. Sintering issues encountered in this work can be of interest for future research and development on sintering processes for generation IV type reactors.

Due to the chemical reaction between CeO_2 and SiC to form $\text{Ce}_2\text{Si}_2\text{O}_7$ and the inability to obtain dense, non-brittle samples, a different UO_2 surrogate matrix had to be selected for SiC -containing samples. ZrO_2 was selected for these specific SiC -containing pellets. Sintering SiC with ZrO_2 allowed us to create dense and uniform samples. Due to possible cracking occurring during sintering, which could reduce the overall thermal conductivity of the pellet, samples were sintered with two types of ZrO_2 : natural zirconium oxide (anisotropic monoclinic/tetragonal phase, sample ID: TZ0/ SiC) and 8 mol. % yttrium stabilized zirconium oxide (isotropic cubic phase, sample ID: TZ8YS/ SiC). The use of these two matrix crystal structures also allowed us to examine potential effects of irradiation induced anisotropic swelling of the matrix material on the overall performance of the composite. Both were consolidated using conventional sintering at 1600 °C in argon atmosphere to prevent oxidation of the SiC particles. Both ZrO_2 matrices produced uniform pellets without any visible agglomeration of the SiC platelets. Some debonding was observed in the anisotropic natural zirconia sample as well as intergranular fracture, further decreasing the density of the sample to 93 %. The stabilized zirconia pellet possessed a better interfacial contact with the second phase, allowing the sample to reach a slightly higher final density of 94 % TD. Some transgranular fractures were present within the pellet due to volume and strain change between the cubic/monoclinic/tetragonal ZrO_2 phases during sintering (See Figure 4.2). The stabilized zirconia composition is of higher relevance considering that the matrix is a reasonable surrogate for UO_2 , but thermal conductivity and mechanical properties evolution were studied on both ZrO_2 matrix composites due to possible variations from the different porosity within the two samples.

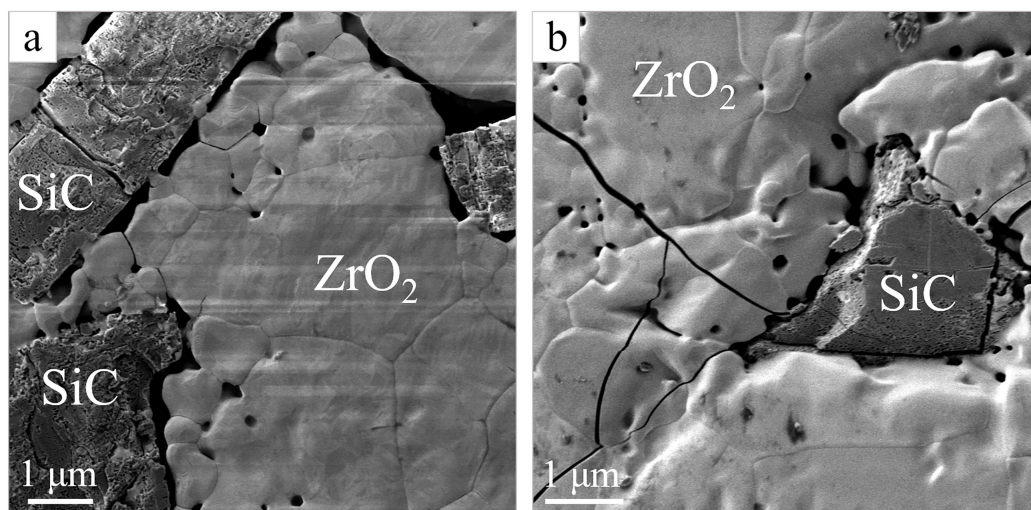


Figure 4.2: SEM images showing the surface evolution of ZrO_2/SiC samples post sintering: (a) TZ0-SiC and (b) TZ8YS-SiC.

4.2 Surface characterization

The evolution of the surface microstructure for $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples was observed using SEM imaging and is shown in Figure 4.3 for the 500 °C irradiation condition. Thermal etching was conducted at 1480 °C for 4 hours on the unirradiated sample in order to reveal grain boundaries and provide information on the pre-irradiation general microstructure. The ion irradiated samples were not subjected to post-irradiation annealing. At 1 dpa, a small trench and rim start to appear around the Al_2O_3 inclusions, while no changes are observed within the CeO_2 matrix grains (Figure 4.3). At 5 dpa, a widening of these trenches around the Al_2O_3 second phase is observed, and the same etching phenomenon is also observed at the grain boundaries. Moreover, the surface etching also starts to happen around smaller Al_2O_3 particles as well as producing surface pores within the matrix. The small rim swelling present around pores, Al_2O_3 inclusions and grain boundaries does not further evolve from that observed at 1 dpa. Finally, important visible surface differences are present in the 15 dpa sample. Both the etched depth at grain boundaries and rim swelling height are increased. The CeO_2 surface morphology appeared transformed, creating an intergranular scale-like surface feature covering all CeO_2 grains. The Al_2O_3 particles were not affected by this phenomenon.

Surface morphology and topography mapping of the 15 dpa irradiated $\text{CeO}_2/\text{Al}_2\text{O}_3$ sample was further examined using AFM scanning. Figure 4.4 shows two heatmap images of the surface of the 15 dpa, 500 °C $\text{CeO}_2/\text{Al}_2\text{O}_3$ sample taken at two different locations. These scans provide a more quantitative perspective of the different surface features present. In order to get an accurate average of all these surface changes, more than 30 single measurements were averaged together over more than 5 scanned areas. With this method, we were able to determine the average CeO_2 grain boundary depth to be 406 ± 37 nm and its width to be 1.2 ± 0.032 μm . The ridge swelling height present around Al_2O_3 particles was found to be 229 ± 45 nm. Finally, the scale-like ridges forming over the CeO_2 grains were measured to have an average height of 176 ± 14 nm.

Figure 4.5 shows the surface microstructure evolution of yttria stabilized ZrO_2/SiC samples after irradiation up to 15 dpa at 500 °C. No apparent changes on the SiC

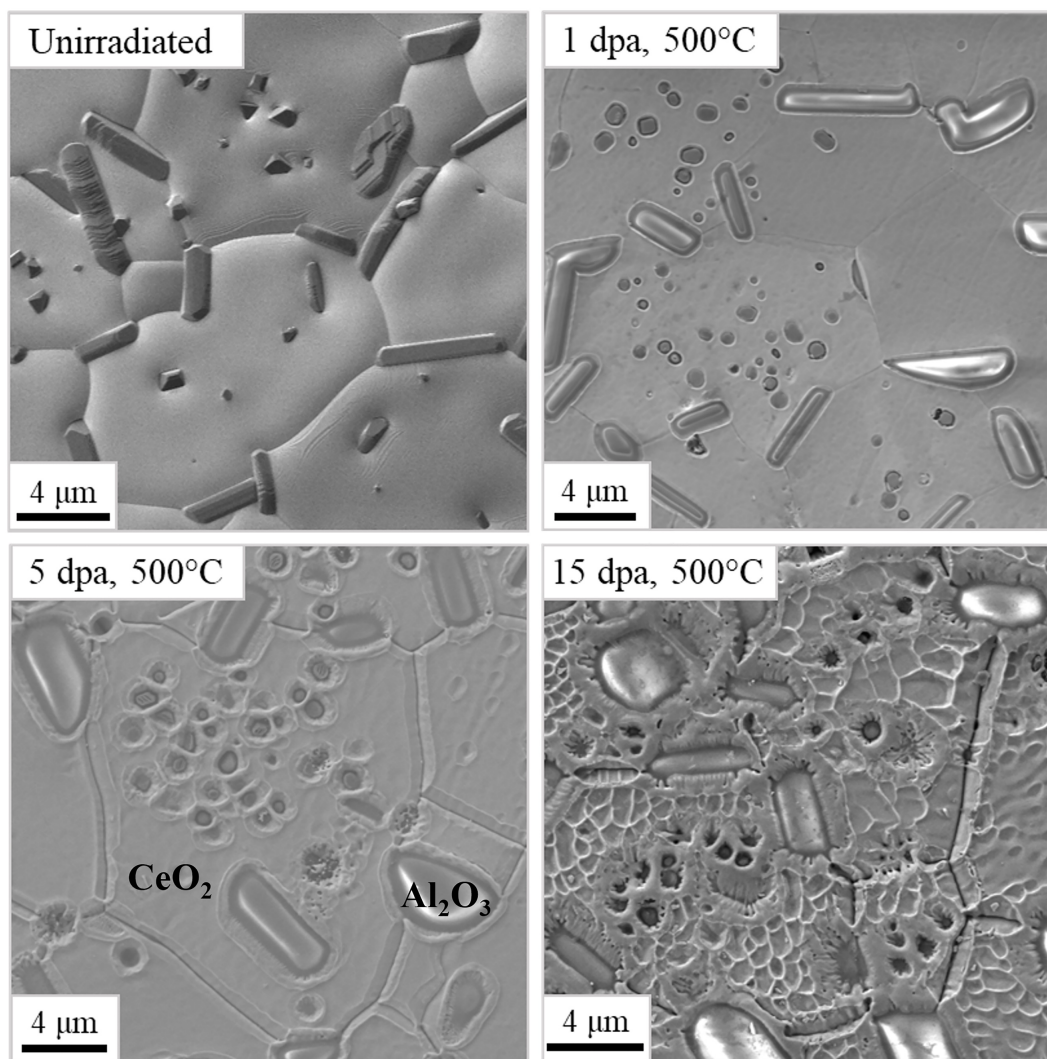


Figure 4.3: SEM images showing the surface evolution vs dpa at 500 °C for ion irradiated $\text{CeO}_2/\text{Al}_2\text{O}_3$.

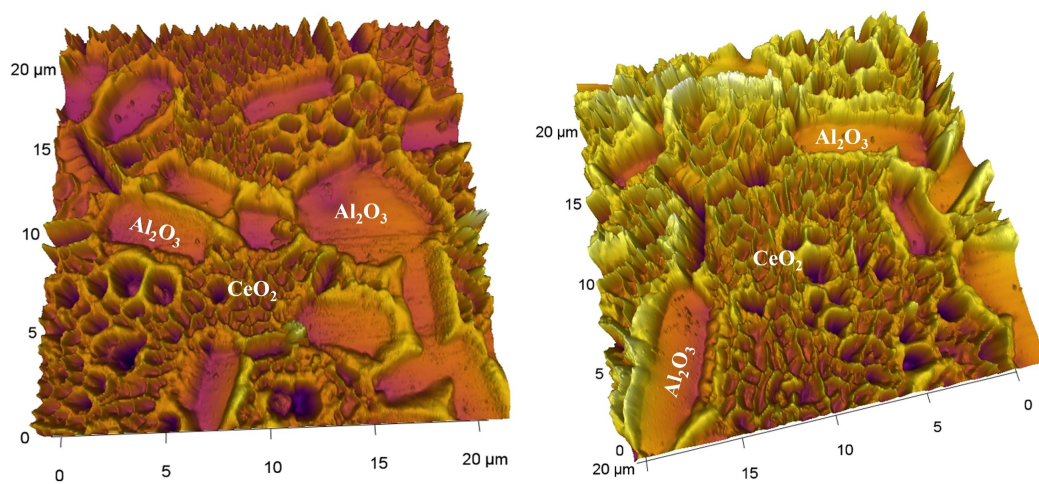


Figure 4.4: Typical AFM heatmaps from two regions of the CeO₂/Al₂O₃ sample ion irradiated at 15 dpa, 500 °C.

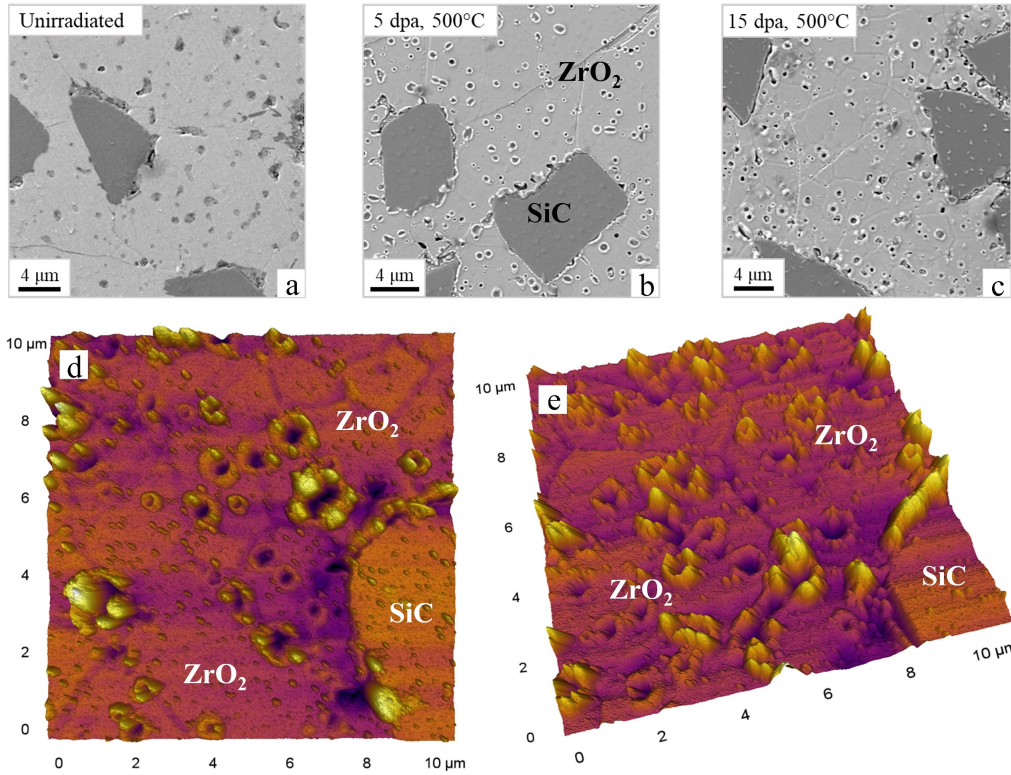


Figure 4.5: (a-c) SEM images showing the surface evolution vs dpa at 500°C for ion irradiated yttria stabilized ZrO_2/SiC and (d-e) AFM heatmap of the sample irradiated at 15 dpa, 500°C .

inclusion surface is noticeable. SiC appears to be stable even at the highest irradiation condition (15 dpa, 500 °C). The zirconia matrix appears to be similarly stable. Some very small microstructural etching can be seen, lightly revealing the grain boundaries, with the phenomenon more noticeable at higher dpa. The only visible change is a small swelling around the rim of the matrix's pores (qualitatively similar to but less pronounced than the one observed for the $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples at 1 and 5 dpa). Some slight swelling is also visible to a slight extent around the zirconia / silicon carbide interface. Using AFM allowed us to quantify these results and compare them to the CeO_2 matrix. Several areas were scanned over the 15 dpa, 500 °C irradiated sample allowing us to find an average surface uplifting value of 48 ± 6 nm surrounding surface pores and SiC particles. As opposed to the $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples, the small quantified swelling does not differ between the matrix and second phase particle in the ZrO_2/SiC sample.

4.3 Thermal conductivity

Experimentally measured thermal conductivity values vs. test temperature of the three sintered compositions are shown in Figure 4.6. Pure CeO_2 as well as ZrO_2 (yttria stabilized and pure) values from the literature are also plotted [145, 104, 54, 132]. Both compositions with additives show an increase in thermal conductivity compared to the monolithic CeO_2 and ZrO_2 data. Compared to an average of recent literature data on CeO_2 (Suzuki and Nelson) [145, 104], our CeO_2 composite showed a 42 % increase in thermal conductivity from 100 to 900 °C. The two ZrO_2 -based composites (natural zirconia and yttria-stabilized zirconia) with SiC additives showed different final thermal conductivity values. The natural zirconia composite behaved like typical moderate-conductivity ceramics, with a large thermal conductivity increase compared to pure ZrO_2 due to the addition of the SiC and a general decrease in thermal conductivity with increasing temperature. This phenomenon is due to well-known phonon-phonon scattering effects. At high temperature, where the Umklapp scattering dominates, the number of available phonons increases while their mean free path decreases. With the scattering rate being proportional to the phonon population, the mean free path of phonons is inversely proportional to the temperature [101, 180].

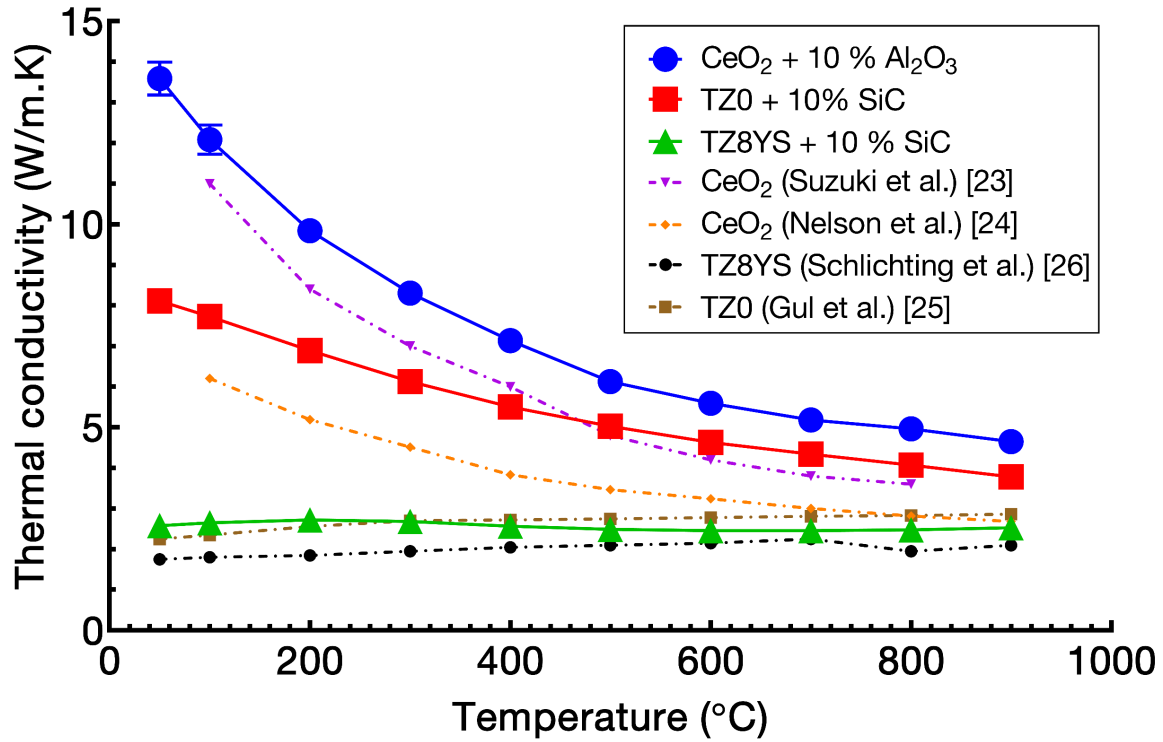


Figure 4.6: Thermal conductivity vs test temperature of the sintered samples before irradiation and literature values of CeO₂ and ZrO₂ (Yttria stabilized and pure ZrO₂). Dashed lines represent literature data.

The presence of a limited fraction of interface debonding/intergranular fracture features (Fig. 4.2) did not seem to affect heavily the final thermal conductivity values. As opposed to this, the stabilized zirconia +10 vol. % SiC composite samples, which included deeper and more dispersed transgranular fractures (Fig. 4.2) than the pure ZrO_2 +10 vol. % SiC composite sample, exhibited a relatively low thermal conductivity that did not show much temperature dependence and followed a similar profile as stabilized zirconia without SiC [54]. It still exhibited a ≈ 30 % thermal conductivity increase at all temperatures compared to the stabilized ZrO_2 data without additive.

4.4 Grazing Incidence X-Ray Diffraction

Using Rietveld refinement, the lattice parameter evolution for the CeO_2 matrix in the ion irradiated $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples was determined (Figure 4.7). Several phenomena can be observed within these results. First, a statistically significant lattice expansion is observed compared to the unirradiated CeO_2 matrix for all three irradiation temperatures and at all doses. The near equivalence of the irradiated lattice parameters for a given irradiation temperature at 1 and 5 dpa suggests that a saturation of defects responsible for the lattice parameter swelling occurs by 1 dpa [36]. This approximate plateau is followed by a slight decrease at 15 dpa for the 500 °C condition (although all lattice parameter values are much higher than the unirradiated value for all irradiation conditions). At a given dose, the lattice parameter swelling decreases monotonically with increasing irradiation temperature. There is some indication for a decrease in lattice parameter swelling at 5 dpa compared to 1 dpa at the higher irradiation temperatures with increasing dose. This has been reported to be associated with increased coarsening of small defect clusters into large dislocation loops and network dislocations (with a corresponding smaller amount of lattice swelling compared to a high density of smaller defect clusters) [174, 89]. It is worth noting that the magnitude of the lattice parameter increase only amounts by a maximum of 0.14 % compared to the unirradiated value.

Lattice parameter measurements performed on the stabilized zirconium oxide matrix samples and presented in Figure 4.8 showcase a very stable matrix, as only minimal

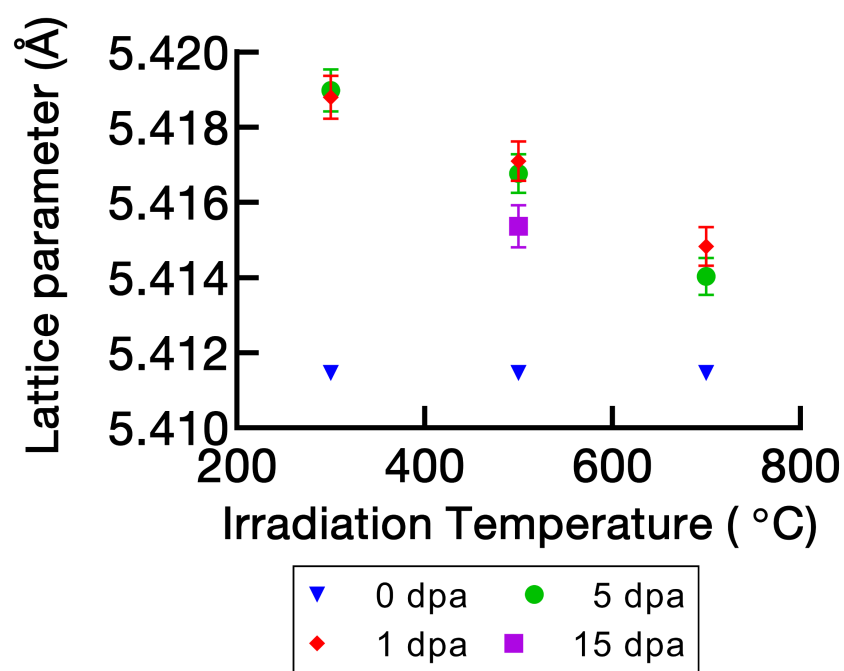


Figure 4.7: Lattice parameter evolution of CeO_2 matrix with ion irradiation dose and temperature.

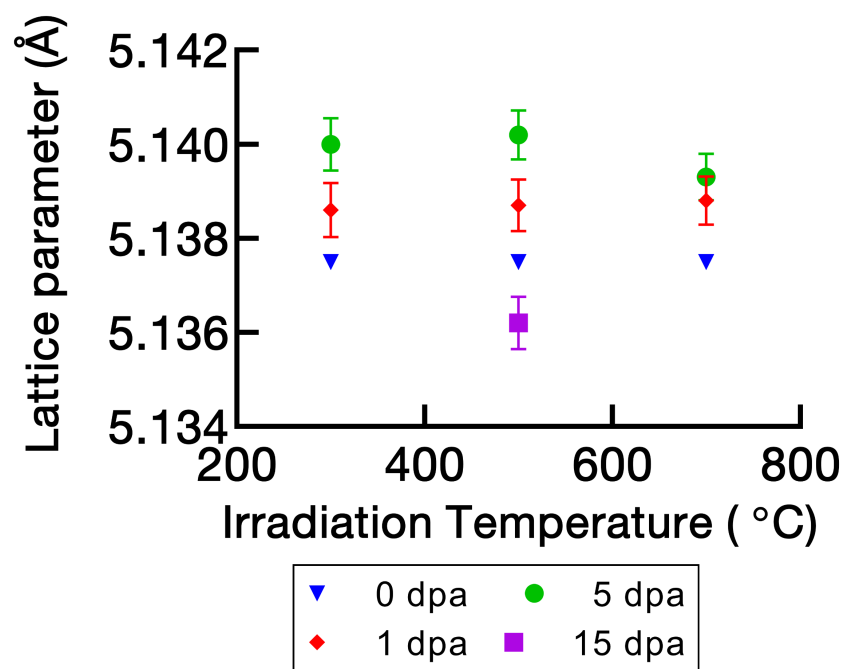
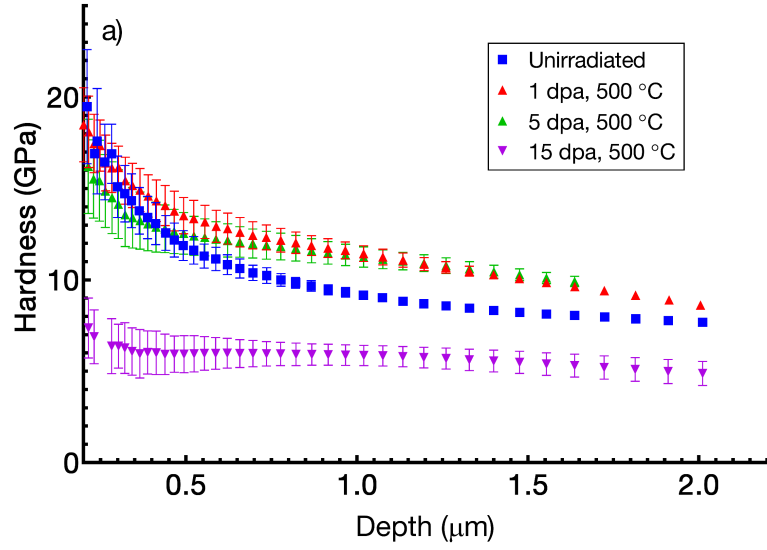


Figure 4.8: Lattice parameter evolution of ion irradiated yttria stabilized ZrO_2 matrix.

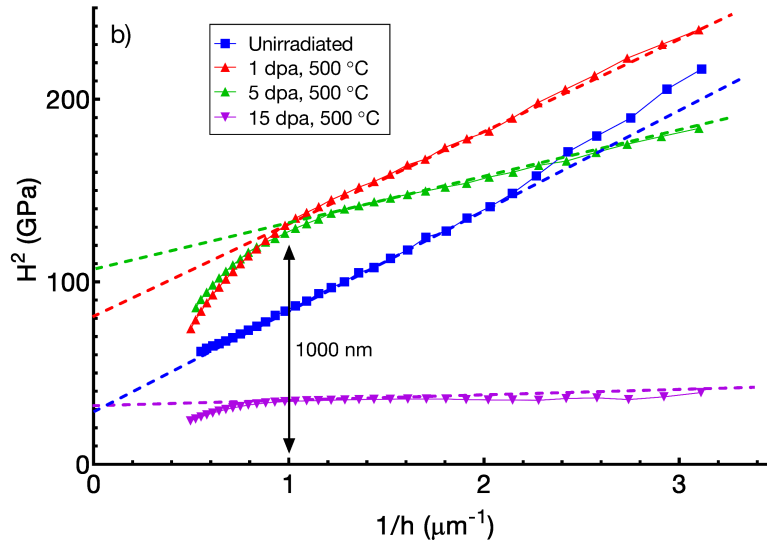
lattice parameter swelling occurred (below 0.04 %) at any examined irradiation condition. Furthermore, specimens from all tested irradiation temperatures seemed to behave in a similar manner. Qualitatively similar behavior as seen for the CeO_2 matrix is observed, with a lattice parameter increase at low dose followed by a drop at 15 dpa. Unlike the CeO_2 results where peak lattice swelling occurred at 1 dpa, the peak swelling at all three temperatures appeared to occur at 5 dpa for the stabilized ZrO_2 specimens. Since the surrogate matrix was supposed to mimic, at best, UO_2 behavior, only the yttria stabilized ZrO_2 data are being presented here, as natural zirconia does not have the same crystal structure. The mixture of monoclinic and tetragonal phases within the natural ZrO_2 matrix allowed for a more important swelling of this matrix. All of the lattice parameters (a, b, c) in the monoclinic phase exhibited similar trends, where lattice swelling was observed by 1 dpa (≈ 0.28 %) followed by a drop and plateau at 5 and 15 dpa (≈ 0.15 % swelling compared to unirradiated value). Similar values were found for the 300 °C and 500 °C samples while 700 °C showed slightly less pronounced swelling. The tetragonal phase had its “a” parameter stable up to 5 dpa then showed a 0.13 % lattice parameter reduction at 15 dpa. Finally, its “c” parameter evolved the most, with a constant lattice parameter increase up to 15 dpa (0.58 % swelling at the highest dose).

4.5 Nanoindentation

As is typically observed in unirradiated and irradiated materials, the hardness vs. depth exhibited a pronounced indentation size effect where the hardness decreased with increasing depth [107]. According to literature [120], the elastic strain from the indent extends five to ten times the indenter depth. Therefore, indent depths up to ≈ 1 micrometer should predominantly measure the ion irradiated hardness region. In order to experimentally quantify the indentation hardness transition point between the irradiated and unirradiated region in our results and to extract the approximate bulk hardness values from the near-surface irradiated region, the Nix-Gao model [107] was used. Figure 4.9 summarizes the measured hardness vs. indent depth as well as the Nix-Gao plots of hardness squared vs. inverse indent depth for the ceria matrix regions of the $\text{CeO}_2/\text{Al}_2\text{O}_3$ ion irradiated specimens.



(a)



(b)

Figure 4.9: (a) Room temperature hardness (H) vs indent depth (h) and (b) H^2 vs $1/h$ curves after 20 MeV Ni^{6+} ion irradiation at 500 °C for $\text{CeO}_2/\text{Al}_2\text{O}_3$.

It can be observed that the indentation size effect becomes progressively less pronounced with increasing dose and in particular the 15 dpa sample exhibits significantly less indentation size effects compared to the unirradiated and lower dose irradiated samples. From the Nix-Gao plots, a transition depth of 1000 nm was found for all three of the ion irradiated specimens which corresponds to about 1/6 of the calculated ≈ 5500 nm extent of the ion irradiated region discussed in section 3. Figure 4.10 (a, b) summarizes the evolution of hardness (obtained from Nix-Gao plots) and elastic modulus for the $\text{CeO}_2/\text{Al}_2\text{O}_3$ composite sample after ion irradiation at 300, 500, and 700 °C to midrange doses of 1, 5, and 15 dpa. The measured hardness increased by 10 to 20 % after irradiation to both 1 and 5 dpa, where hardness values were found to increase from 9.1 (unirradiated) to 11 GPa (irradiated). Under the same irradiation conditions, the modulus was unchanged from the unirradiated result with values around 245 GPa. The 700 °C irradiated hardness was slightly lower than the 300 and 500 °C hardness at 1 and 5 dpa, although the values were within one standard error of each other. The biggest change occurred at 15 dpa, where both hardness and modulus were found to dramatically decrease. The hardness decreased from a 9.1 GPa unirradiated value (and ≈ 11 GPa at 1 and 5 dpa) to 5.8 GPa after 15 dpa. Moreover, the measured elastic modulus also dropped from 249 GPa to 169 GPa. Evaluated hardness and elastic modulus data as determined from Nix-Gao analysis on the ion irradiated yttria stabilized ZrO_2 (TZ8YS)/SiC specimens are shown in Figure 4.10 (c, d). Its behavior is qualitatively similar compared to the $\text{CeO}_2/\text{Al}_2\text{O}_3$ results. At 1 and 5 dpa, the hardness remained constant and the elastic modulus showed a ≈ 10 to 20 % decrease (as opposed to a slight hardness increase and constant modulus in the $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples). Hardness values remained near 12.4 ± 1 GPa up to 5 dpa and modulus decreased from 185 GPa (unirradiated) to around 150 GPa. Finally, as previously observed with the $\text{CeO}_2/\text{Al}_2\text{O}_3$ composition, a pronounced softening occurred at 15 dpa, with hardness values dropping from 12.4 (unirradiated) to 6.8 GPa and modulus decreasing from 185 GPa (unirradiated) to 105 GPa. The datapoint for the 1 dpa, 500 °C ZrO_2 (TZ8YS)/SiC sample is not present in Figure 4.10 (c, d) because it was misplaced during the nanoindentation process.

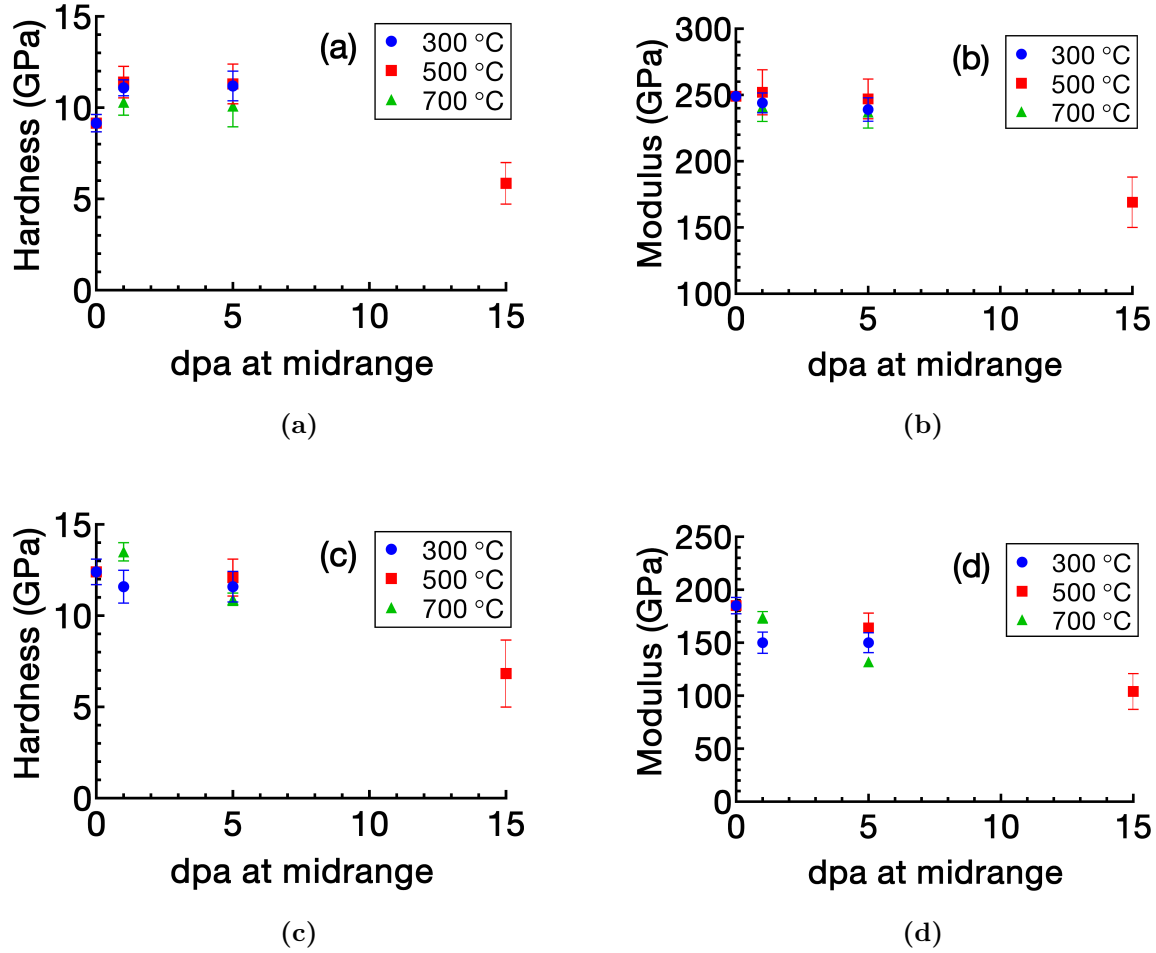


Figure 4.10: Room temperature hardness and elastic modulus evolution vs dpa after 20 MeV Ni ion irradiation at 300 °C, 500 °C, and 700 °C for (a, b) CeO₂/Al₂O₃ and (c, d) ZrO₂ (TZ8YS)/SiC as determined from Nix-Gao fitting.

4.6 Transmission Electron Microscopy

The matrix microstructure of the 500 °C irradiated CeO₂/Al₂O₃ samples was observed using STEM-BF imaging techniques. Furthermore, the evolution of the interface between the matrix and the high conductivity phase was also examined. As summarized in Figure 4.11, the typical depth-dependent damage pattern observed throughout the irradiated matrix areas consisted of tangled dislocation lines near the irradiated surface, followed by dislocation loops, and finally a fine scale defect cluster microstructure. No evidence of interfacial debonding between the CeO₂ matrix and Al₂O₃ particles is evident for the 500 °C condition (1, 5, 15 dpa midrange irradiation) and good interface bonding was also observed in the unirradiated region.

In the 1 dpa CeO₂/Al₂O₃ sample, tangled dislocations were present from the surface to a depth of 2.6 µm with some dislocation loops also found within the first 1 µm from the irradiated surface. Fine scale defect clusters were observed past a depth of 2.6 µm corresponding to the peak damage and implanted ion region. In the 5 dpa midrange dose sample, dislocation lines were the predominant microstructural feature within the first $\approx$ 1 µm depth range, followed by dislocation loops from 0.9 µm to 1.6 µm and then fine scale defects from 1.6 to 3.8 µm. Finally, in the 15 dpa midrange dose sample, numerous dislocation lines were formed from the surface to 1.5 µm depth and dislocation loops were observed from 1.5 to 2.2 µm. The fine scale defect cluster area spread from 2.1 to 4.3 µm and a few dislocation lines were once again found within a few µm after that. For the 1 and 5 dpa midrange dose samples, the fine scale defect cluster region ended at the same depth (3.8 µm) but started closer to the surface for the higher dose condition (1.6 vs 2.6 µm for 1 vs. 5 dpa). At the highest midrange dose (15 dpa), the fine scale defect cluster region covered the same depth as it did for the 5 dpa irradiation but started 0.5 µm deeper. Figure 4.12 shows an overview of the depth distribution and the average diameter and number density for dislocation loops in the CeO₂/Al₂O₃ samples from 1 to 15 dpa at 500 °C. Bins of 100 nm were chosen to plot these datasets. Detailed STEM images of the representative loop microstructure regions are also shown in the bottom three images in Fig. 4.12 to showcase the typical loop structure within the matrix. The irradiated surface is located towards the

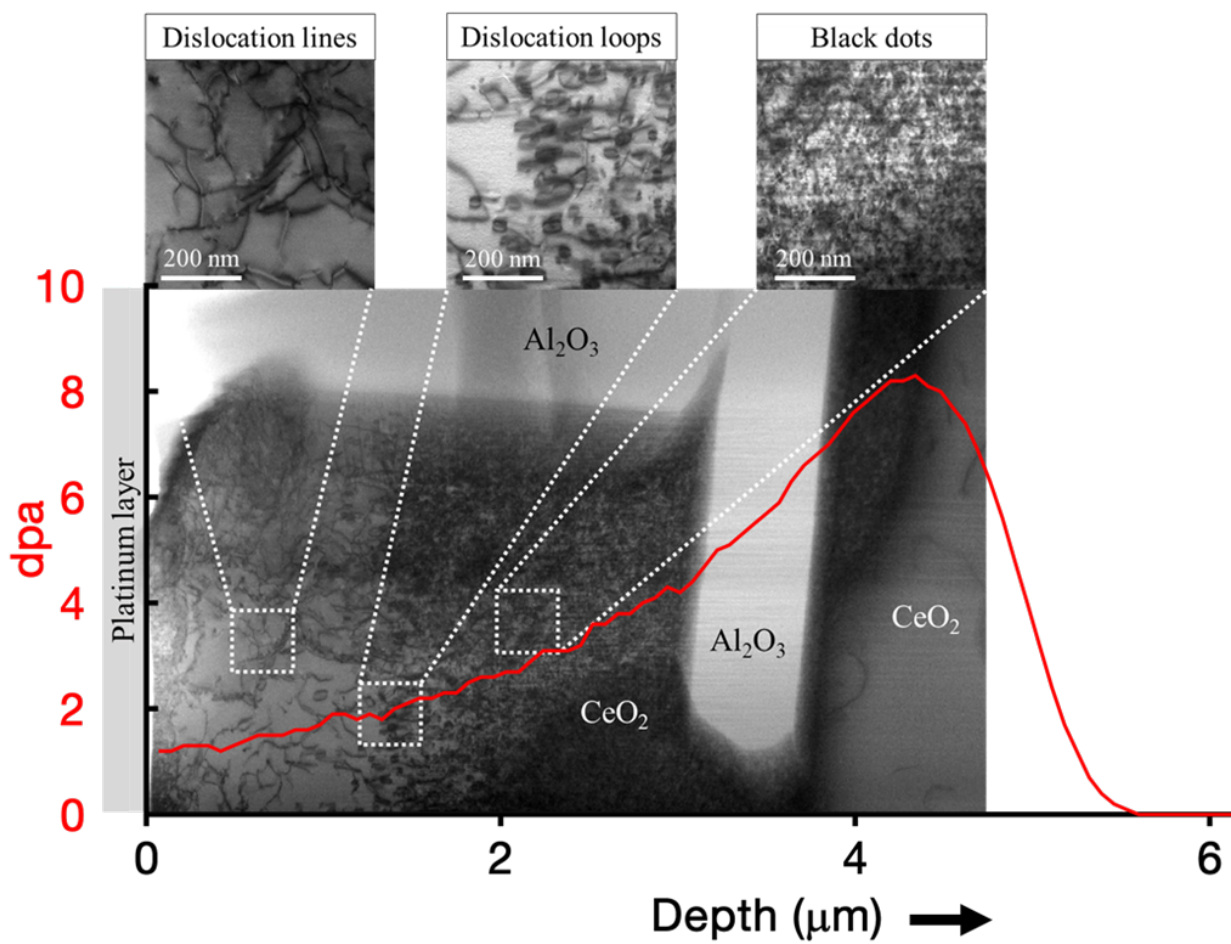


Figure 4.11: STEM-BF images of the irradiated depth-dependent microstructure for the 5 dpa, 500 °C irradiated $\text{CeO}_2/\text{Al}_2\text{O}_3$ sample. SRIM-calculated damage added in red to compare it with actual observed damage.

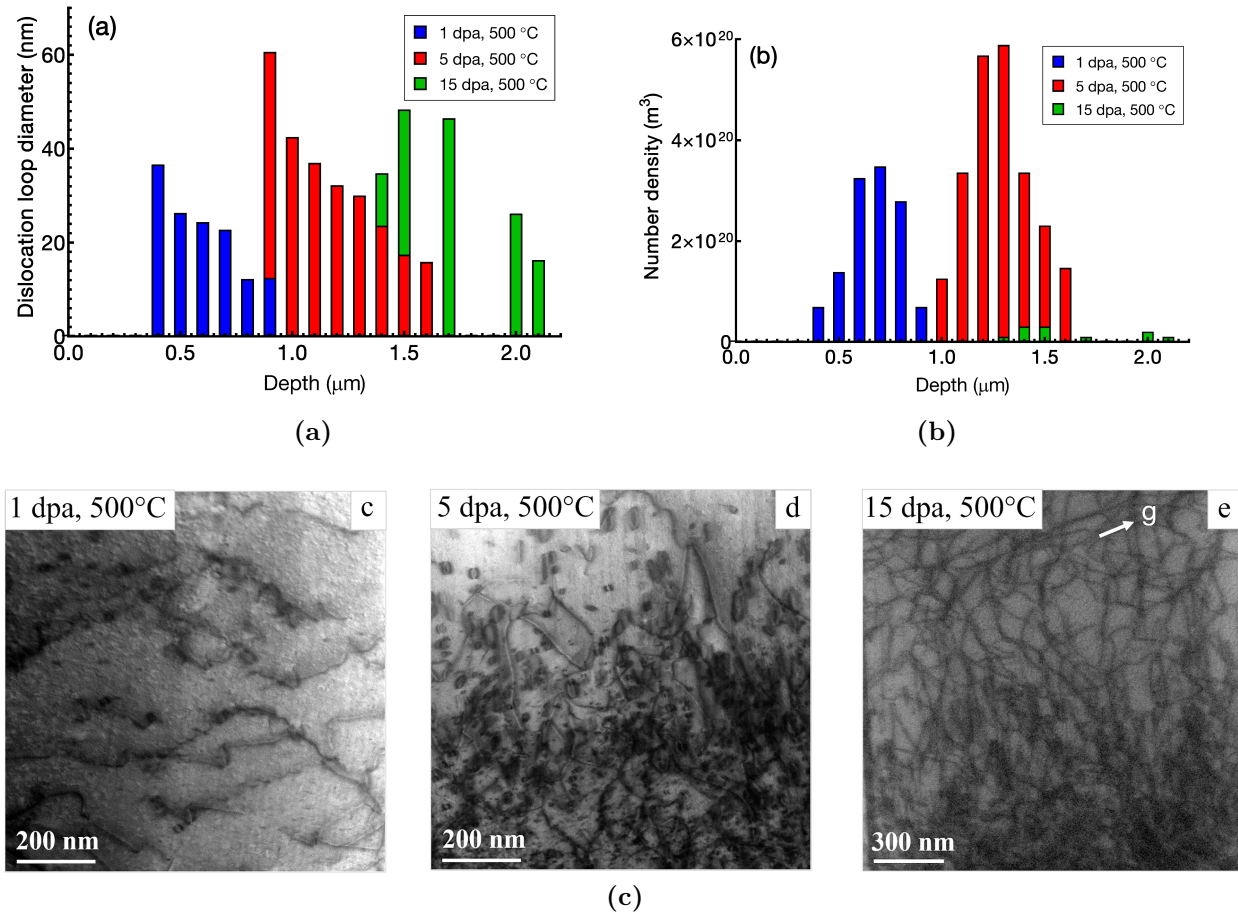


Figure 4.12: (a, b) Depth distribution for average dislocation loop diameter and number density in CeO_2 matrix for the ion irradiated $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples. (c-e) Representative STEM mode images centered around the depth containing the highest number density of loops at 500 °C are shown in the lower three images for 1, 5, and 15 dpa, respectively. (Images captured close to $[112]$ zone axis and $g\langle\bar{2}20\rangle$).

top in all three images. The 1 dpa image was taken at a depth around 0.6 μm , whereas the 5 and 15 dpa images were taken around 1.5 microns deep. As summarized in the dislocation loop size and density plots in Fig. 4.12, irradiation to a damage level of 1 dpa at 500 °C produced a moderately high density of ≈ 1 to $3 \times 10^{20}/\text{m}^3$ loops with a diameter of ≈ 20 nm at midrange depths. Slight loop growth to ≈ 30 nm with a slight increase in volumetric density occurred after 5 dpa. For the 15 dpa specimen, many of the loops had converted to network dislocation tangles (presumably via physical impingement) and the remaining loop density was consequently about one order of magnitude lower than for the 5 dpa midrange dose condition. Figure 4.13 illustrates the microstructural features near the CeO_2 matrix and the Al_2O_3 second phase. As illustrated in images a and b, it was observed for all irradiated doses that dislocations are formed within the matrix perpendicular to the second phase platelets and tend to create aligned dislocation features. Image c shows an example of an Al_2O_3 grain boundary within the Al_2O_3 inclusion as well as CeO_2 matrix/ Al_2O_3 interfaces and confirms that no microcracks were observed at the interface for the $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples, from 1 to 15 dpa. This indicates that differential lattice parameter swelling differences between CeO_2 matrix and the Al_2O_3 inclusion was not sufficiently high to induce cracking along the interface, although the observation of dislocation arrays in the CeO_2 matrix suggests the presence of significant swelling mismatch stresses between the inclusion and the matrix. TEM was also used to look at the $\text{CeO}_2/\text{Al}_2\text{O}_3$ interface outside the irradiated area and no similar dislocation array was found in the unirradiated area. Fine scale radiation-induced defect clusters (2-3 nm) were also observed within the Al_2O_3 grains under high magnification (not visible in Fig. 4.13).

4.7 Discussion

The general evolution of the surface microstructure appears to be primarily dependent on dose, and irradiation temperature between 300 and 700 °C does not seem to have an important impact on the sample surface microstructure. The only small observed temperature effect is enhanced thermal etching of the grain boundary at higher temperatures (as expected), but overall, dose has a more important impact on the sample surface, including

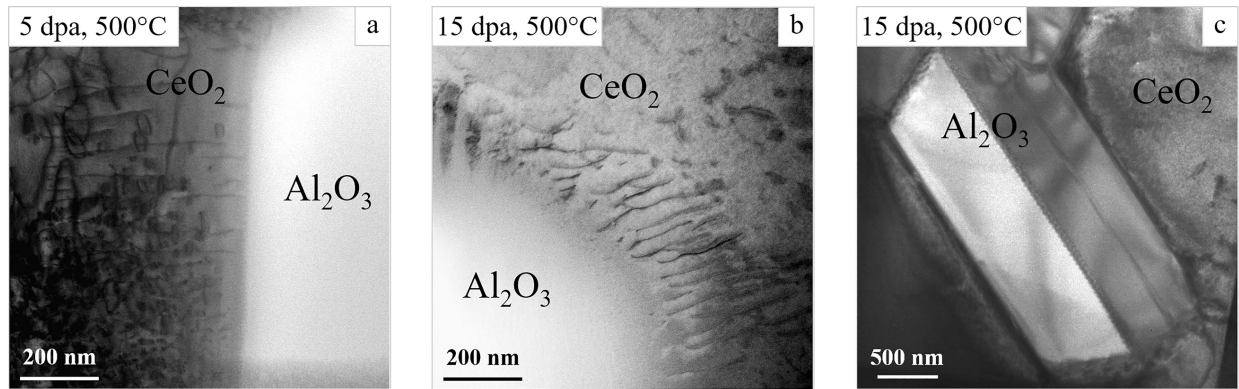


Figure 4.13: TEM images of CeO_2/Al_2O_3 interaction; images captured along $[110]$ zone axis. (a, b: STEM mode, $g<002>$); c: TEM-BF mode).

grain boundary etching. The observation of surface features in CeO_2 and dislocation structures in CeO_2 near the interface of the additive phase may be speculated to be evidence of significant differential stress associated with differential point defect swelling. The surface features might be associated with radiation enhanced plastic flow under stress: this has been reported in a few ion irradiated ceramics studies [119, 83, 157, 21]. These scale-like ridges on the CeO_2 grains were quantified using AFM, but it is still unclear as to why these features appeared and whether it is a unique CeO_2 related phenomenon or would also occur for UO_2 . As observed in Figure 4.3, no changes were observed on the Al_2O_3 second phase from 1 to 15 dpa aside from a small rim swelling present around it in the CeO_2 matrix. A similar swelling was observed around pores present within the CeO_2 matrix, reinforcing the hypothesis that it is a matrix driven phenomenon. While looking at CeO_2 grains not containing Al_2O_3 particles in or around them, the scale-like surface features was still observed, which is a good indication that it would also be observed in pure CeO_2 . Previous literature work on irradiated cerium oxide using heavy ions at high temperature revealed the possible formation of transgranular embossed shapes, resulting from self-organization by sputtering competing with surface diffusion [99]. While our observed phenomenon differs from this one due to its different shape and by being an intergranular phenomenon, similarities exist between both such as the formation of rounded dents at the surface and the outward transformation of the surface morphology. These pronounced surface topological features were not observed on the surface of the ZrO_2 grains, and these samples also did not show any major surface microstructure evolution aside from limited swelling located around the matrix pores and SiC particles. Zones without SiC particles were observed at the surface, and the same behavior was observed, allowing us to believe that this swelling was present due to the matrix and the second phase particles had little effect on it. As opposed to the $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples, ZrO_2/SiC samples showed both poor particle-matrix bonding as well as matrix cracking (expected due to phase change during sintering) which affected their thermal conductivity.

Quantification of the improvement in thermal conductivity for the as-consolidated $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples is somewhat complicated, since CeO_2 purity heavily impacts its sintered thermal conductivity. A large discrepancy exists between recent “pure” CeO_2 literature values with thermal conductivity data varying between 6 to 11 W/m.K (measured at 100

°C, the lowest communal temperature between all literature data used) and causes for such discrepancies were assumed to come from both stoichiometry differences as well as impurities [100, 101]. Differences can also be linked with the sintering processes used and final microstructures of the samples. With that said, results presented within the current investigation showed a substantial improvement in thermal conductivity compared to non-doped CeO₂ values (Fig. 4.6). To further quantify the thermal conductivity results obtained through this work, two models were utilized: the rule of mixtures and the Maxwell model. The rule of mixtures (equation 4.1) is a simple linear model where K represents the thermal conductivity and V the volume fraction for both the matrix (m) and the additive phase (a) [15].

$$K_{eff} = K_m V_m + K_a V_a. \quad (4.1)$$

The Maxwell model is often used as an alternative model to evaluate the thermal conductivity of a two-phase composite when the volume fraction of the additive is relatively low [117]. As shown in equation 4.3, K_m and V_m are the thermal conductivity and volume fraction of the matrix and K_a and V_a are the thermal conductivity and volume fraction of the additive phase.

$$K_{eff} = K_m \times \frac{K_a(1 + 2V_a) - K_m(2V_a - 2)}{K_m(2 + V_a + K_a(1 - V_a))}. \quad (4.2)$$

In this study, the thermal conductivity used to model these results were pulled from the literature. Suzuki's (11 W/m.K at 100 °C) [145] and Gul's (2.4 W/m.K at 100 °C) [54] data were respectively used to model the CeO₂ and ZrO₂ matrix values. Al₂O₃ (21.6 W/m.K at 100 °C) data was collected from Touloukian's manuscript [152] while SiC values (64.2 W/m.K at 100 °C) were obtained from McCluskey et al. [96]. Considering that the thermal conductivity of stabilized zirconia does not show a significant difference compared to ZrO₂ and that we observed (Fig. 4.6) no temperature dependence with the inclusion of SiC, presumably due to the important transgranular fracturing present within this sample, this dataset was not modeled here.

As shown in Figure 4.14, both the Maxwell model and the rule of mixtures are in a similar agreement regarding the thermal conductivity of the $\text{CeO}_2/\text{Al}_2\text{O}_3$ composite. Both model predictions slightly underestimated the experimental results for the $\text{CeO}_2/\text{Al}_2\text{O}_3$ composite which may be explained by the uncertainties surrounding the temperature dependent thermal conductivity values used in this study for both CeO_2 and Al_2O_3 . Conversely, the ZrO_2/SiC modeling gave divergent results, with neither model agreeing with the experimental data. The rule of mixtures overestimated the thermal conductivity of the ZrO_2/SiC composite by 10-30 %, which may be attributed to several causes. First, this simple rule of mixtures model tends to overemphasize the thermal conductivity of the additive phase, which is more noticeable when it is much greater than the matrix conductivity. Furthermore, as discussed in the results section and shown in Figure 2.3, cracking, porosity, and a bad interfacial contact were observed in these samples, which would degrade the thermal conductivity of the specimens compared to the ideal crack-free prediction. The Maxwell model greatly underpredicted the conductivity of the ZrO_2/SiC composite at low temperatures (by more than a factor of two). This is because the Maxwell model does not work well when the additive phase conductivity is much higher than the matrix phase. Additional thermal conductivity models such as the Lewis-Nielsen model [117] were also tried to model the composite thermal conductivity but did not produce results significantly different from the Maxwell model. Considering both composites, the rule of mixtures produced a better overall agreement to the measured composite thermal conductivity values compared to the Maxwell model.

Using surrogate material such as CeO_2 and ZrO_2 was useful to provide a general behavioral trend, especially for post irradiation studies, but it is important to keep in mind that differences between ZrO_2 and UO_2 were encountered during the fabrication process. The yttria-stabilized ZrO_2 composition showed only a small improvement of its thermal conductivity with the SiC addition as opposed to the natural zirconia composite (cf. Fig. 4.6), and this was attributed to deep transgranular matrix cracking as well as imperfect bonding between the yttria-stabilized ZrO_2 matrix and the SiC. Granular fracturing and debonding of the second phase as well as pronounced porosity can be avoided with an improvement of the sintering parameters. These sintering issues were not reported in previous

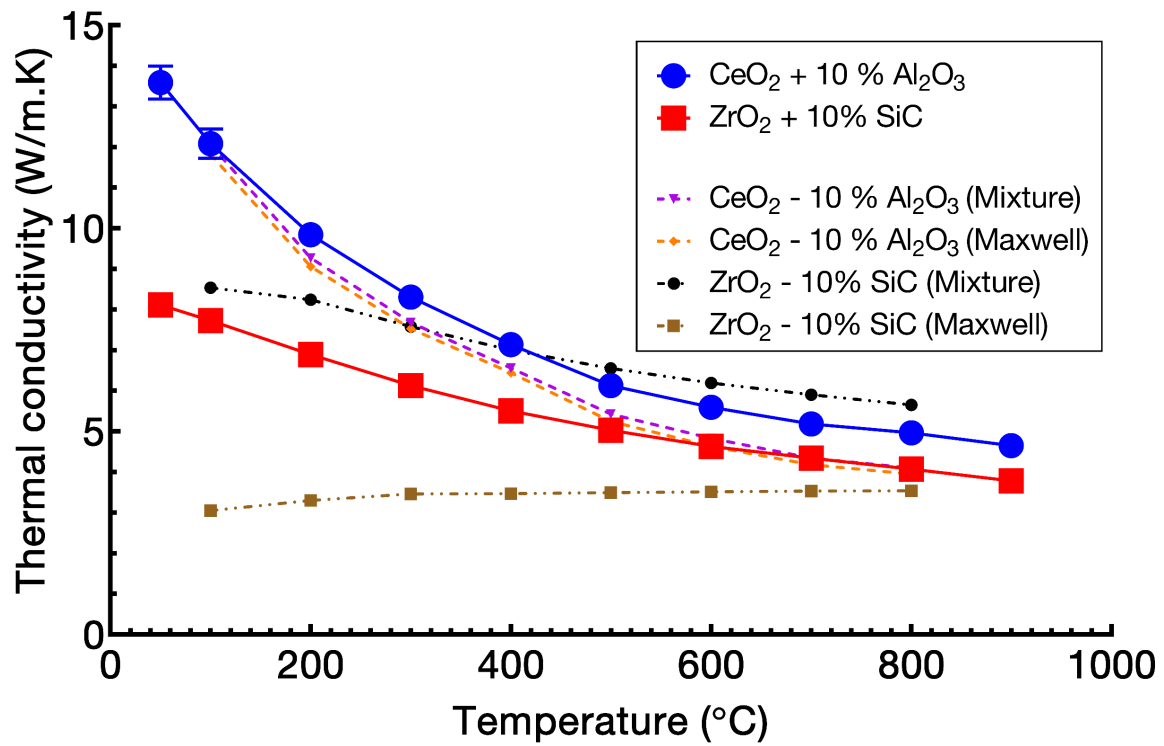


Figure 4.14: Experimentally obtained and calculated thermal conductivity values for $\text{CeO}_2/\text{Al}_2\text{O}_3$ and ZrO_2/SiC composites. Dashed lines represent model predictions.

studies of high thermal conductivity composites when using UO_2 instead of a surrogate matrix. While stabilized zirconia samples were of higher interest (being a reasonable surrogate for UO_2), both natural and stabilized zirconia were used to study the possible differences in sintering behavior as well as to bring further insight on the effects of anisotropic phases on the irradiation behavior of multiphase fuel forms. This process demonstrated the sort of increase one could observe using SiC additive when the matrix/second phase doesn't show transgranular cracking and proved the lack of thermal conductivity increase when cracks are present.

Prior irradiation studies on ceramic materials have often reported similar saturation in lattice parameter swelling at similar temperatures for doses above 0.1 dpa [140, 161, 69, 99]. In this work, both peak broadening and decrease in peak intensity were observed in the irradiated results compared to the unirradiated XRD pattern at room temperature. This phenomenon previously observed in the literature [36] is due to the presence of heterogenous microstrain in the material due to the presence of point defects / defect clusters. As observed in Figure 4.7, lower swelling was reported at higher temperature due to the reduced concentration of defects formation of more complex ones explained by the thermal annealing of defects at high temperature. This observation is in agreement with other ceramics such as CeO_2 , Al_2O_3 and SiC within comparable irradiation temperature regime [140, 161, 69, 99]. It is worth noting that while a decrease in swelling was observed at higher dose and higher temperature, the lattice swelling was always greater than zero. At the highest investigated dose (midrange damage level of 15 dpa), there was evidence of a reduction in lattice parameter swelling compared to the 1 and 5 dpa exposures (Figs. 4.7, 4.8). Previous studies of several irradiated ceramics including Al_2O_3 and AlN have reported that after reaching an apparent saturation swelling level at relatively low doses of ≈ 0.1 to 1 dpa, a reduction in lattice parameter swelling can occur at higher doses; this has been attributed to a reduction in lattice strain associated with the transformation of small defect clusters into large loops and/or network dislocations, with accompanying reduction in lattice swelling [169, 161, 69, 70, 38]. Reported lattice swelling in this work correlates well with literature values on CeO_2 and ZrO_2 without additives [36, 99, 66]. Cureton et al. reported a swelling of 0.17 % for CeO_2

while we found a value of 0.14 % after ion irradiation [36]. Degueldre et al. reported a lattice swelling in cubic zirconia around 0.06 % after $1.8 \times 10^{16} \text{ cm}^{-2}$ Xe irradiation at room temperature and Kalita et al. measured a lattice swelling around 0.05 % after ion irradiation at high temperatures (850 °C) compared to 0.04 % presented in this paper [66, 39]. These agreements seem to indicate that 10 % of additive did not affect the properties of the matrix in a significant manner. As calculated by Beschnitt et al. [17], the vacancy diffusion energy for Ce in undoped CeO₂ systems is greater than 8 eV. As opposed to this, Nolan et al. reported a calculated oxygen vacancy diffusion of $\approx 0.52 \text{ eV}$ (possible values between 0.46 – 1.08 eV depending on the stoichiometry of CeO₂) [108]. The very large Ce vacancy diffusion enthalpy allows us to expect loop coarsening to be slow and void swelling to be negligible in irradiated CeO₂ even for temperatures above 1000 °C due to the low Ce vacancy mobility (i.e., the overall vacancy-based evolution will be controlled by the very slow vacancy diffusion on the Ce sublattice). In order to observe and characterize the oxygen and zirconium diffusion in ZrO₂ in its fluorite cubic phase, it has to first be stabilized using a lower-valent oxide such as $> 8 \text{ mol. \%}$ of Y₂O₃ which makes the cation diffusion data analysis much more complicated as opposed to CeO₂. Above 1000 °C, it has been reported that 8YSZ (8 mol. % Yttria Stabilized ZrO₂) has a cation vacancy diffusion energy of 4.8 eV while its oxygen vacancy diffusion energy is just 0.5 eV [45], showcasing a fast anion vacancy diffusion similar to the CeO₂ system. To a larger extent, it has been demonstrated in the literature that this phenomenon is observable within compounds with the fluorite structure, which has a preference for relatively high anion migration vs relatively low cation migration. A monotonic decrease in lattice parameter swelling with increasing temperature (300 to 700 °C) was observed in the ion irradiated CeO₂ and ZrO₂ matrix materials. The low cation migration energy indicates that the lattice swelling regime (where lattice parameter swelling monotonically decreases with increasing temperature) will extend up to very high temperatures in excess of 1000 °C for both of these materials. Of course, in an actual UO₂ matrix composite, pronounced gaseous fission product formation will induce bubble swelling in addition to the lattice parameter swelling, with the gaseous fission product swelling generally becoming predominant at high burnup levels and temperatures.

Considering the uncertainties in the data for the nanoindentation results, the room temperature hardness and elastic modulus evolution are primarily dependent on dose only and do not exhibit a pronounced dependence on ion irradiation temperature at least up to 700 °C. The 15 dpa ion irradiation was performed only at 500 °C, so any possible irradiation temperature dependence at this highest dose is uncertain. Nanoindentation measurements indicated that the nanoindentation mechanical properties for all investigated compositions were rather stable up to ≈ 5 dpa but they all subsequently exhibited a pronounced decrease of their mechanical properties after irradiation to 15 dpa. The observed general trend of stable (slightly increasing or decreasing strength) up to doses of 1 to 5 dpa is in general agreement with prior studies on ion or neutron irradiated monolithic ceramics [140, 161, 30, 113, 44, 137, 181]. Sickafus et al. [137] measured the low temperature (-153 °C) ion irradiated properties of zirconia using nanoindentation. The elastic modulus was found to be stable up to doses around 34 dpa. A slight hardness increase was observed below 1 dpa, and no changes were noticed at higher doses. Other work done at room temperature can also be found [137, 98, 85]. These articles tend to present similar results, with a generally stable elastic modulus at doses below 1 dpa and a slight increase observed in the hardness. At 7.7 dpa, Sickafus et al. [137] reported a small ($\approx 9\%$) decrease in both hardness and modulus for 72 MeV ion irradiated cubic-stabilized zirconia at room temperature, similar to what was pictured in Figure 4.10 (c, d).

A decrease in strength at high doses (similar to that observed in the present study, Fig. 4.10) has been observed in several ceramics with anisotropic crystal structures and has been attributed to grain boundary cracking phenomena associated with anisotropic swelling within individual randomly oriented grains [72, 56, 161, 69, 67, 170, 27]. We did not observe evidence for grain boundary or matrix-particle interface cracking in the $\text{CeO}_2/\text{Al}_2\text{O}_3$ samples (Figs. 4.4, 4.11, 4.13). Furthermore, it is worth noting in the present investigated samples that the lattice swelling as monitored by x-ray diffraction (Fig. 2.8, 2.9) decreased as the midrange dose increased from 5 to 15 dpa, so the potential anisotropic matrix strain associated with lattice swelling should have lessened in this dose range. However, some evidence of matrix strain was observed in the form of localized dislocations in the matrix, adjacent to the second phase interface (Fig. 4.13). Alternatively, as Dienst observed in SiC, Al_2O_3 and AlN [43],

strength decrease following irradiation may not be affected by the grain size of the particles but may correlate with the overall volumetric swelling instead.

In order to be viable for LWR use, the ceramic fuel should exhibit good stability to neutron-relevant displacement damage up to at least 20 dpa (and simultaneously exhibit good resistance to structural and property changes associated with fission recoil ion track damage up to much higher damage levels). The observed mechanical properties degradation coincides with the pronounced surface topological changes in the $\text{CeO}_2/\text{Al}_2\text{O}_3$ sample (cf. Fig. 4.3 and 4.4). While a similar degradation was observed through nanoindentation measurements on the ZrO_2/SiC sample at 15 dpa, no surface modification was observed that could hint at this mechanical property degradation. Overall, the observed deterioration of mechanical properties at the highest investigated dose of 15 dpa raises some concerns regarding the viability of composite fuels involving high conductivity additives with anisotropic crystal structures.

TEM observations of the microstructure of the ion irradiated specimens are consistent with the dose dependent swelling observed using GIXRD and is supported by similar literature work done on other ceramics under irradiation, including pure CeO_2 and ZrO_2 [174, 137, 166]. At low dose, production and accumulation of Frenkel pair defects create a pathway towards formation of dislocation loops. With increased dose, these loops will grow in size and density until reaching a critical level where loops interaction will lead to the formation of a dense dislocation network. This phenomenon was observed during this work (Figures 4.7, 4.8 and 4.12). There was no evidence for radiation induced amorphization or cavity formation for any of the conditions investigated in the current study.

Defect cluster evolution within all samples appeared to follow the same pattern. Fine scale defect clusters and a low density of dislocation lines with some network dislocations appeared at low doses. At intermediate doses, easily resolvable dislocation loops intermixed with some finer scale defects were observed, along with some network dislocation lines. At high doses, the dislocation loop density decreased, and the extent of network dislocations was more pronounced. Several observations can be made from these trends. First of all, dislocation lines seemed to always appear between the surface and the start of the fine scale defect cluster

region regardless of the specific depth location of the fine scale clusters. Additionally, more dislocation lines were found towards the deep end of the irradiated region. The dislocation loop maximum depth formation increased with increasing dose and loops were preferentially formed within the matrix, away from the second phase grains. Several published studies have shown that most ceramic materials have mobile interstitials and immobile vacancies within the observed temperature range (above recovery Stage I and below Stage III) due to their very high melting point [185, 27, 188, 158, 192]. Within this point defect swelling regime, void nucleation/swelling is suppressed. Consequently, the build-up of interstitial type defects will saturate at low damage level (often varying between 1 – 10 dpa depending on each ceramic material). Therefore, any pronounced degradation due to differential point defect swelling between the matrix and the second phase should already be observable at doses around 10 dpa. This doesn't preclude the possibility of additional fuel degradation from happening (due to fission recoil damage or chemical effects), but this behavior would be predominantly occurring in the fissile phase. To confirm this, future ultra-high dose neutron irradiation studies should be conducted using actual UO_2 as matrix.

No microcracks were observed at the interface regions of the irradiated $\text{CeO}_2/\text{Al}_2\text{O}_3$ system. This implies the CeO_2 radiation-induced swelling at the investigated conditions was sufficiently low (≤ 0.14 % lattice parameter swelling, Fig. 4.7) and the Al_2O_3 anisotropic swelling was also sufficiently low to prevent crack formation due to differential swelling between the matrix and second phase. The absence of interface cracking may be due in part to the relatively small second phase particle sizes, since microcracking due to anisotropic swelling increases with increasing particle or grain size [171, 72, 161, 69, 27, 28, 33, 47, 57, 68]. Numerous studies of irradiated ceramics with anisotropic crystal structures have reported that grain boundary cracking and loss of mechanical strength occurs when the differential swelling exceeds a critical value that is inversely dependent on grain size. The critical differential strain for inducing interfacial fracture can be estimated from the following expression derived by Clarke et al. [28]:

$$\mathcal{E} \approx \left(\frac{24\gamma}{El} \right)^{\frac{1}{2}}. \quad (4.3)$$

Using $\gamma = 1.5 \text{ N/m}$ for the grain boundary surface energy, $l = 5.5 \text{ }\mu\text{m}$ as grain radius, and $E = 350 \text{ GPa}$, we get: $\mathcal{E}$, the critical differential strain $\approx 0.45 \text{ }\%$.

Diffraction patterns from the irradiated Al_2O_3 platelets were examined in an attempt to quantify the lattice parameter swelling of the Al_2O_3 second phase. Unfortunately, we were unable to tilt to suitable low index zone axes in the randomly oriented Al_2O_3 platelets in the TEM liftout foils, and therefore we could not obtain detailed information on the actual basal vs. prism direction anisotropic swelling in the irradiated Al_2O_3 platelets. Data from published lattice swelling values in neutron irradiated Al_2O_3 at 0.5 to 5 dpa [161?] indicates that the difference between swelling in the c-axis versus a-axis direction is $\approx 0.04\text{--}0.1 \text{ }\%$ at $80\text{--}390 \text{ }^\circ\text{C}$, $\approx 0.25 \text{ }\%$ at $600 \text{ }^\circ\text{C}$, and $\approx 0.35 \text{ }\%$ at $750 \text{ }^\circ\text{C}$. Therefore, the differential swelling in the Al_2O_3 platelets in the present study is predicted to be below the critical strain level required to induce interfacial cracking. Cracking would be predicted to occur if larger diameter platelets were utilized.

Chapter 5

Nitride Ceramics

5.1 Grazing Incidence X-Ray Diffraction

Evolution of both a and c-axis lattice parameters and the associated volumetric swelling of Si_3N_4 are presented in Figure 5.1 and was calculated using equation 5.1:

$$\frac{\Delta V}{V} = \frac{\Delta c}{c} + 2\left(\frac{\Delta a}{a}\right). \quad (5.1)$$

At 1 and 15 dpa, the a and c lattice parameters appear to exhibit a slight gradual decrease with increasing temperature. The 15 dpa lattice swelling was found to be slightly higher than that at 1 dpa, suggesting that doses above 1 dpa are needed to approach point defect swelling saturation at these temperatures. A volumetric swelling increase up to 15 dpa was found (0.51 % at 300 °C). A large discrepancy was observed at 50 dpa in the 700 °C ion irradiated sample where a swelling of 0.55 % was measured while a saturation value close to 0.2 % was expected as observed with both 1 and 15 dpa irradiations.

Lattice expansion and corresponding volumetric swelling associated only with lattice expansion of the ZrN samples following Ni ion irradiation are summarized in Figure 5.2 and was calculated using equation 5.2:

$$\frac{\Delta V}{V} = 3\left(\frac{\Delta a}{a}\right). \quad (5.2)$$

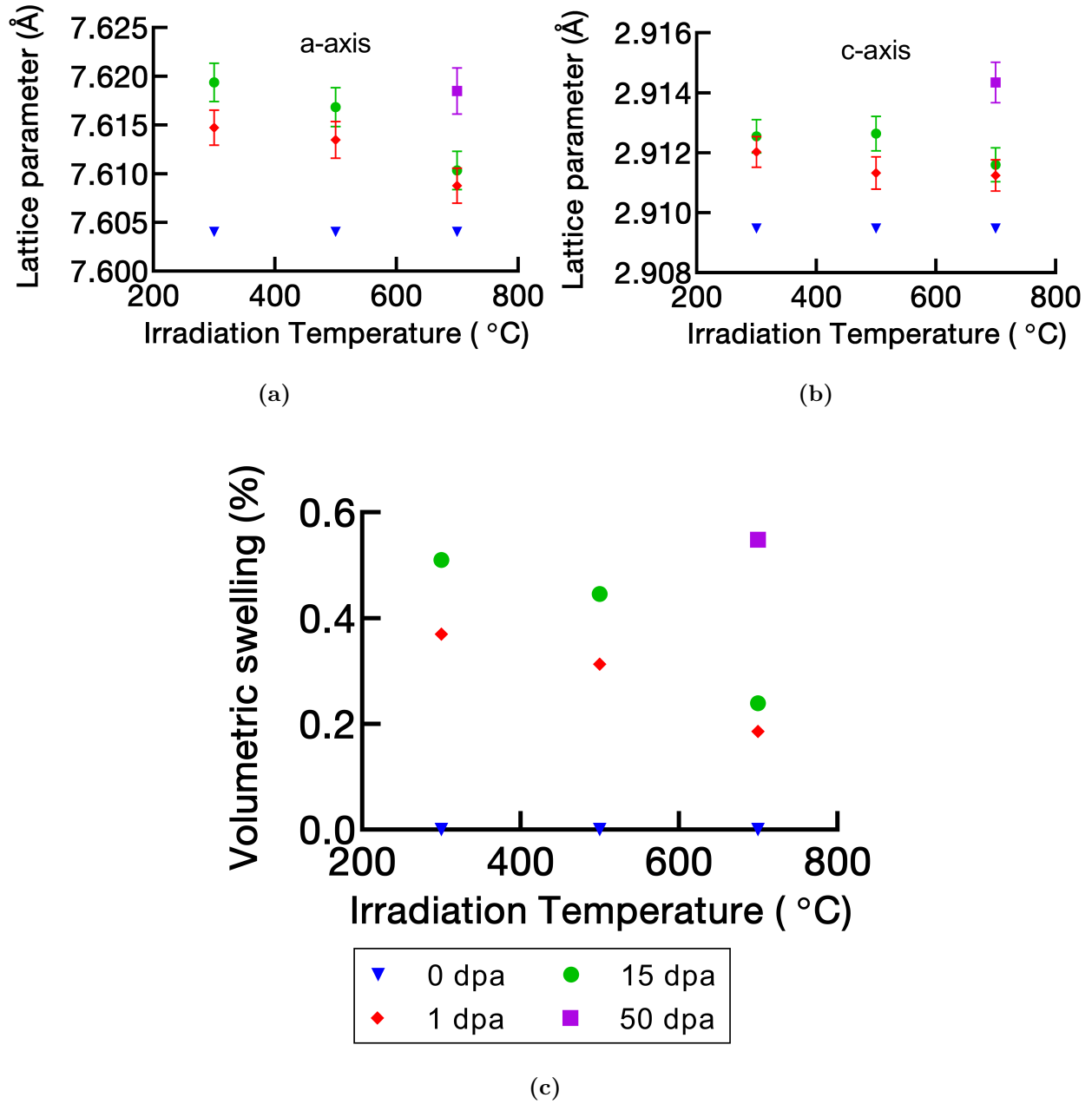
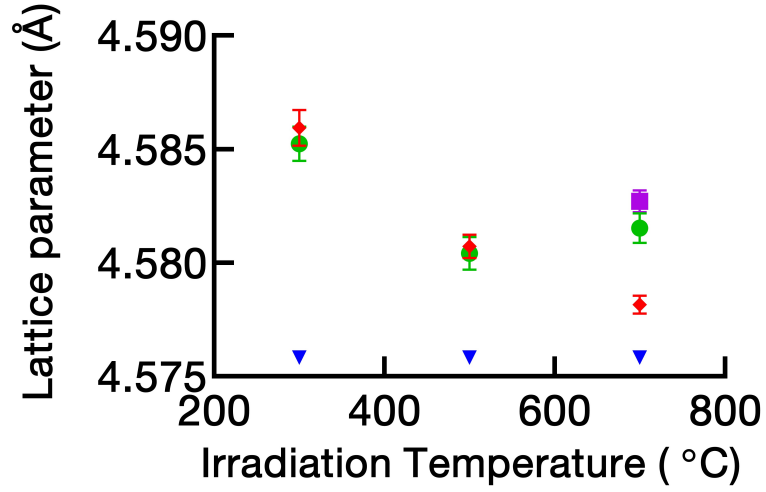
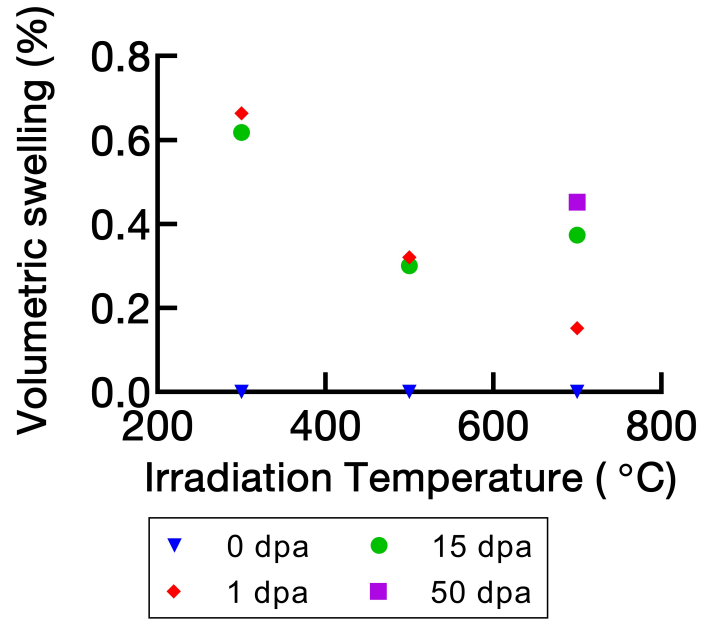


Figure 5.1: (a, b): a-axis and c-axis lattice parameter evolution and (c): corresponding volumetric swelling associated with lattice swelling for Si_3N_4 following 15 MeV Ni ion irradiation.



(a)



(b)

Figure 5.2: (a): Lattice parameter evolution and (b): corresponding volumetric swelling associated with lattice swelling for ZrN following 15 MeV Ni ion irradiation.

For irradiations conducted at 300 and 500 °C, results showed that a saturation in the surviving defect fraction is apparently reached by 1 dpa, as indicated by the similar lattice parameter measured at both 1 and 5 dpa. The temperature dependence of the lattice parameter swelling exhibited a monotonic decrease with increasing irradiation temperature at 1 dpa; the lattice swelling after 0.1 dpa at 700 °C was $\approx 0.1X$ vol. %, approximately five times lower than the corresponding swelling at 300 °C [186]. The 700 °C experiments displayed a different behavior at higher doses (15 and 50 dpa), where its lattice parameter swelling increased with increasing dose up to 50 dpa and did not display saturation behavior below that dose. Volumetric swelling was calculated using the same experimental lattice parameter values. Volumetric swelling data indicated a maximum swelling for ZrN around 0.67 % at 300 °C, and a swelling increase up to 0.45 % at 700 °C. Overall, both ceramics showed a maximum volumetric swelling below 0.7 % which allows us to assume a good dimensional stability up to 50 dpa. If we normalize these results to published SiC data also measured via GIXRD, we get ≈ 25 % SiC swelling for Si₃N₄ from 300 to 700 °C and 43 to 27 % SiC swelling for ZrN at 300 and 500 °C.

5.2 Surface microstructure characterization

The evolution of the surface microstructure for both Si₃N₄ and ZrN samples was observed using SEM imaging and is shown in Figures 5.3 and 5.4. The ion irradiated samples were not subjected to post-irradiation annealing. Small thermal etching at the surface of both ceramics was observed starting at 500 °C and surface evolution of the microstructure was more evident at 700 °C. A different surface roughness was observed in Si₃N₄ grains starting at 15 dpa. This effect is a bit more apparent at 50 dpa. Figure 5.3 does not include an unirradiated micrograph due to pronounced charging at the surface (even at low voltage). ZrN grains did not present this dose-dependent behavior. White light interferometry was used to quantify this surface roughness evolution and showed an important dependence with dpa but a small dependence on temperature. As seen in Figures 5.3 and 5.4, this phenomenon was more prominent in Si₃N₄ than ZrN. For Si₃N₄, an average surface roughness value of 15.2 nm was measured on the unirradiated sample, 20.7 nm at 1 dpa, 36.2 nm at 15 dpa and

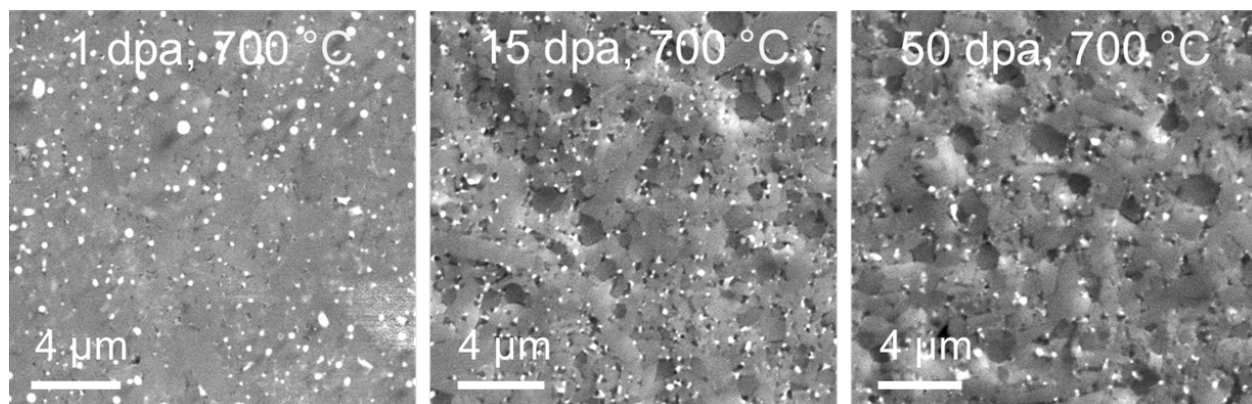


Figure 5.3: SEM images of surface evolution of Ni ion irradiated Si_3N_4 at 700 °C.

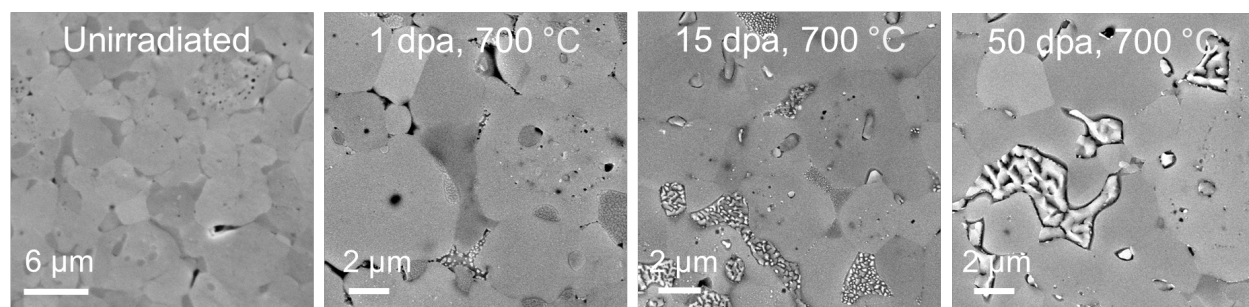


Figure 5.4: SEM images of surface evolution of Ni ion irradiated ZrN at 700 °C.

90.3 nm at 50 dpa. Irradiated ZrN values remained quite stable with 59 nm at 1 dpa, 56.8 nm at 15 dpa and 54.4 nm at 50 dpa (20.7 nm was measured on the unirradiated sample).

5.3 Thermal conductivity

Spatial domain thermoreflectance (SDTR) was used to determine the thermal conductivity of the bulk nitrides as well as their ion irradiated layers. Corresponding thermal diffusivity plot can be seen in Figure 5.5. Error bars of 10 % are associated with these readings and are mostly dependent on the time per measurement: a longer runtime would be needed in order to reduce them. All measurements were conducted at room temperature. Both silicon nitride and zirconium nitride presented a similar behavior in their thermal diffusivity evolution following ion irradiation. First, a thermal diffusivity increase can be observed with increasing irradiation temperature, and values similar to unirradiated ones were measured at 700 °C. In Si_3N_4 , a 44 % decrease was measured between the unirradiated value and the 1 dpa irradiated sample at 300 °C. Meanwhile, only a 22 % decrease was observed at 1 dpa and 700 °C. A similar behavior can be seen in ZrN at 300 °C (48 % decrease) while a complete recovery can be seen at 700 °C (+13 % increase, within error of unirradiated value). Second, both Si_3N_4 and ZrN presented a decrease in thermal diffusivity with increasing dose, suggesting that the degradation saturation has not yet been reached by these irradiation doses.

5.4 Nanoindentation

Figure 5.6 shows the hardness and elastic modulus evolution for both Si_3N_4 and ZrN after 1, 15 and 50 dpa irradiation at 300, 500, and 700 °C, as determined from nanoindentation measurements. The Nix-Gao method described in previous chapters was used to extract the bulk equivalent hardness from the midrange irradiated region. A 37 % increase in hardness compared to the unirradiated value can be observed at 300 °C for doses of 1 and 15 dpa for silicon nitride while the corresponding elastic modulus increased by 15 % compared to the unirradiated value (Fig. 5.6: a, b). At 500 °C, peak hardening can be seen by 1 dpa (30

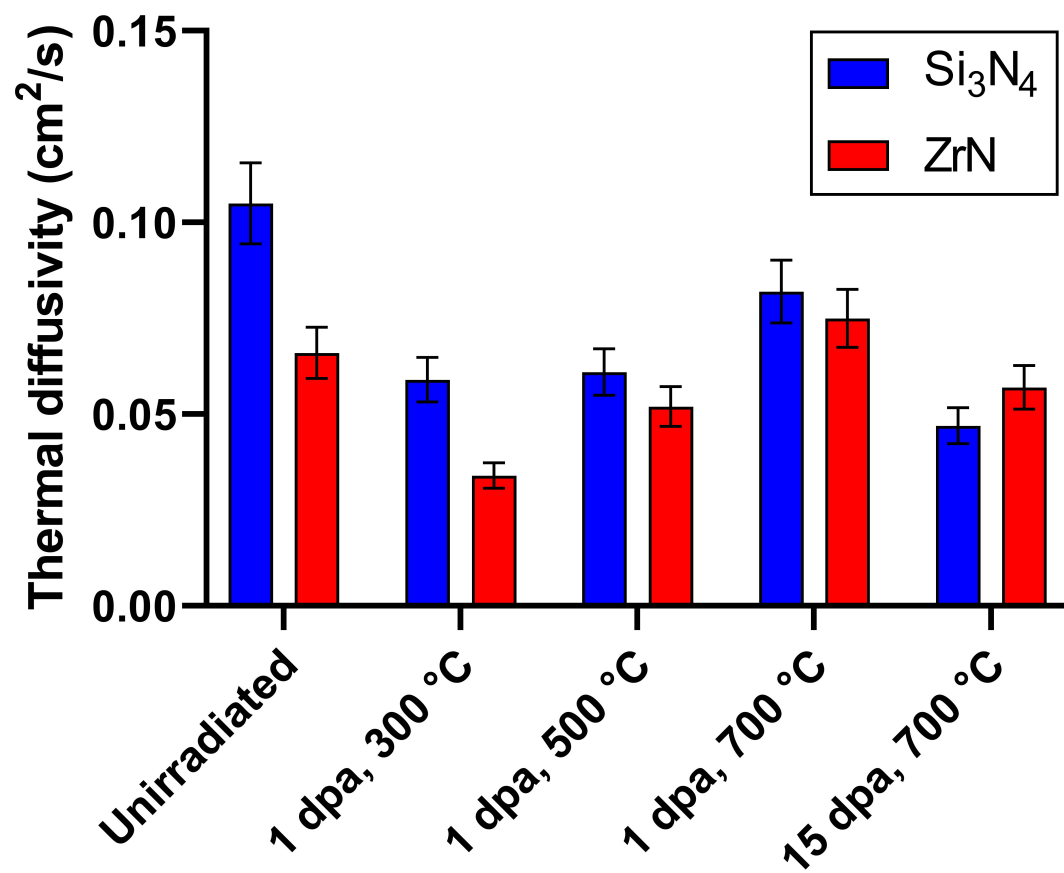
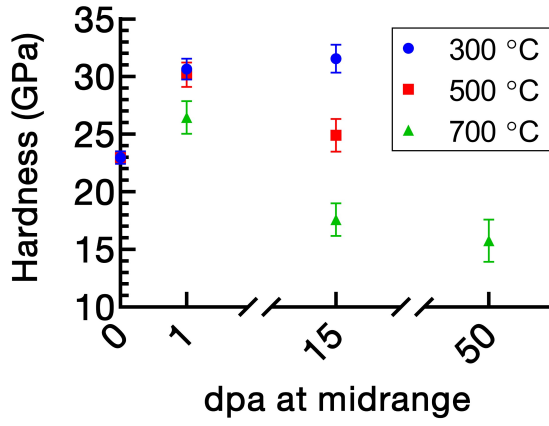
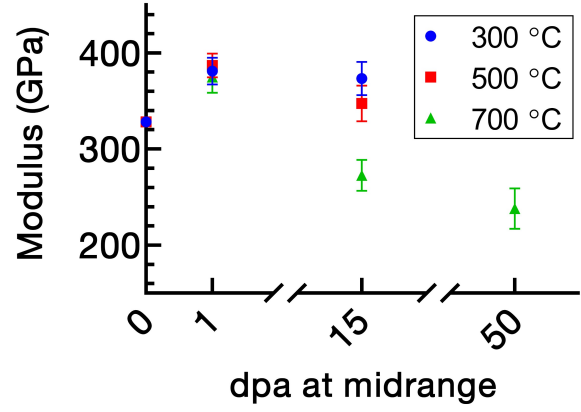


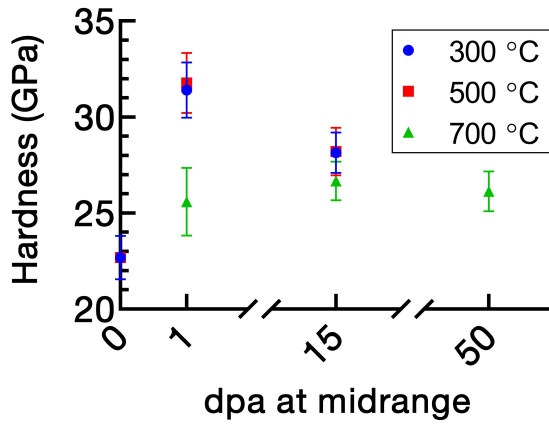
Figure 5.5: Thermal diffusivity evolution following Ni ion irradiation for Si_3N_4 and ZrN .



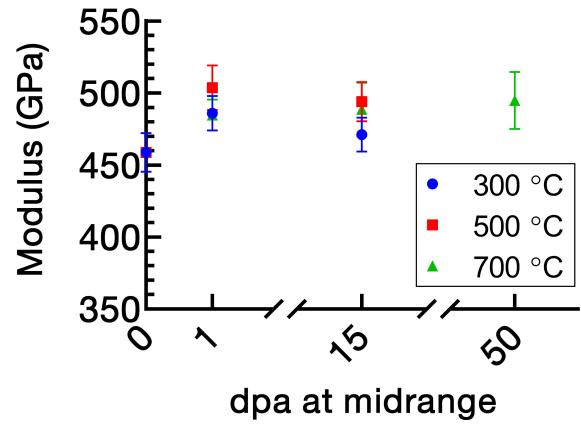
(a)



(b)



(c)



(d)

Figure 5.6: Room temperature hardness and elastic modulus evolution vs dpa after 15 MeV Ni ion irradiation at 300 °C, 500 °C, and 700 °C for (a, b) Si₃N₄ and (c, d) ZrN.

% hardness increase) while 15 dpa data look similar to unirradiated values (8 % hardness increase). Elastic modulus values followed a similar trend with an 18 % increase at 1 dpa and a 6 % increase at 15 dpa. At 700 °C, while increases in the mechanical properties can be observed at 1 dpa (13 % hardness and 14 % modulus increase), a dramatic drop in both hardness and modulus was observed at higher doses (30 % hardness and modulus decrease compared to unirradiated values at 50 dpa). The ZrN data summarized in Figure 5.6 (c, d) shows a qualitatively similar increased hardness and elastic modulus behavior at 1 dpa. However, different trends are observed at higher dose. The elastic modulus showed an 8 % increase at 1 dpa and remained stable up to 50 dpa at all irradiated temperatures. A gradual hardness increase can be observed at 700 °C up to 15 dpa (23 to 27 GPa, 18 % increase), followed by a plateau until 50 dpa. 300 and 500 °C irradiations showed an initial 35 % hardness increase by 1 dpa and reached the same 700 °C plateau by 15 dpa.

5.5 Transmission Electron Microscopy

5.5.1 Microstructure characterization of irradiated silicon nitride

TEM-BF and STEM-BF was used to characterize the defect microstructure in both Si_3N_4 and ZrN samples. Figure 5.7 presents the Si_3N_4 low-magnification (full damage range) microstructure evolution versus temperature (300 vs. 700 °C) at low dose (1 dpa), and the dose effect at high temperature (700 °C). At 1 dpa and 300 °C, most of the defects observed within the irradiated region are fine scale point defects. Some dislocation lines can be observed between the surface and 1.5 μm . Finally, a very small amount of isolated dislocation loops was also observed in multiple grains. At 700 °C and 1 dpa, while most of the defects observed remained fine scale point defects, dislocation lines can now be sparsely observed throughout the entire irradiated area. A similarly low amount of isolated dislocation loops can again be seen within Si_3N_4 grains. At 15 dpa and 700 °C, some dislocation loops and dislocation lines can be observed within the sample in a similar manner as the 1 dpa 700 °C condition. Fine scale point defects also appear to be concentrating around the peak irradiation region (4.5 μm). Delamination at the Si_3N_4 grain boundaries can be seen in the

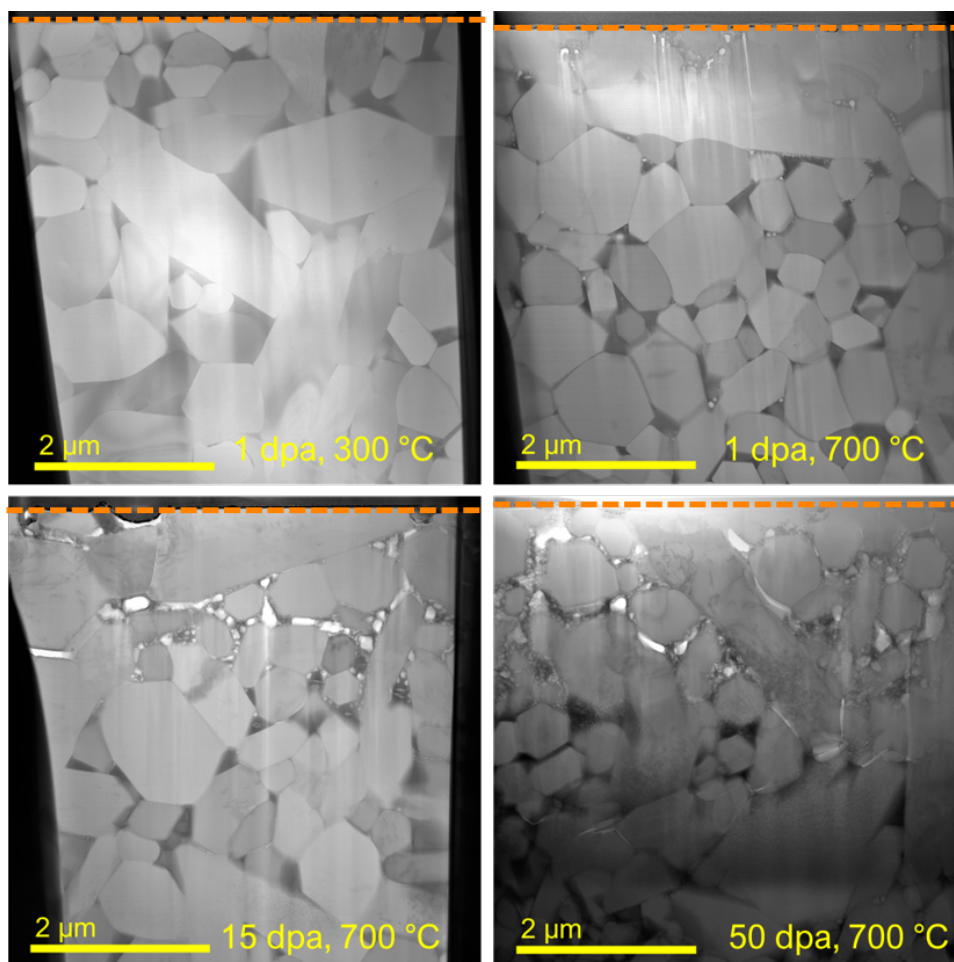
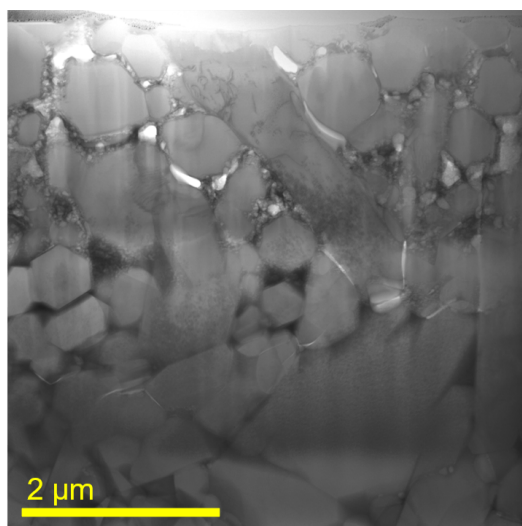


Figure 5.7: Low magnification (30kX) STEM-BF on-zone overview images of different Ni ion irradiation conditions for Si_3N_4 samples. Original sample surface located at the orange dotted line.

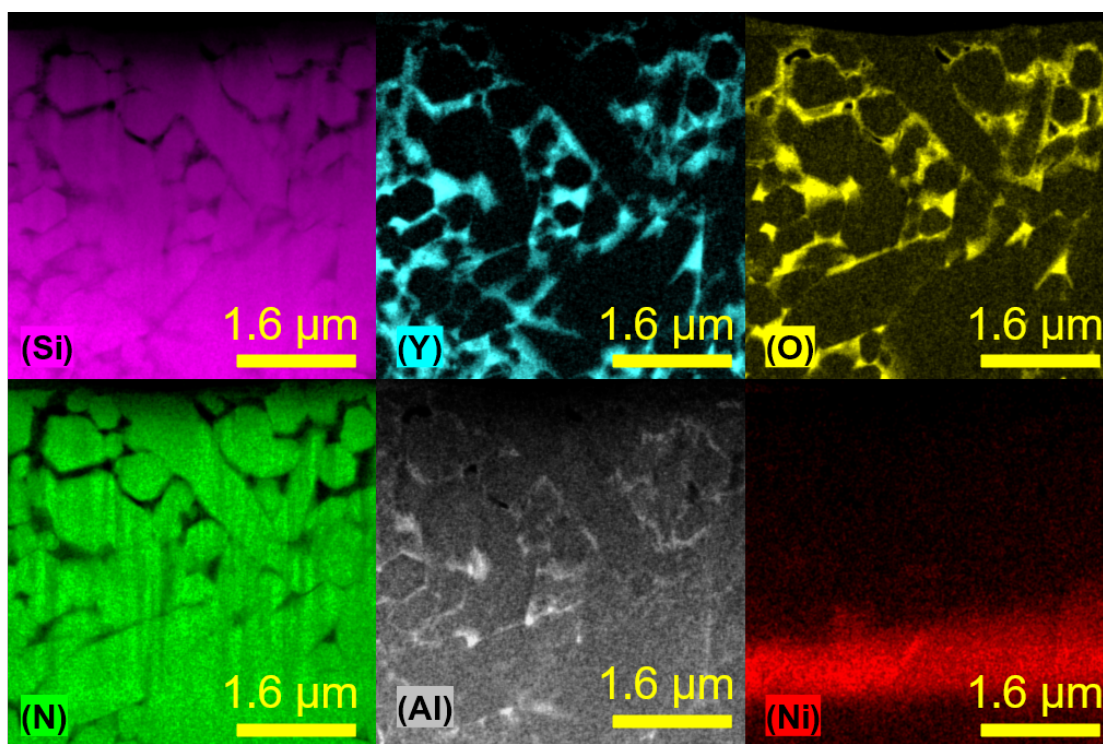
15 dpa, 700 °C sample, a phenomenon not observed at lower irradiation conditions. Finally, at 50 dpa and 700 °C, all the radiation-induced microstructural defects can be observed in a more prominent way. Dislocation lines are observed, and a higher amount of aligned dislocation loops were seen around the midrange damage area (around 2/2.5 μm). The saturated fine scale point defect region can be seen clearly and extends from 3.2 to 5 μm deep. Si_3N_4 grain boundary delamination is more pronounced and extends the entirety of the ion irradiated region.

Figure 5.8 illustrates the different elements mapped in the Si_3N_4 samples using EDS. The elemental mapping (b) shows the presence of a sintering aid, YAG, or Yttrium Aluminum Garnet, and its preferential formation at grain boundaries. The nickel implantation from the actual irradiation experiment follows the trend described by SRIM calculation and confirmed our studies to be primarily conducted in a very low nickel implanted area (around midrange damage); there was no evidence of significant radiation enhanced diffusion of the implanted Ni ions into the midrange irradiated regions. The EDS mapping did not show the presence of any unexpected or unwanted element in the sintered Si_3N_4 samples. Combined with the TEM overviews of the irradiated region found in Figure 5.7, the sintering aid behavior under irradiation can be described. Multiple cavities were observed at the YAG-enriched Si_3N_4 grain boundaries within the first 2 μm (around 10 to 60 nm in diameter) while a few isolated cavities in the YAG sintering aid started to appear at similar grain boundary locations from 2 to 4 μm depths at 1 dpa and 700 °C. At 15 dpa and between 500 to 700 °C, the cavities found in the YAG grain boundary phase within the first 2 μm depth region were observed to be more common and of larger size (60+ nm). The larger space present between Si_3N_4 grains started to produce significant grain boundary separation. From 2 to 4 μm in depth, a higher number density of cavities can be observed vs the 1 dpa condition yet the average size remained within 10 to 60 nm. At 50 dpa and 700 °C, a multitude of smaller cavities appear to have been formed around and over the larger cavities and now extends up to 3 μm below the surface. A few isolated cavities are also observed in deeper irradiated regions.

A high density of tiny cavities was observed within the interior of Si_3N_4 grains under all irradiated conditions and pictured in 5.9. As shown in Figure 5.10, cavity diameter remained stable, around 1.4 nm up to 15 dpa and 700 °C. After 50 dpa at 700 °C, a small increase

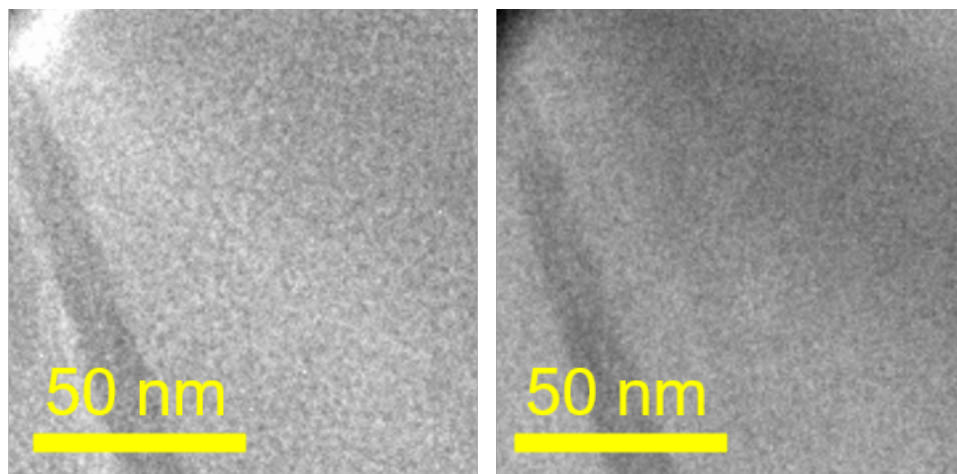


(a)

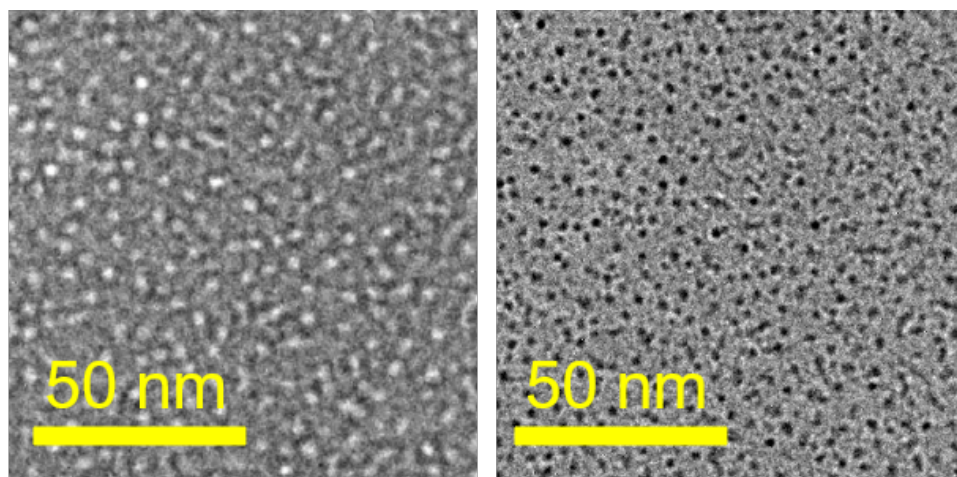


(b)

Figure 5.8: (a) STEM-BF overview cross-section image and (b) corresponding EDS mapping of 50 dpa, 700 °C Ni ion irradiated Si_3N_4 sample.

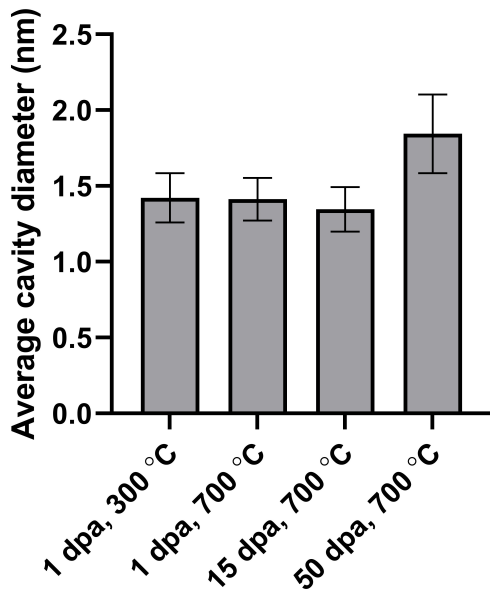


(a)

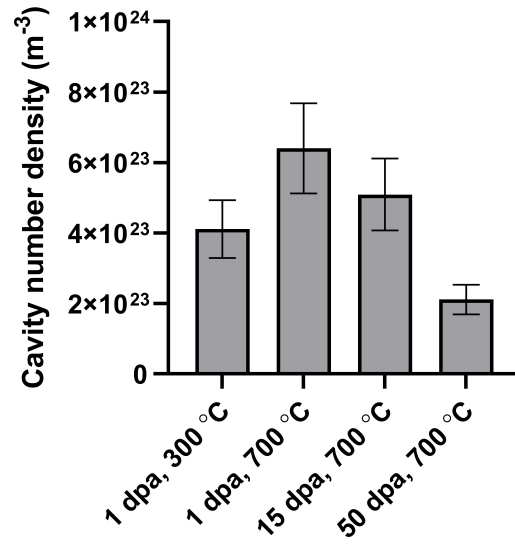


(b)

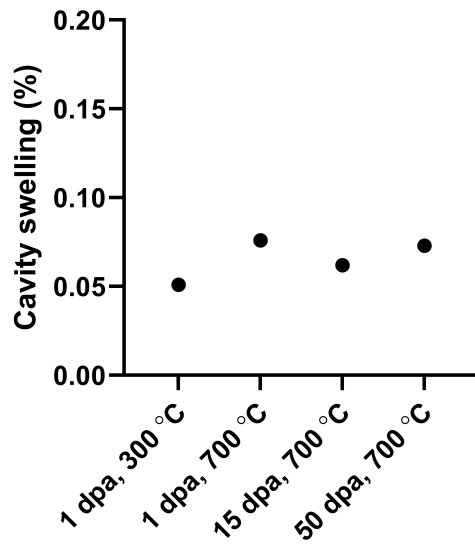
Figure 5.9: Under/Over focused TEM-BF micrographs of cavities in Si_3N_4 : (a) Unirradiated material (b) Irradiated material.



(a)



(b)



(c)

Figure 5.10: (a) Average cavity diameter and (b) number density and (c) cavity swelling for several irradiation condition in Si_3N_4 .

to 1.8 nm diameter was observed. The cavity number density appeared to average around $4 \times 10^{23} \text{ m}^{-3}$ up to 15 dpa and 700 °C (slightly higher density at 700 °C compared to 300 °C). The cavity density decreased to $2 \times 10^{23} \text{ m}^{-3}$ at 50 dpa, indicating slight coarsening of the cavity distribution for this irradiation condition. The calculated void swelling due to cavities appeared to slightly increase with increased temperature, but in all cases the volumetric swelling associated with cavities was well below the lattice parameter volumetric swelling (Fig. 5.1). The cavity volumetric swelling was calculated to be 0.051 % at 1 dpa and 300 °C, and 0.062 to 0.076 % from 1 to 50 dpa at 700 °C.

5.5.2 Microstructure characterization of irradiated zirconium nitride

STEM-BF overview images of the irradiated zirconium nitride samples can be found in Figure 5.11. At 1 dpa and 300 °C, most of the defects observed from the surface to the peak irradiated damage region are fine scale defects and clustered point defects (around 3 to 4 nm diameter). At 1 dpa and 700 °C, the same defects can be observed with a slight increase in size: Clustered defects were measured to be between 5 to 7 nm in diameter, and the evolution into small dislocation loops can be sparsely seen. Under these irradiation conditions, these defects are present at a high number density and their quantification could not be determined due to their projected image superposition within the thin foil. At 15 dpa, defect coarsening was observed. While some coarse point defects and stray dislocation lines can be seen, most defects appear as dislocation loops.

In the present work, loop characterization was conducted using diffraction contrast with the two-beam kinematic bright field (KBF) imaging technique. The Burgers vector of the loops was determined via the invisibility criteria, $\mathbf{g} \cdot \mathbf{b} = 0$ (where $\mathbf{g}$ = diffraction vector and $\mathbf{b}$ = Burgers vector) by focusing on one specific area and tilting the sample to get images under different $\mathbf{g}$ vectors and different low-index zone axes. 54 % of the loops were found to be faulted loops (with corresponding Burgers vector $\mathbf{a}/3\langle 111 \rangle$ and $\mathbf{a}/3\langle \bar{1}11 \rangle$) while 46 % were found to be perfect loops (with corresponding Burgers vector $\mathbf{a}/2\langle 110 \rangle$, $\mathbf{a}/2\langle 011 \rangle$ and $\mathbf{a}/2\langle 10\bar{1} \rangle$). The dislocation number density and average loop diameter versus loop

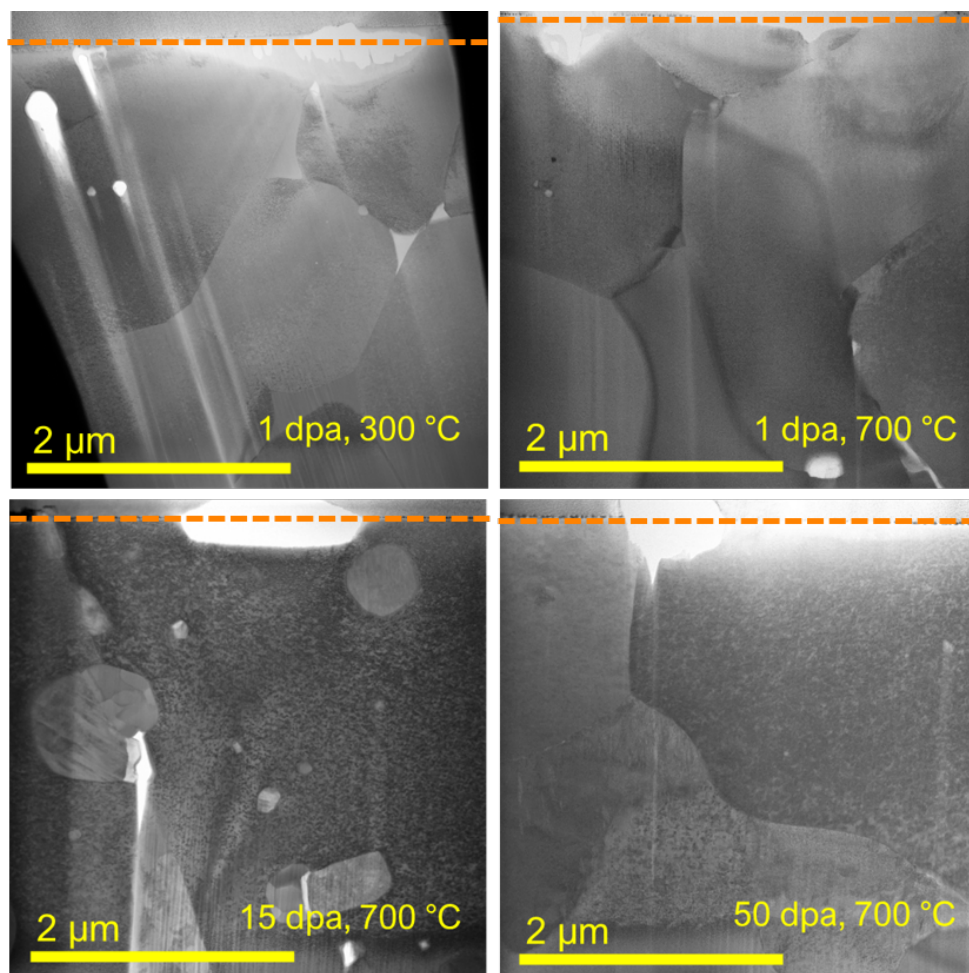
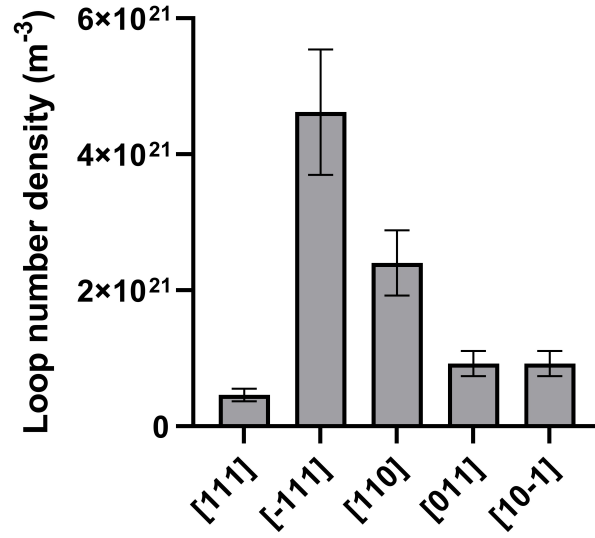


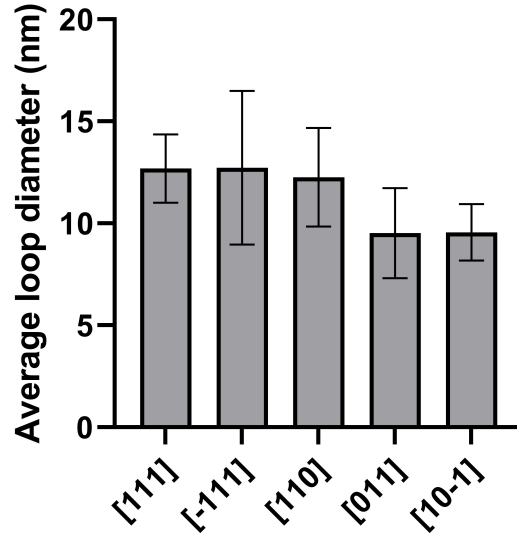
Figure 5.11: Low magnification (40kX) STEM-BF on-zone overview images of different Ni ion irradiation conditions for ZrN samples. Original sample surface located at the orange dotted line.

type are shown in Figure 5.12. The loop number density exhibited some anisotropy for the different loop habit planes. This may be associated with anisotropic stresses in the out of plane vs. in-plane directions associated with the ion irradiation induced lattice swelling [182]. Despite the different loop types, they were found to have a similar loop diameter of around 12 ± 3 nm. Based on typical loop evolution sequence in irradiated materials (initial formation of faulted loops on closest packed planes, and then unfauling to perfect loops when the loop size and density exceeds a critical value [186]), this suggests that the loop unfauling process is well developed after 15 dpa at 700 °C. After 50 dpa, a larger percentage of faulted loops have been converted to perfect loops. 33 % of the loops were found to be faulted loops (with corresponding Burgers vector $a/3\langle 111 \rangle$ and $a/3\langle \bar{1}\bar{1}1 \rangle$) while 67 % were found to be perfect loops (with corresponding Burgers vector $a/2\langle 110 \rangle$, $a/2\langle \bar{1}\bar{1}0 \rangle$, $a/2\langle 011 \rangle$ and $a/2\langle 10\bar{1} \rangle$). While a majority of the loops remained on the 111 habit planes, some were observed to have rotated and form pure edge-on loops on the 110 habit planes. As summarized in Figure 5.13, a similar dislocation loop number density was measured between 15 and 50 dpa at 700 °C, around $1 \times 10^{22} \text{ m}^{-3}$. The average loop diameter increased to 16.5 ± 3.5 nm compared to the 15 dpa irradiation. The 50 dpa, 700 °C sample exhibited anisotropic distribution of loops on the analyzed habit planes (similar to the behavior observed at 15 dpa), which may be associated with anisotropic stresses in the ion irradiated samples due to constraint by the unirradiated substrate. Under both higher dose conditions, fine scale defect clusters were observed to concentrate around the peak damage irradiated depth.

In Figure 5.14, elemental mapping is presented for the 50 dpa, 700 °C sample. As detected using XRD and described in a previous section, some zirconium oxide grains can be observed below the surface based on the high oxygen content for some grains in the EDS map. EDS mapping was utilized to ensure the study of only ZrN grains for the detailed TEM microstructural characterization. The EDS mapping also confirmed the absence of second phases or precipitate formation. The nickel implantation map agrees with SRIM calculations regarding the maximum implantation depth but exhibited evidence for substantial diffusion of Ni into the midrange regions of the irradiated sample, in contrast to the Ni mapping results for Si_3N_4 . TEM imaging and defect characterization was conducted around or before the midrange damage region in order to minimize potential effects associated with the implanted



(a)



(b)

Figure 5.12: (a) Dislocation loop number density and (b) average dislocation loop diameter vs loop type for 15 dpa, 700 °C Ni ion irradiation in ZrN.

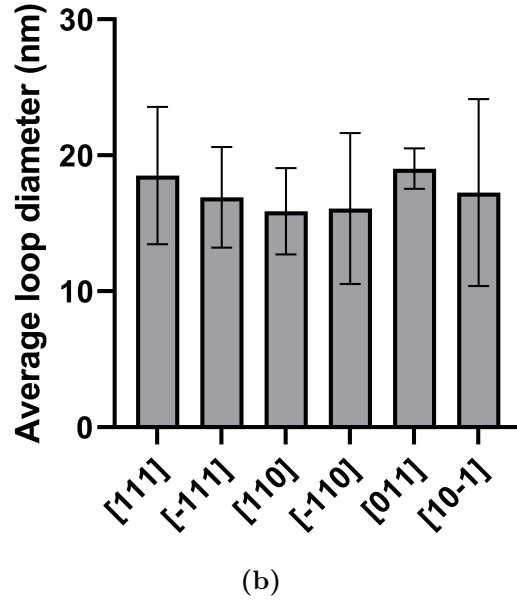
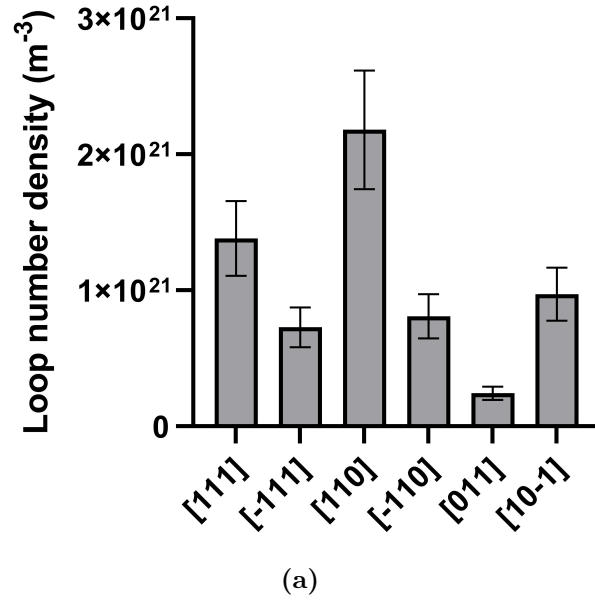
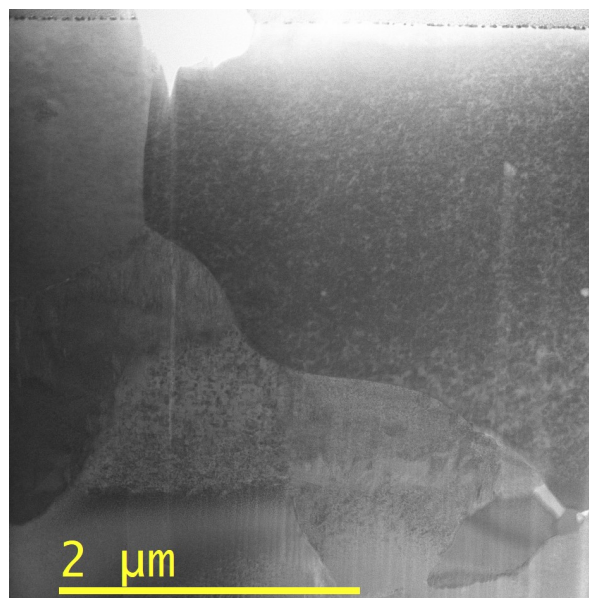
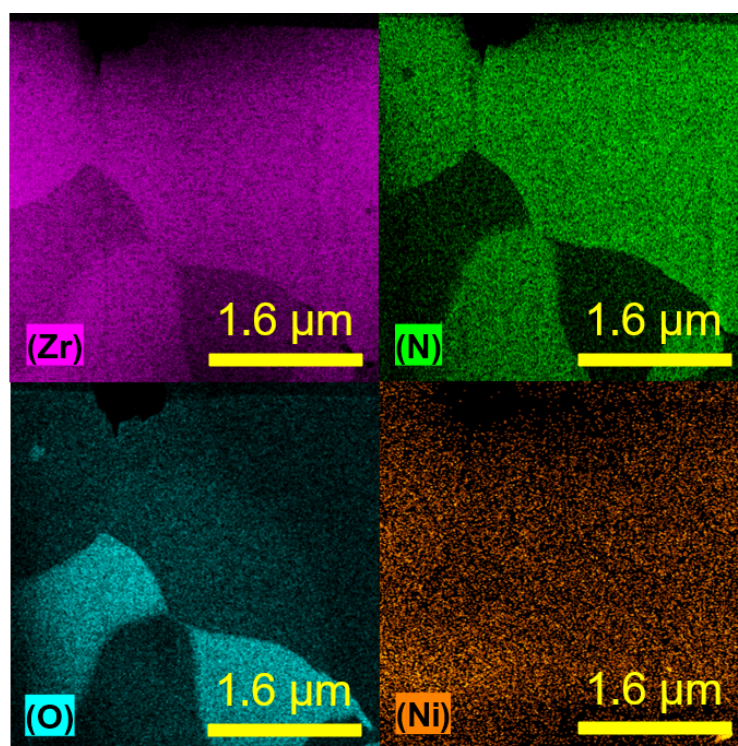


Figure 5.13: (a) Dislocation loop number density and (b) average dislocation loop diameter vs loop type for 50 dpa, 700 °C Ni ion irradiation in ZrN.



(a)



(b)

Figure 5.14: (a) STEM-BF overview cross-section image and (b) corresponding EDS mapping of 50 dpa, 700 °C Ni ion irradiated ZrN sample.

Ni, but the dramatically higher radiation enhanced diffusion behavior for Ni in ZrN compared to Si₃N₄ indicates that some implanted ion effects may occur in the high dose 700 °C ZrN specimen. The diffusion of Ni into the midrange region may contribute to some of the unanticipated high lattice parameter swelling in the high dose 700 °C ZrN specimen (Fig. 5.2).

Similar to the observations for Si₃N₄, a high density of tiny cavities were also observed in ZrN for all irradiated conditions, including the 300 °C, 1 dpa sample and are presented in 5.15. Examination of unirradiated grains adjacent to the ion irradiation region confirmed the absence of cavities outside the irradiated regions. The cavity number density remained similar up to 50 dpa (around $2.5 \times 10^{23} \text{ m}^{-3}$). Void diameter was observed to slightly increase from 1.6 nm at 1 dpa (for both 300 and 700 °C) to 2.1 nm for 15 and 50 dpa at 700 °C. These differences are illustrated in Figure 5.16. The volumetric swelling due to cavity formation was smaller than the corresponding swelling associated with lattice parameter expansion (Fig. 5.2) and slightly increased with increasing temperature at 1 dpa (0.068 % to 0.083 % from 300 °C to 700 °C). For an irradiation temperature of 700 °C, cavity swelling increased by nearly a factor of two (from 0.083 % to 0.15 %) with increasing dose of 1 to 50 dpa.

5.6 Discussion

While surface imaging using SEM did not reveal major differences between unirradiated and irradiated samples, a few interesting results were observed after GIXRD measurements. The lattice parameter of silicon nitride presented a gradual decrease with increasing temperature at 1 and 15 dpa up to 700 °C and zirconium nitride showed the same behavior up to 700 °C at 1 dpa and up to 500 °C at 15 dpa. This general trend is consistent with what has been described previously in the literature for samples irradiated at temperatures below the onset of long-range vacancy motion [33, 150, 70, 161, 186, 18, 140, 27, 148]. It is associated with a reduction of the concentration of defect formation due to the enhanced point defect recombination and thermal annealing of defect clusters occurring at higher temperature. This lattice reduction goes along with a lattice saturation often occurring for ceramics at doses around 0.1 to 1 dpa. Si₃N₄ lattice parameter swelling at 15 dpa is slightly

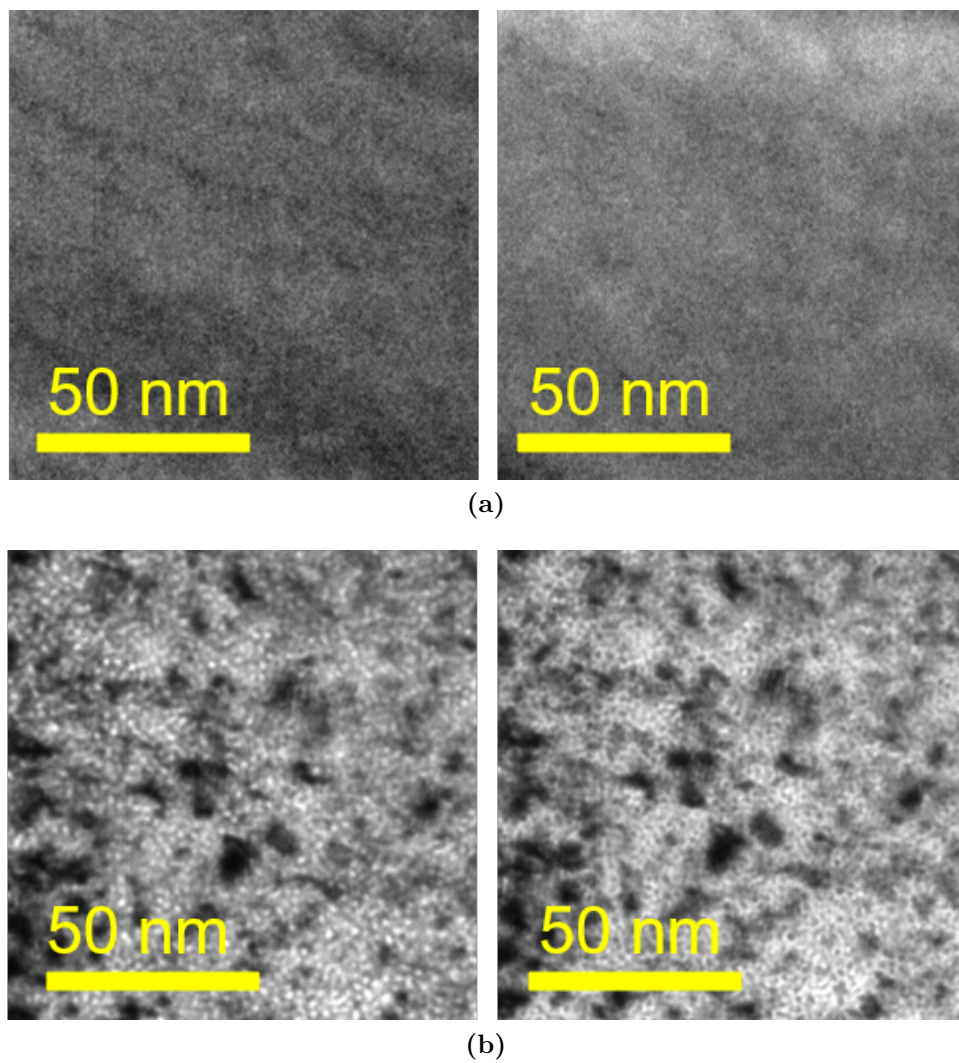
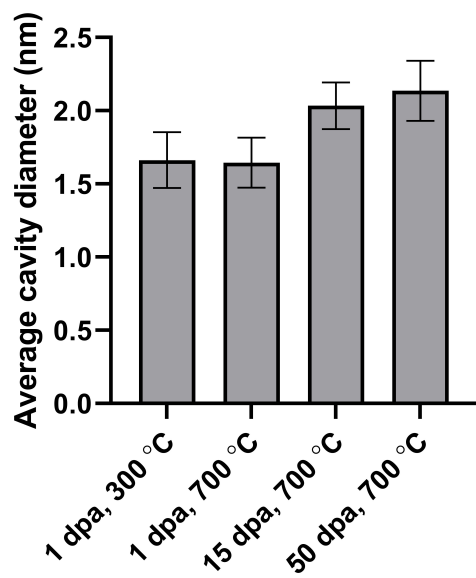
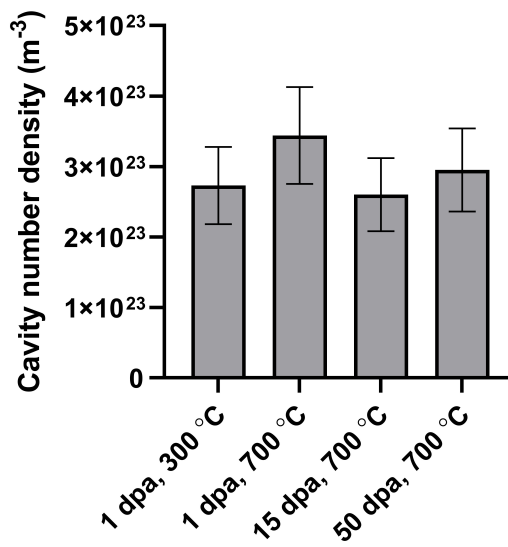


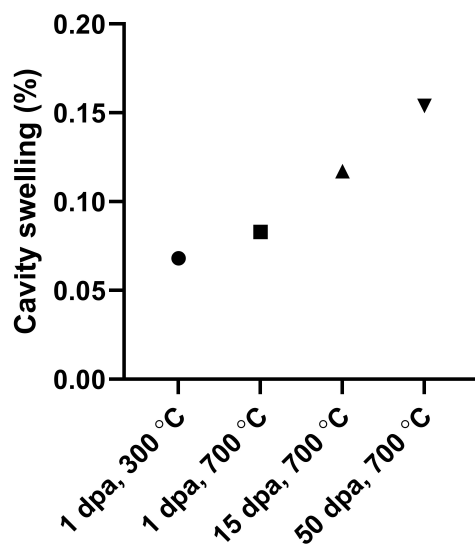
Figure 5.15: Under/Over focused TEM-BF micrographs of cavities in ZrN: (a) Unirradiated material (b) Irradiated material.



(a)



(b)



(c)

Figure 5.16: (a) Average cavity diameter and (b) number density and (c) cavity swelling for several irradiation condition in ZrN.

higher than at 1 dpa, indicating the approach of the saturation regime at the investigated temperatures. The saturation behavior can clearly be seen in the ZrN results up to 500 °C. Lattice parameter evolution for Si₃N₄ showed an unexpected result at 50 dpa and 700 °C, where a swelling value of 0.55 % was measured when a value closer to 0.2 % (as it was found with both 1 and 15 dpa irradiations) was expected. STEM overview of the irradiated microstructure found in Fig. 5.8 showed important grain boundary delamination within the 50 dpa, 700 °C sample, a phenomenon that has been reported previously by Tada et al. [146]. This behavior reflects the anisotropic crystal structure of Si₃N₄ and was not observed in isotropic materials such as ZrN. We assume that it may be a possible reason why the lattice parameter shows such a large discrepancy under this irradiation condition. While the constraint by adjoining grains could suppress an important level of lattice swelling, grain boundary cracking above a critical dose (associated with anisotropic stresses) could allow for a constraint-free swelling within individual grains.

ZrN irradiation at 700 °C also revealed a lattice parameter swelling behavior that did not follow the trends set at lower temperature: the lattice parameter swelling increased with increasing dose up to 50 dpa and did not display any evidence of a swelling saturation behavior below that dose. The few studies present in the literature involving the observation of the lattice parameter over increasing dose in zirconium nitride showed rapid saturation similar to expected trends and results presented here at 300 and 500 °C [155, 35, 94, 92]. One possibility for the different behavior observed at 700 °C in the ion irradiated ZrN could be radiation enhanced diffusion of the implanted nickel ions into the midrange region where the GIXRD analysis was performed, which could produce lattice expansion. As it was shown above in Figs. 5.8, 5.14, EDS mapping of the implanted nickel in ZrN revealed its presence throughout the entirety of the ion irradiated region. While the Ni content is concentrated around the peak damage area, a significant amount of Ni can be observed throughout the midrange irradiated region and extending to the original surface (deposited platinum layer). This behavior was not observed in Si₃N₄, where its peak damage area was formed deeper into the material and the Ni content was largely localized close to the implanted ion region predicted by SRIM (as shown in Figures 5.14). A second possibility could be radiation enhanced radiolysis of zirconium nitride in the ion irradiated region, where ZrN would release

some nitrogen and thus change the Zr:N stoichiometry. As published by Toth and presented in Fig. 2.9, the lattice parameter of ZrN was shown to increase when a reduction of the N/Zr ratio occurred in unirradiated ZrN [151].

As discussed in Wolfer [163], the point defect swelling regime ends when the onset of vacancy motion begins (recovery Stage III), which is typically around 0.2 Tm. While this onset of vacancy motion at a temperature near ≈ 0.2 Tm has been experimentally validated for multiple materials, exceptions do exist: for example, whereas vanadium and niobium have higher melting temperatures than chromium, the latter possesses a much higher stage III recovery temperature and in all three of these cases the Stage III recovery occurs at ≈ 0.1 -0.2 Tm [186, 163]. The onset temperature for vacancy migration on either the cation or anion sublattice has not yet been accurately determined for the two nitride ceramics investigated. A limited number of studies have been conducted on self-diffusion in silicon nitride [134, 77, 133, 84]. This has been due to several factors such as its decomposition at 1900 °C, the lack of suitable radioactive tracers, difficult synthesis, and impurity contamination [19]. Schmidt et al. reported similar nitrogen and silicon self-diffusion coefficients in Si₃N₄ if compared at the same temperature between 1200 and 1700 °C [134]. They also discussed the migration energies of nitrogen vacancies in silicon nitride and reported values between 1.8 to 3.6 eV. Despite this, details on point defect formation and migration in silicon nitride remain quite lackluster, and more work must be done to better understand these migration processes. No reliable vacancy migration energies have been reported for zirconium nitride. Only one publication from Desmaison and Smeltzer reported migration energies for nitrogen in sub-stoichiometric ZrN of 1 eV for ZrN_(0.71–0.79) and 1.59 eV for ZrN_(0.93) [42]. Therefore, the empirical correlation of 0.2 Tm is assumed for the onset of vacancy migration.

In our case, 0.2 Tm would be equivalent to ≈ 380 °C for Si₃N₄ and 596 °C for ZrN. Volumetric swelling calculated from experimentally measured lattice parameter swelling using GIXRD is plotted in Figure 5.17 for both ceramics, as well as literature values for BeO and SiC. In general, the lattice parameter swelling for all four plotted materials tends to monotonically decrease with increasing irradiation temperature up to $\approx 0.25/0.4$ Tm, in general agreement with expectations for irradiation at temperatures where vacancies are immobile [70]. This figure appears to show a good correlation between Si₃N₄ values and the

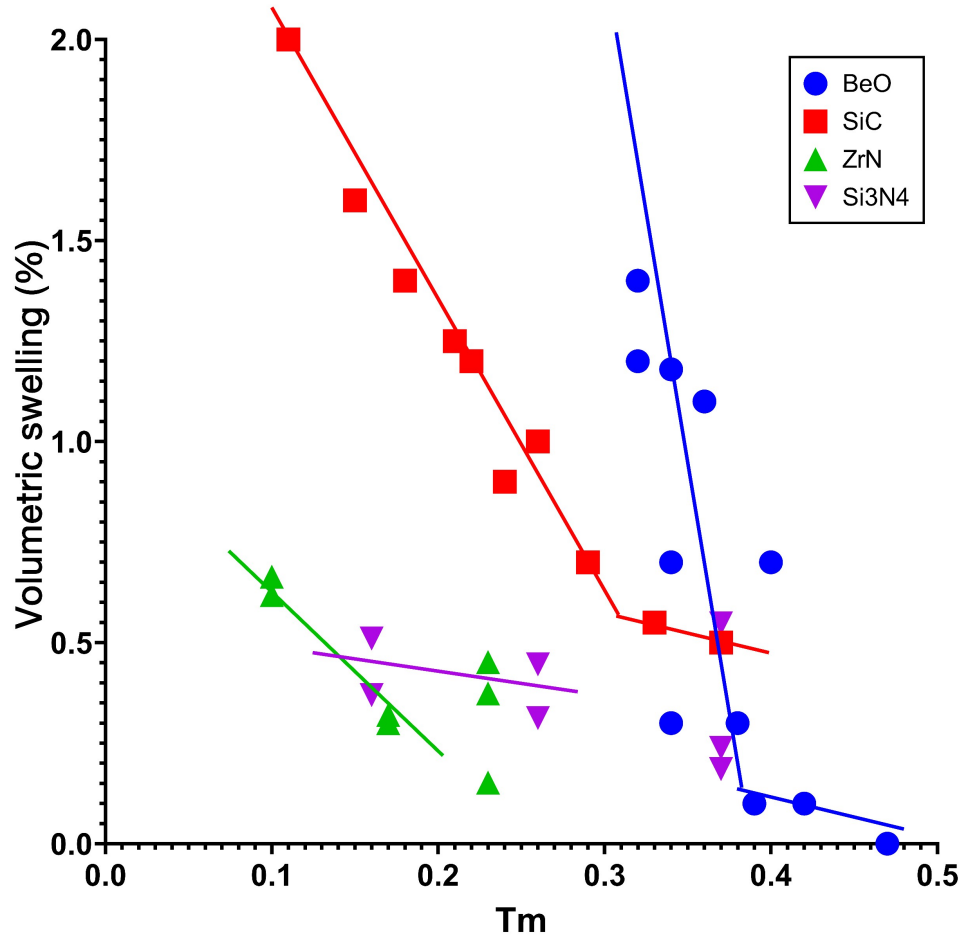


Figure 5.17: Volumetric swelling evolution calculated from lattice expansion versus melting temperature for multiple ceramic materials mentioned in this document. BeO and SiC literature values adapted from Zinkle et al. [192]. ZrN and Si₃N₄ experimental values from this work.

$\approx 0.2/0.3$ Tm onset of vacancy motion. All ZrN irradiations were done below 0.3 Tm and a linear trend is observed up to 1 dpa and to 500 °C for higher doses. Figure 5.18 presents the total swelling (lattice parameter + cavity swelling) calculated for these irradiation conditions in both Si₃N₄ and ZrN and summarizes the impact of both dose and temperature. Lattice parameter swelling was predominant contributor to overall volumetric swelling under all irradiation conditions, and a regime transition where the swelling would be dominated by cavity formation (typically occurring after relatively high doses at irradiation temperatures between ≈ 0.35 and 0.6 Tm) was not observed.

The origin of cavity formation in these nitride ceramics remains to be determined, and the high temperature results should be taken lightly due to the adverse reactions discussed above. They include drop in mechanical properties above 15 dpa and 500 °C for silicon nitride, attributed to the poor radiation stability of the sintering aid present at grain boundaries, and the lattice parameter increase with increasing dose without showing a saturation behavior at 700 °C in zirconium nitride.

Cavity formation, an indication of significant vacancy mobility in irradiated materials, has been generally described to occur between ≈ 0.2 (defect recovery stage III) to 0.55 Tm. [186]. The three irradiation temperatures studied during this work represented 0.16/0.27/0.38 Tm for Si₃N₄ and 0.1/0.17/0.24 Tm for ZrN. While a few metals exhibit void formation at temperature as low as 0.2 Tm such as tungsten, niobium, and tantalum, they all possess a bcc crystal structure [139]. The typical void swelling range in fcc materials range from 0.35 to 0.6 Tm [139, 34]. TEM characterization of the irradiated Si₃N₄ and ZrN in the current study clearly showed small cavity formation in both Si₃N₄ and ZrN, at 300, 500, and 700 °C. The cavity number density remained approximately constant for all investigated doses and temperatures, and the cavity diameter slightly increased with increasing dose at 15 and 50 dpa. There have been no previous reports of cavity formation in these materials around or below those irradiation conditions unless insoluble gas is implanted [119, 184]. We also confirmed that the cavity formation was limited to the ion irradiated region and confirmed the absence of cavities in the unirradiated regions of the observed specimens (see Figs. 5.9, 5.15), so the cavity formation was not associated with a specimen preparation artifact.

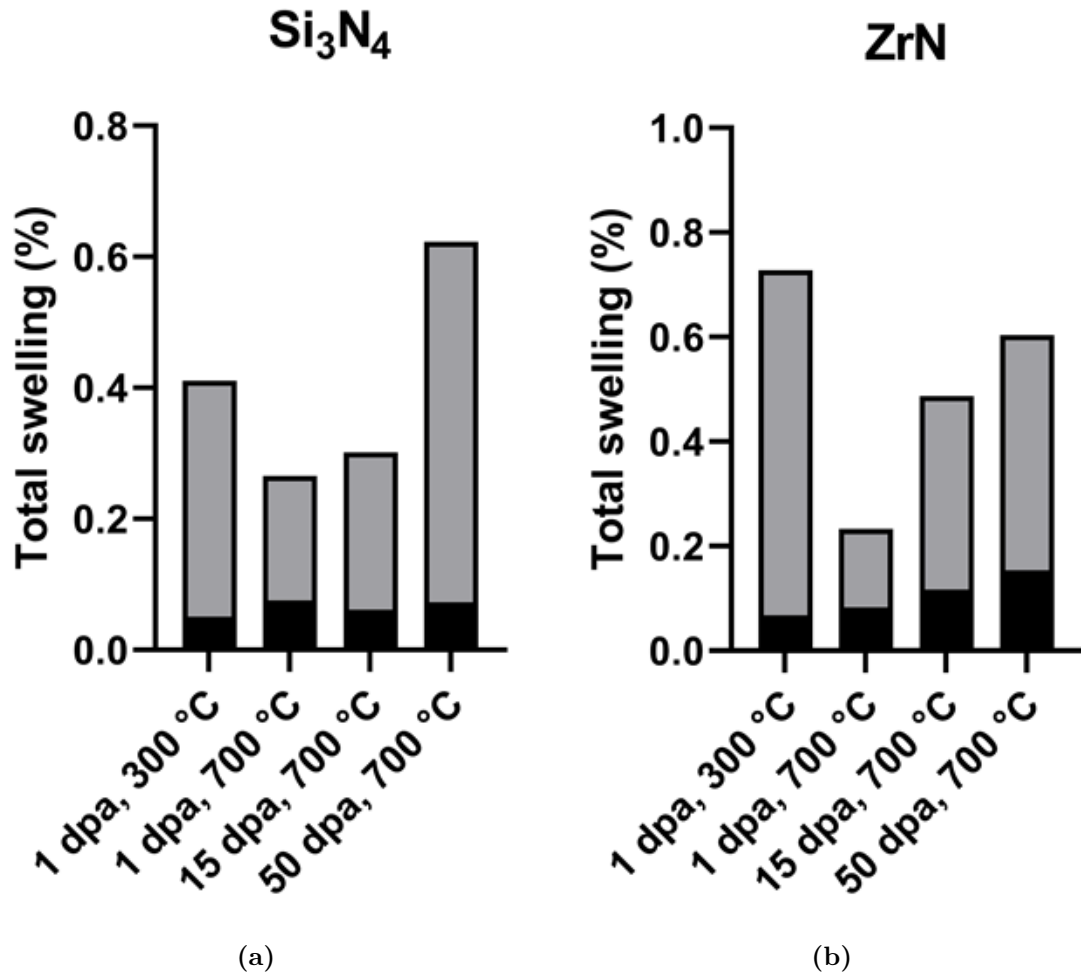


Figure 5.18: Total swelling in (a) Si₃N₄ and (b) ZrN. Grey bars represent lattice swelling while black bars represent cavity swelling.

While this radiation-induced cavity formation behavior remains quite puzzling, the cavity formation may arise from ionization enhanced radiolysis of these two nitride ceramics. Another potential contributing factor may be if the nitrogen sublattice displacement rate was much higher than the zirconium or silicon one. The excess nitrogen interstitials could accumulate at small cavity nuclei and help promote cavity stabilization (high nucleation rate of cavities). However, this would not explain why previous studies have not reported cavity formation as it should occur in a wide range of irradiation spectra. Some materials (organic materials, quartz, alkali halides) have been described in the literature as susceptible to displacement damage from radiolysis reactions [1, 50, 65, 136]. Ionizing radiation can be especially strong during light ion irradiation due to the high amount of ionization per dpa. It can produce behaviors such as enhanced diffusion, bond ruptures and localized electronic excitations [190, 20, 183]. In this scenario, a partial decomposition of our nitride materials would release some free nitrogen which could behave similarly as He and form small cavities in the material. As noted earlier, this speculated radiolytic decomposition of ZrN may be able to explain to some extent the lattice parameter increase in ZrN at 700 °C: when unirradiated ZrN becomes ZrN_{1-x} , its lattice parameter should increase due to the reduction in the N/Zr ratio [151]. To contrast with this data published by Toth, some publications on B1 cubic materials including one on zirconium nitride discussed unit cell contraction following irradiation [92, 81, 13, 177]. Lu et al. observed a small unit cell contraction up to 1.42 % in nano sized ZrN after irradiations using 300 keV Ne^+ and 350 keV O^+ . A reduction in N:Zr ratio to 0.88 was measured and assumed to be due to the production of displaced nitrogen atoms as well as fast diffusion along grain boundaries [92].

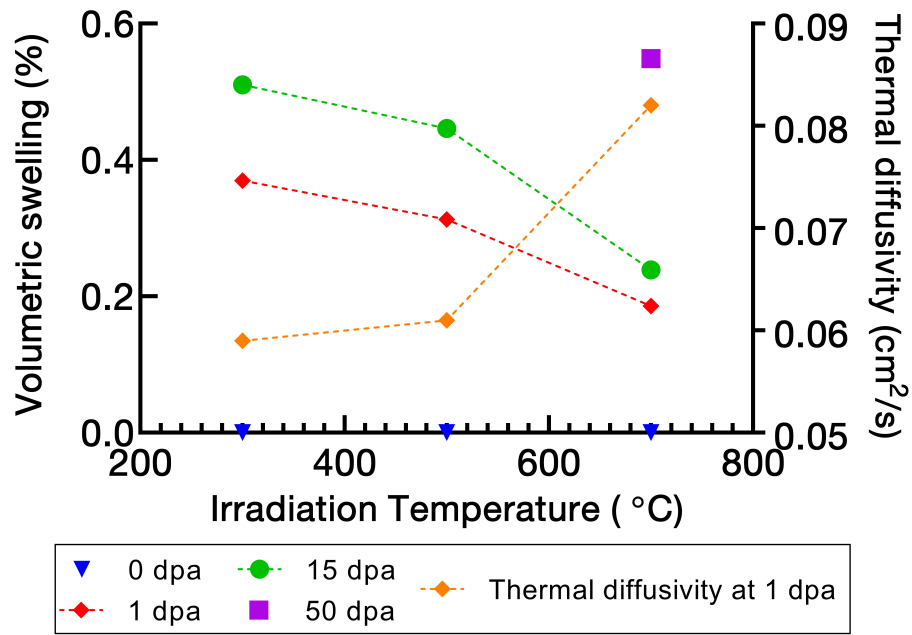
Past work has presented and discussed the thermal diffusivity evolution of Si_3N_4 following neutron and electron irradiation using a wide range of dose, temperature, and including measurements post annealing [5, 8, 7]. Thermal diffusivity was measured using laser flash analysis in these published results, which only allows for bulk property measurement and is not suited for ion irradiated materials due to the shallow irradiated depth. In this study, the thermal diffusivity of nitride ceramics was measured using spatial domain thermoreflectance (SDTR) which allows for accurate isolation and measurement of the thermal properties of an irradiated layer without negative effects from the bulk [74, 73]. Akiyoshi et al. conducted

thermal conductivity measurements on a variety of Si_3N_4 samples, varying temperature, dose, and annealing [5, 8, 7]. They reported its evolution following both electron and neutron irradiation. First, degradation of the thermal conductivity was observed with increasing dose up to 30 dpa where saturation occurred. This behavior indicated the stability of Si_3N_4 's thermal diffusivity for high fluence applications. After reaching saturation, thermal diffusivity evolution became only dependent of the irradiation temperature: an increase can be observed with increasing irradiation temperature. The evolution of the thermal diffusivity with the microstructure of irradiation induced defects was also discussed. At low temperature, the mobility of interstitial atoms was not high enough to allow for loop formation or annihilation with adjacent vacancies, allowing for a high density of isolated defects while clear dislocation loops were observed at higher temperatures. Thermal diffusivity results reflected this behavior, where a lower thermal diffusivity was found at lower temperature [8]. The same behavior was confirmed in this work, using ion irradiation and thermoreflectance measurements, as shown in Figure 5.19. Moreover, we can also correlate it with lattice swelling, where a reduction can be seen with increased temperature due to the smaller defect concentration / thermal annealing of defects.

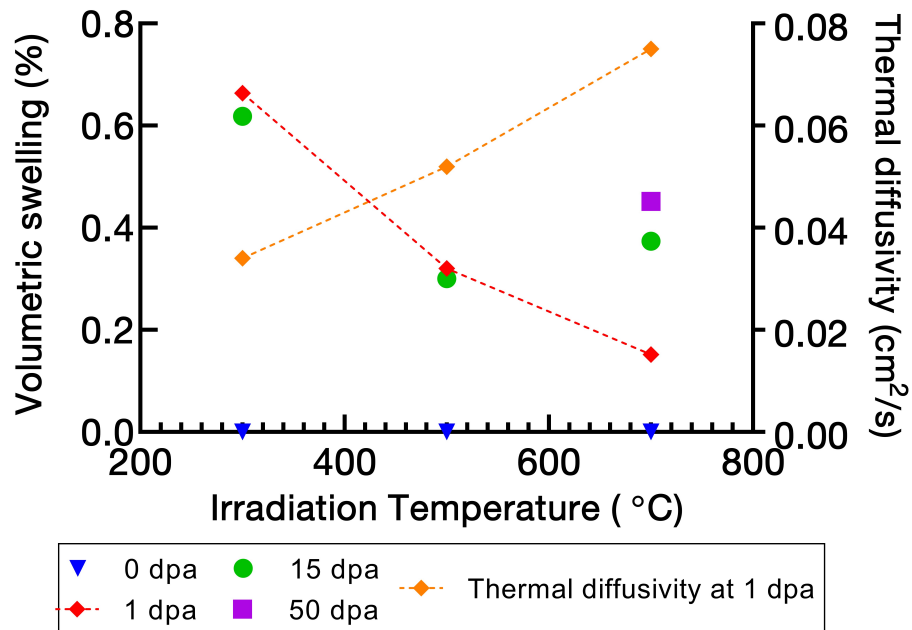
The thermal defect resistance can be defined the difference of the reciprocal of irradiated and unirradiated thermal conductivity as shown in Eq. 5.3:

$$\frac{1}{K_{Rd}} = \frac{1}{K_{irr.}} - \frac{1}{K_{Unirr.}}. \quad (5.3)$$

It can also be correlated with the defect type and defect concentration present in irradiated ceramics [140, 141]. Assuming that the thermal defect resistance is due to point defects, a linear increase should be observed if the defect production was linear (valid for temperatures with limited point defect mobility and below the saturation dose for defect accumulation) and this trend should be broken when the material reached onset of vacancy motion as discussed by Snead and coworkers [140, 141]. Figure 5.20 presents the thermal defect resistance evolution versus lattice swelling for both Si_3N_4 and ZrN , which correlate with the defect microstructure observed using TEM. This behavior appears to be

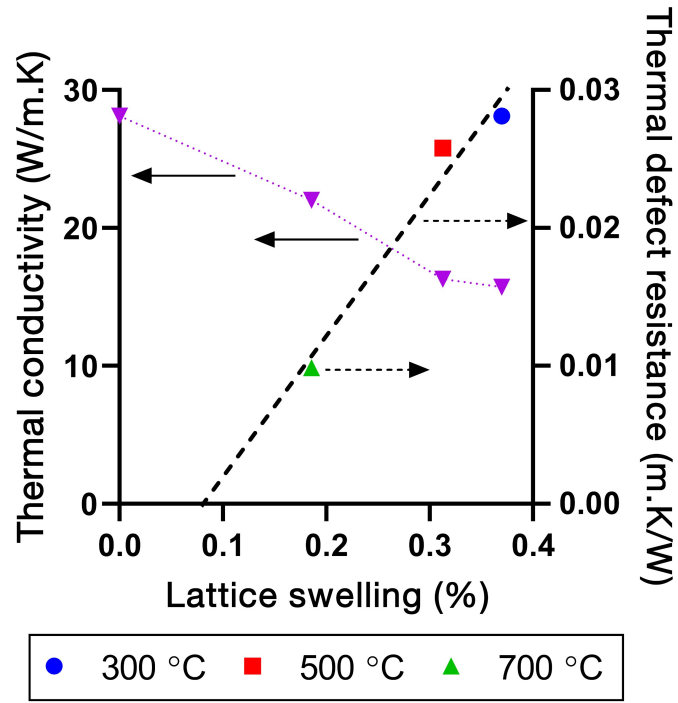


(a)

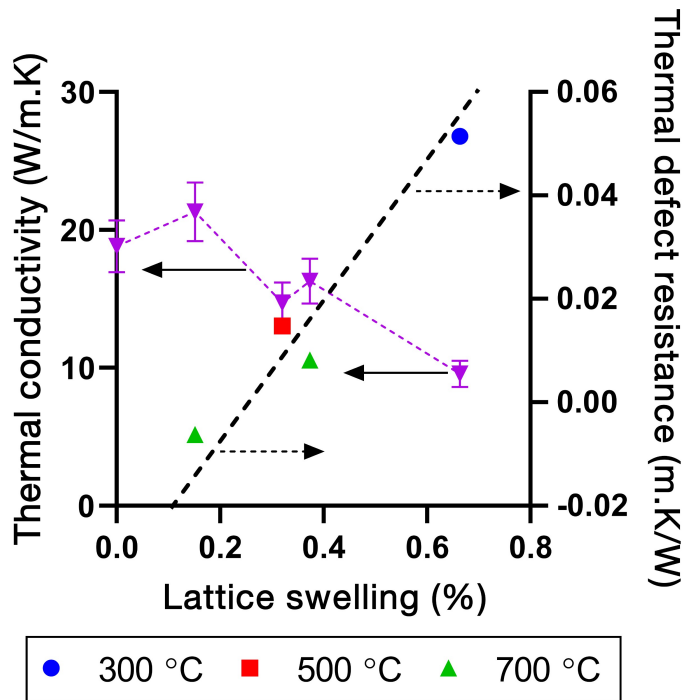


(b)

Figure 5.19: Corresponding volumetric swelling associated with lattice swelling and thermal diffusivity evolution following Ni ion irradiation for: (a) Si₃N₄ and (b) ZrN.



(a)



(b)

Figure 5.20: Corresponding volumetric swelling associated with lattice swelling and thermal diffusivity evolution following Ni ion irradiation for: (a) Si_3N_4 and (b) ZrN .

temperature independent indicating that the defects controlling lattice swelling and thermal conductivity are one and the same.

While Si_3N_4 showed some irradiation induced hardening at 300 °C, a drop in mechanical properties was observed starting at 15 dpa and 500 °C and accentuated at 700 °C. STEM and EDS mapping characterization (Figs. 5.7, 5.8) allowed us to conclude that a sintering aid (yttrium aluminum garnet, or YAG) was present in the sample and preferentially located at grain boundaries. This sintering aid phase was observed to degrade under ion irradiation. Large swelling of the grain boundary phase was observed in the 15 dpa, 500 °C Si_3N_4 sample for irradiation depths up to 2 μm , and the grain boundary phase swelling was observed up to depths of 3 μm after 50 dpa at 700 °C. The intergranular phase expansion caused the Si_3N_4 grains to lose grain to grain contact, creating space between them and reducing the continuous path throughout the sample, which will affect the mechanical properties and final thermal conductivity of the sample. The different effects of sintering Si_3N_4 with additives have been discussed by Klemm [79]. While some advanced sintering aids such as Lu_2O_3 and Sc_2O_3 were reported to allow for a superior temperature resistance due to crystallization of the grain boundary phase, others such as Al_2O_3 were found to be problematic due to low eutectics [110, 61, 106, 26]. Al^{3+} ions presence will allow for the formation of a soft oxidation layer and important oxygen diffusion into the silicon nitride causing degraded fracture behavior and poor oxidation resistance at high temperatures [80].

Grain boundary sliding would be expected to become pronounced in Si_3N_4 above 15 dpa at 500 °C due to the lack of structural integrity at the grain boundaries. Therefore, the observed hardness degradation (softening) of Si_3N_4 measured in this work for the higher doses and irradiation temperatures is considered to be an artifact due to the presence of the YAG phase's presence and is not representative of the intrinsic mechanical properties behavior of Si_3N_4 . Based on the microstructural observations at high temperatures and high doses, a moderate hardness increase compared to the unirradiated value would be expected even at 50 dpa, 700 °C for pure Si_3N_4 .

In general, consolidation of ceramics such as Si_3N_4 to a high fraction of its ideal density requires a sintering aid. Therefore, additional research is needed to identify a suitable sintering aid for Si_3N_4 that doesn't react poorly during irradiation. To support this point,

Tada et al. reported the Vickers microhardness of Si_3N_4 following neutron irradiation at 3.9 dpa ($3.9 \times 10^{25} \text{ n/m}^2$) and 680 °C as well as 55 dpa ($5.5 \times 10^{26} \text{ n/m}^2$) at 710 °C [146]. They observed a microhardness increase at both doses, 12 % at 3.9 dpa and 16 % at 55 dpa. While not knowing the possible additives in their commercial material (purchased from the Nikkato company), TEM micrographs did not reveal any nefarious behavior at grain boundaries, suggesting the absence of a YAG phase in their material. Results from their work matches the trend observed in our experiments at lower dose: We observed a 13 % hardness increase at 1 dpa and 700 °C (Fig. 5.6). Based on microstructural characterization of the Si_3N_4 , it is reasonable to assume that a similar hardness increase around 16 % would have been observed at 50 dpa and 700 °C if no sintering aid (or a suitably radiation-resistant one) would have been present. This speculated behavior is indicated by the dashed line in Figure 5.21.

Nanoindentation results demonstrated a good resistance to irradiation damage for ZrN. Both hardness and modulus exhibited a moderate increase (compared to unirradiated values) up to the highest tested condition of 50 dpa and 700 °C. No temperature effect was observed at medium to high dose while a greater hardness increase was observed at 300 and 500 °C at 1 dpa. Some work has been done in the past on unirradiated and irradiated ZrN using nanoindentation and has been discussed in the literature. Hardness evolution in irradiated samples has been reported between 20 to about 28 GPa in unirradiated and irradiated materials respectively [123, 165, 156, 14, 49, 48, 167]. Yang et al. discussed the microhardness change in proton irradiated ZrN at 1073 K [167]. They measured a 9.5 % increase at 0.35 dpa and 14.6 % increase at 0.75 dpa as well as a hardness recovery after annealing at 1673 K. They argued that most of the defects formed were point defects and unstable defect clusters that will self-annihilate rather than grow. Egeland et al. reported nanoindentation results on both hardness and modulus following 300 keV Xe ions irradiation at cryogenic temperature and at fluences varying from 1×10^{14} to $1 \times 10^{16} \text{ ions/cm}^2$ (0.9 dpa, 9 dpa, and 90 dpa) [48]. They noted an increase in hardness with a possible plateau being reached at higher dose as well as insignificant changes in modulus. Robertson conducted 4 MeV Au ion irradiations at room temperature to a fluence of $5 \times 10^{16} \text{ cm}^2$ (around 200 dpa at midrange) [123]. He revealed a nanohardness increase from 22 GPa (unirradiated) to 28

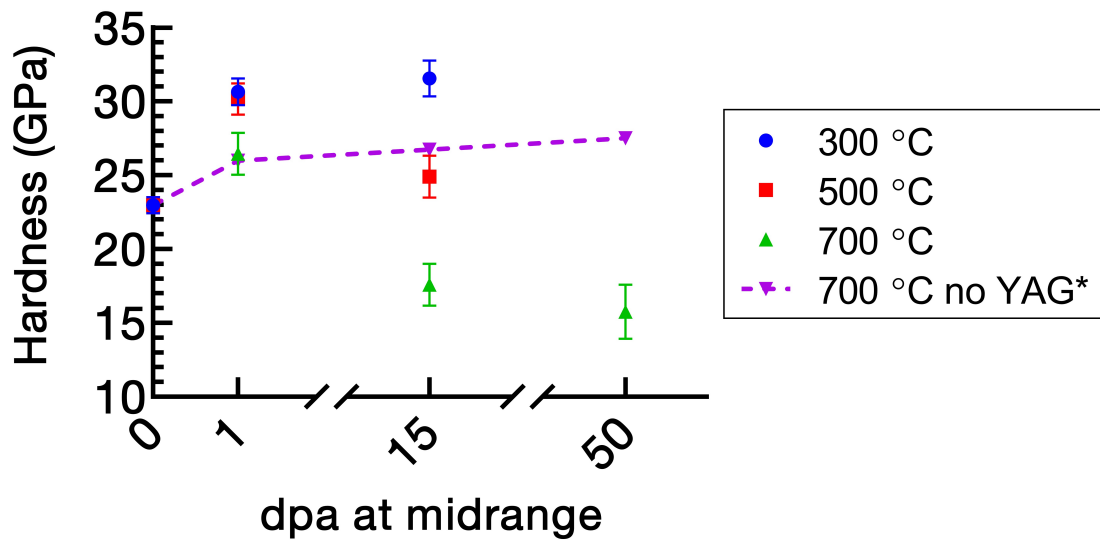


Figure 5.21: Experimental hardness evolution in ion irradiated Si_3N_4 and hypothetical 700 °C trendline without sintering aid failure.

GPa (irradiated) while Young’s modulus increased from 460 GPa (unirradiated) to 515 GPa (irradiated) in his zirconium nitride samples.

Our experiments agree closely with the general trends set by these findings and bring forth confirmative evidence of the behavior of ZrN above room temperature and up to 700 °C. A rapid hardness increase occurred at low dose and reached saturation by 20 dpa. At higher dose, from 50 dpa (this work) up to 200 dpa (Robertson’s [123]), no hardness drop can be detected, reinforcing the idea that the hardness increase is conserved with increasing dose. This rapid initial hardness increase can be linked to the formation and accumulation of point defects and defect clusters. This behavior contrasts with that of Si₃N₄ at mid to high dose and elevated temperatures, but that observed softening was attributed to the poor radiation stability of the sintering aid and not to any other effects such as its hcp crystal structure. No sintering aid was added to the ZrN powder, and no new phase was detected at grain boundaries post irradiation. While irradiated ZrN showed an increase in modulus compared to unirradiated material, very little change in modulus was measured between the different irradiation conditions (and reported in the literature: Young modulus stability under irradiation was expected due to its primary relation with crystal structure and atomic bonding and not with extrinsic defects [186, 48]). No phase change was also reported for ZrN, maintaining its fcc crystal structure with increasing temperature.

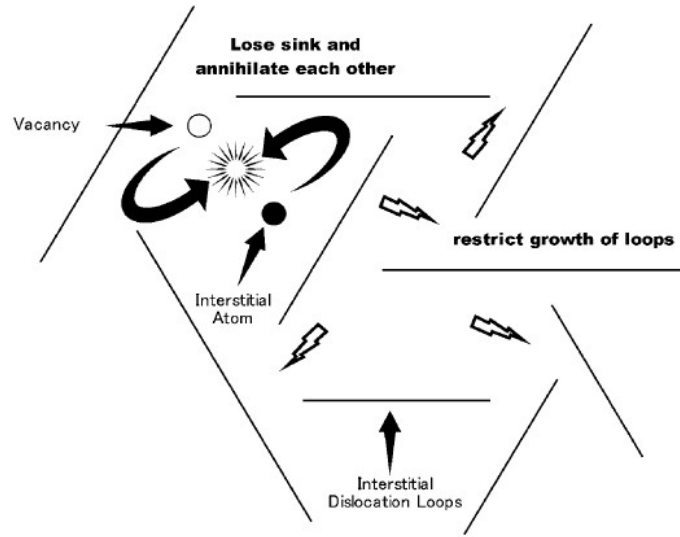
Several types of defects are induced during neutron irradiation in ceramic materials and can be replicated to an extent using ion irradiation. At low temperatures, Frenkel pairs and small point defect clusters are expected to be the predominant surviving defects (due to limited atomic mobility at low temperatures). The defect cluster number density should approach a saturation value after ≈ 0.1 to 1 dpa with a value that can be directly correlated with the point defect recombination radius. With increasing temperature, the higher mobility of point defects facilitates enhanced defect clustering and the formation of dislocation loops or voids (the latter occurring if vacancies are mobile). These dislocation loops are mostly found with habit planes corresponding to the closest-packed planes. Fine scale point defects were observed in our irradiated Si₃N₄ samples and isolated dislocation loops formed with increasing temperature. Overall defect cluster concentration in irradiated Si₃N₄ increased

with increasing dose and small defect clusters appeared prominently at 50 dpa while the dislocation loop number density seemed to be somehow restrained.

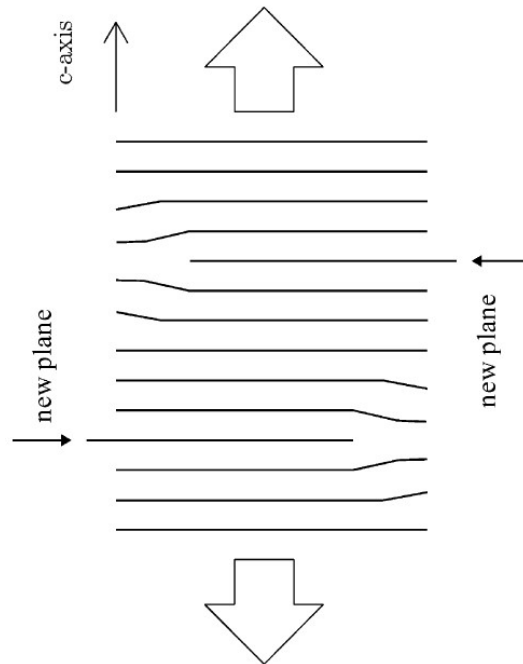
This behavior can be explained by having a closer look at the Si_3N_4 crystal structure and its close-packing planes. The atoms site can be described as multiples of about $1/12$ of the unit cell on the a-axis while SiN_4 tetrahedra are projected as equilateral triangles if we imagine the (0001) plane. The close-packed plane corresponds to $(10\bar{1}0)$ and interstitial dislocation loops are formed on it with a Burgers vector of $b = 1/6\langle 023 \rangle$ (extra layer of SiN_4 tetrahedra on the $(10\bar{1}0)$ plane). In the hexagonal lattice, the $(10\bar{1}0)$ plane family have three equivalent planes (rotated 60 and 120° from (100)). A second type of planar defect can also be found on the $(11\bar{2}0)$ planes (also having three equivalent planes) with a Burgers vector $b = 1/6\langle 223 \rangle$ [55]. Finally, these two types of defects never intersect, which limit dislocation loop growth and restrict the nucleation of new loops [9].

These dislocation loops were described by Akiyoshi et al., and they named this restrictive structure “nano-partition” [3]. A schematic reference is presented in Figure 5.22. This loop growth restriction will limit the amount of swelling generated from the material (as opposed to ceramics such as Al_2O_3 and AlN which allows for the c-axis to swell without constraints). As discussed by Akiyoshi and coworkers, the close packed plane for Al_2O_3 and AlN is the (0001) basal plane and interstitial dislocation loops are preferentially formed on it, and piling up in parallel as sketched in Figure 5.22. This structure does not limit loop growth and coalescence or loop formation, causing unrestrained swelling on the c-axis, which led to intergranular cracking.

Yano et al. observed small planar defects (below 4 nm) in Si_3N_4 at low dose and temperature (4 dpa, 377 °C) [173]. While temperature increase to 727 °C did not substantially modify the size of the defects, dose increase up to 37 dpa produced a higher number density on both $(10\bar{1}0)$ and $(11\bar{2}0)$ planes and interstitial-type dislocation loops were clearly resolvable. Tada et al. [146] observed interstitial type dislocation loops as well as small “black dot” defect clusters after neutron irradiation at 700 °C and 55 dpa for Si_3N_4 . All these previous observations are in general agreement with what was observed in ion irradiated Si_3N_4 during this work.



(a)



(b)

Figure 5.22: (a): Nano-partition schematic model in Si_3N_4 and (b): schematic of piled up dislocation formed on the (0001) plane in Al_2O_3 (Reproduced from Akiyoshi et al. [3]).

Defect formation in irradiated ZrN followed expected fcc ceramic behavior and was consistent with literature data on irradiated ZrN by Yang et al. and Bao et al. [14, 167]. Yang et al. [167] observed loops with an average size of 2.23 nm at 0.35 dpa and 800 °C after 2.8 MeV proton irradiation and observed loops with an average diameter of 2.35 nm at 0.75 dpa and 800 °C. Bao et al. irradiated ZrN samples using 4 MeV Au ions to a midrange dose of 200 dpa [14]. Their defect microstructure was described to be divided in four unique regions: the first two include dislocation lines, with very high density and hard to resolve near the surface and easily resolvable just below the near-surface region. The third layer is composed of a very high density of dislocations, and dislocation loops of around 50 nm in diameter can be observed at the boundary between the second and third layer as well as randomly distributed throughout. The final region includes no resolvable dislocations and showed a dark saturated contrast. Smaller (around 15 nm) loops can be seen past it close to the unirradiated region. Our experimental results, including defect type and dislocation loops details (compared in Figure 5.23) follow the same trend observed by these literature data. While our dislocation loop number density remained stable with increasing dose, the average loop size increased with increasing dose. As shown in the results section, the 1 dpa irradiations presented small indistinct loops and defect clusters between 5 to 7 nm in diameter.

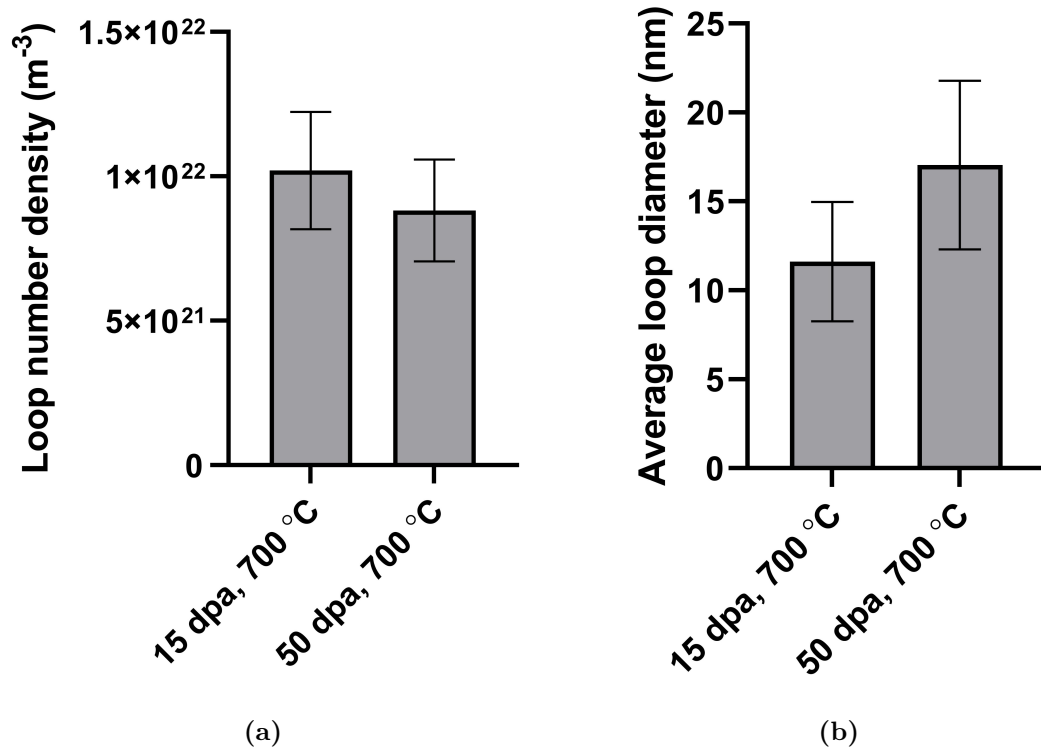


Figure 5.23: (a) Comparison of dislocation loop number density and (b) average dislocation loop diameter vs loop type for 15 and 50 dpa, 700 °C Ni ion irradiation in ZrN.

Chapter 6

Summary and Conclusions

The purpose behind this dissertation was to improve our fundamental understanding of irradiation effects in proposed ceramic materials for advanced nuclear fuels applications. The two studied concepts were the addition of a high thermal conductivity second phase (Al_2O_3 or SiC) to an UO_2 surrogate matrix and nitride ceramics (Si_3N_4 and ZrN). 15 to 20 MeV Ni ion irradiation was used to irradiate the materials, and several characterization techniques were performed to quantify their stability post irradiation.

Composite surrogate fuels were successfully sintered, and high sintered densities were achieved (around 95 % of ideal density). Moreover, thermal conductivity increase due to the inclusion of second phase additives was demonstrated using laser flash analysis: 42 % increase was measured in $\text{CeO}_2/\text{Al}_2\text{O}_3$ composites from 100 to 900 °C and 192 % (at 50 °C) to 50 % (at 900 °C) was measured in ZrO_2/SiC composites. The different sintering techniques used during this work helped demonstrate the important differences in sintering behavior in surrogate materials vs UO_2 . While UO_2/SiC composites have been successfully sintered in the past, issues arose when SiC was sintered with CeO_2 . Chemical compatibility issues were observed and attributed to the Red/Ox differences between lanthanide vs actinide elements and were observed as low as 1150 °C. A ZrO_2 matrix was chosen instead to study the properties of a SiC composite surrogate fuel. Despite promising literature work presenting the measurements of the thermal conductivity in ion irradiated layers, both transient grating spectroscopy and modulated thermorefectance failed to present decisive results. No signal was obtained via thermorefectance, suggesting technique limitations

when used on composite samples with similar particle size. Modulated thermorefectance produced a readable signal but the postprocessing of those data was far off the expected trends, which was also attributed to the particle size and composite aspect of the material. Both composite surrogates appeared to be stable at temperatures between 300 and 700 °C following ion irradiation up to 5 dpa. At 15 dpa, a pronounced decrease of their mechanical properties was witnessed. While a softening of the matrix could reduce fuel-clad mechanical interaction, the observed deterioration of the mechanical properties at 15 dpa raised some concerns towards the viability of these high thermal conductivity fuel forms. Additionally, the $\text{CeO}_2/\text{Al}_2\text{O}_3$ composite presented a unique surface reaction at 15 dpa, where rounded dents and intergranular scale-like protrusions were seen covering all of the CeO_2 grains. The reason behind this formation remains unknown at the moment. One of the questions behind hcp-based additives was whether or not microcracks will be induced at grain boundaries after irradiation due to anisotropic swelling in the hcp phase. Modeling followed by experimental observations were able to confirm the absence of cracks at the matrix/additive interface, suggesting that particles less than 15 micrometers in diameter were sufficiently small to prevent crack formation. However, aligned and clustered dislocation lines were observed in the matrix grains, perpendicular to the second phase grains, which may be evidence of high stresses in the matrix when adjacent to the second phase material.

Based on these experimental results and conclusions drawn here, the following recommendations are made for future research based on composite nuclear fuel including a high thermal conductivity second phase:

- Additional post irradiation characterization should be conducted on UO_2 -based composites, to further study matrix/interface behaviors and to avoid surrogate-based reactions during sintering.
- Information on the stability of these composite fuels to fission track damage and fission product recoil implantation as well as their impact on structural and properties changes up to around 1000 dpa will also be needed. Precipitation/segregation could be observed at the interface, which would greatly reduce the overall thermal conductivity of the fuel.
- Improvement of laser-based techniques to determine the thermal conductivity of ion irradiated layers should be pursued. Both transient grating spectroscopy and modulated

thermoreflectance showed promise towards thermal conductivity determination in metals, single crystals, and simple ceramic materials. Yet, this work has showed their limitations around more complicated samples such as multiphase composite materials.

The ion irradiation studies of silicon nitride and zirconium nitride allowed us to fill a gap in the literature as well as to bring forth some interesting behavior that will help shape future research based on these ceramics. Modulated thermoreflectance was successfully used to determine the thermal conductivity evolution of both Si_3N_4 and ZrN before and after irradiation. Results were coherent with literature data, where a decrease in thermal diffusivity with increasing dose up to a saturation value (not reached in this work) can be seen as well as a thermal diffusivity with increasing temperatures. The mechanical properties of Si_3N_4 showed improvement up to 15 dpa and 500 °C. At higher dose and temperatures (up to 50 dpa and 700 °C) an important drop was witnessed, associated with the failure of the YAG sintering aid during high temperature, high dose irradiation, preferentially located at grain boundaries. The overall defect resistance of the Si_3N_4 grains combined with literature work indicating no drop in hardness up to similar dose and temperatures would suggest that no negative behavior would be observed in Si_3N_4 without sintering aid or when using a sintering aid with better radiation resistance. Si_3N_4 showed an 36 % increase in both hardness and modulus at 1 dpa and 300 °C while showing around 16 % increase at 50 dpa and 700 °C (simulated value for Si_3N_4 according to literature results). TEM characterization of the microstructure confirmed the failure of the sintering aid (YAG) at 15 dpa and 500 °C where important cavity formation occurred as well as presence of grain boundary delamination, sparsely present at 15 dpa and 700 °C and more visible at 50 dpa and 700 °C. Meanwhile, ZrN showed no unexpected behavior at grain boundaries, and defects evolution matched typical literature knowledge on fcc based ceramics. The necessity of using a sintering aid resistant to radiation at high temperature or no sintering aid at all was reinforced by these observations. Swelling evolution presented both expected and unexpected results. Lattice swelling showed a consistent behavior at low dose, decreasing with increasing temperature but both ceramics displayed a unique behavior at 700 °C. Si_3N_4 irradiated at 50 dpa showed a large lattice swelling increase up to 0.55 % where a saturation value around 0.22 % was expected. ZrN

revealed an increase in lattice swelling with increasing dose at 700 °C, without showing a saturation behavior, up to 50 dpa. Monotonic swelling decrease with increasing irradiation temperature at low dose proved that vacancy migration on the cation or anion sublattice may not occur until temperatures approaching 700 °C. Radiation enhanced diffusion of the implanted nickel ions into the midrange region could contribute to lattice parameter increase and therefore needs to be further evaluated. Finally, a high density of small cavities was observed in both materials, across the entirety of the irradiated region, and under all irradiation conditions. A slight coarsening was observed above 15 dpa (1.5 to 2 nm diameter) and cavity swelling increased with increasing dose (from 0.05 to 0.08 % in Si₃N₄; from 0.06 to 0.16 % in ZrN). No cavities have been previously reported to form in Si₃N₄ and ZrN under neutron or conventional non-gaseous ion irradiation, and cavity formation in ceramics is unusual below 0.2 to 0.3 Tm. Ionization enhanced radiolysis is a potential reason for the formation of these cavities, where freed nitrogen atoms would stabilize cavity formation. Overall, swelling behavior in silicon nitride and zirconium nitride was dominated by lattice swelling and while void swelling was observed to be about two times higher at 700 °C for ZrN, the origin of the observed cavity formation remains mostly unsolved. Despite silicon nitride showing some promising results, it appeared that some limitations were encountered above 15 dpa and 500 °C. When combined with potential effects from its anisotropic crystal structure and its overall lower melting temperature (1900 °C), zirconium nitride would be the recommended ceramic to further investigate in the future for high temperature applications.

From these conclusions, the following propositions were created to orient potential future research on nitride ceramics:

- Unexplained cavities were formed following Ni ion irradiation, and their origin remained unproven. Follow up irradiation work could be conducted to determine the origin of these cavity formation and see if they are nucleating due to possible radiolysis behavior.
- Irradiation studies designed around CVD materials would allow for more in-depth studies designed for coated fuels application.
- Stability of these materials following ion implantation at elevated temperatures could help determine the behavior of fission fragments and their impact on properties evolution.

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Vita

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He was able to conduct an internship at the Oak Ridge National Laboratory (ORNL) through the Advanced Short-Term Research Opportunity (ASTRO) program where he worked on the determination of the thermodynamic properties of francium and continued this research through the Post-Master's Research Associate program.

His passion for research led him to the University of Tennessee, Knoxville, where he was able to complete his Doctor of Philosophy degree through The Bredesen Center for Interdisciplinary Research and Graduate Education.

Mentored by Dr. Steven Zinkle, his work was focused on ion irradiation studies for the developement of advanced nuclear fuels, specifically high thermal conductivity nuclear fuel surrogates and nitride ceramics (Si_3N_4 and ZrN).

He will be working on nuclear fuels R&D as a postdoc at Los Alamos National Laboratory (LANL) starting Fall 2021.