

Ion Irradiation Characterization Studies of MAX Phase Ceramics

A Thesis Presented for the
Master of Science
Degree

The University of Tennessee, Knoxville

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December 2015

ACKNOWLEDGEMENTS

First and foremost I would like to thank my advisor Dr. Steven Zinkle for lending me his knowledge and authority, without which none of this research would have been remotely possible. I would also like to thank him for all that he has taught me in the field of Radiation Effects in Materials and his constant encouragement throughout my time here at the University of Tennessee.

Next I would also like to thank my major collaborators, starting with Darin Tallman from Drexel University for supplying relatively pure, pre-synthesized MAX phase materials, thus providing the foundation upon which this research was made possible. I would also like to thank Dr. Yanwen Zhang and Miguel Crespillo from the University of Tennessee's Ion Beam Materials Laboratory as well as Dr. Lin Shao from Texas A&M Universities Ion Beam Laboratory for their help in performing ion irradiations. Next, I would like to thank both Dr. Maulik Patel from the University of Tennessee and Dr. Chad Parish from Oak Ridge National Laboratory for their direct and significant contributions to X-Ray Diffraction and Transmission Electron Microscopy analysis of the ion irradiated MAX phase samples. I would also like to thank Dr. N.A.P. Kiran Kumar from Oak Ridge National Laboratory for his help creating TEM cross-section foils and Congyi Li from the University of Tennessee for his help analyzing Nano-indentation data.

Next I would like to thank all those who help facilitate my training and use of experimental facilities at both the University of Tennessee and Oak Ridge National Laboratory. This includes Dr. Keith Leonard, Dr. Yutai Katoh, Dr. Maxim Gussev, and Dr. John Dunlap.

Finally, I would like to thank the United States Department of Energy's Office of Fusion Energy Sciences for their research funding through Oak Ridge National Laboratory's "Structural Materials of Potentially Unique Irradiation Resistance" field work proposal ERAT754 as well as the Department of Nuclear

Engineering's sponsorship of my academic career at the University of Tennessee.

ABSTRACT

The family of layered carbides and nitrides known as MAX phase ceramics combine many attractive properties of both ceramics and metals due to their nanolaminate crystal structure and are promising potential candidates for application in future nuclear reactors. This thesis reports on the background, design, and analysis of an experiment focused on determining the effects of energetic heavy ion irradiations on polycrystalline samples of titanium silicon carbide 312, titanium aluminum carbide 312, and titanium aluminum carbide 211. The irradiation conditions consisted of ion doses between 10 and 30 displacements per atom at temperatures of 400 and 700 degrees Celsius, conditions relevant to application in future nuclear reactors, and a relatively unexplored regime for this new class of materials known as the MAX phase. Following irradiation, a comprehensive analysis of radiation response properties was compiled using X-ray diffraction, nanoindentation, scanning electron microscopy, and transmission electron microscopy. In all cases, the materials remain fully crystalline though atomic collisions induce significant damage and disorder into the layered crystalline lattice. X-ray diffraction and nanoindentation show this damage is manifest in anisotropic swelling and hardening at all conditions and in all materials, with the aluminum based MAX phase exhibiting significantly more damage than their silicon counterpart. In all three materials there is little damage dependence on dose, suggesting saturation of radiation damage at levels below 10 displacements per atom, and a high correlation between residual damage and irradiation temperature, with significantly less damage at higher temperatures, suggesting radiation defect annealing. SEM surface analysis showed significant grain boundary cracking and loss of damage tolerance properties in the aluminum based MAX phase irradiated at 400 degrees Celsius, but not in the silicon counterpart. TEM analysis of select samples suggest that interstitials are highly mobile while vacancies are immobile and that all three materials are in the so-called point defect swelling regime

between 400 and 700 degrees Celsius. All results are consistent with previous work involving traditional and MAX phase ceramics. Results show that the aluminum MAX phase are not fit for application near 400 degrees Celsius and that the silicon MAX phase is overall more damage tolerant.

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1 Introduction

The family of layered carbides and nitrides known as MAX phases combine many attractive properties of both ceramics and metals due to their structure, which combines “ceramic” octahedra with intercalated “metallic” layers. It is therefore proposed that this unique combination of pseudo-metallic bonding makes the MAX phases very promising potential candidates for application under extreme radiation conditions. However, the outstanding mechanical properties of the MAX phases are related to their layered microstructure, and as such could be impacted significantly by irradiation. This chapter will discuss the background and motivation for examining the irradiation stability of MAX phase ceramics, analyze the structure and property that makes the MAX phases such a unique family of materials, and provide the goals and outline of this thesis.

1.1 Background and Motivation

Nuclear power currently provides about 18% of the United States’ electrical power, and although it has emerged as a reliable base-load source of electricity, many areas of potential improvement remain. One of the largest technical challenges is with respect to materials. The materials used in existing nuclear reactors provide the basis for and greatly influence the reliability, safety, and economics of these reactors. Power up-rates, reactor lifetime extensions, and fuel integrity are but a few specific examples that are directly affected by material concerns. Material challenges are also expected to be major roadblocks to the development of future fission (Generation IV) reactors and fusion reactors, which generally require materials to reliably operate at higher temperatures and/or radiation damage levels compared to existing water-cooled commercial power reactors. Due to this, there is a renewed interest in advanced and innovative nuclear materials research. A graphic comparing operating temperatures and lifetime doses for different reactor types can be seen in Fig. 1.1.

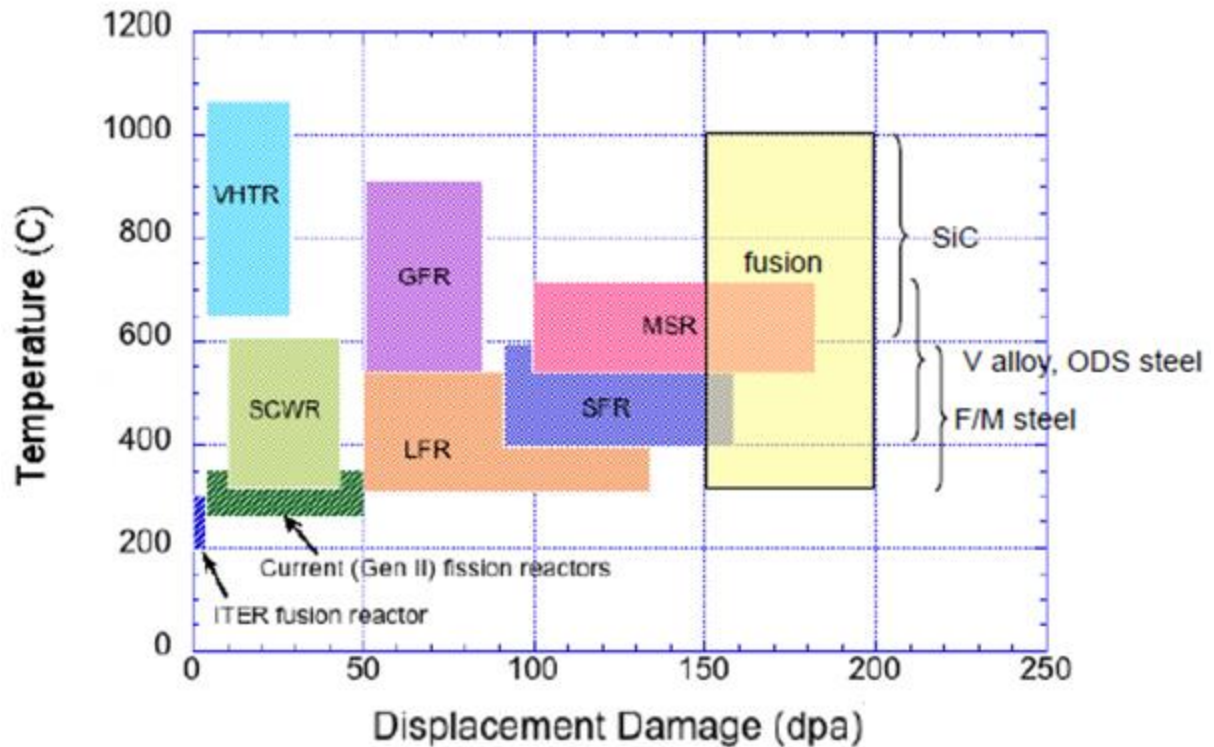


Figure 1.1 Comparison of Generation II, Generation IV, and fusion structural materials environments [1].

A promising but as yet unproven branch of this new materials research involves the class of material known as MAX Phase Ceramics (or simply MAX Phases), a relatively new class of solid best described as *thermodynamically stable nanolaminates*. First stumbled up on in the 1990's, MAX Phases are considered a relatively new family of material, with new subsets still being discovered. While most of the common MAX Phase material properties have been documented, very little is known about the MAX Phases behavior in a reactor environment, especially at high doses and temperatures. Although there has been recent increased interest in irradiation characterization experiments, many of which have begun to show the promise of the MAX Phases with respect to damage tolerance, there is still a large information gap that needs to be filled before MAX Phases are ready for application in nuclear energy systems.

1.2 Structure

The class of material known as MAX Phase [2-4] is a family of layered compounds with chemical formula $M_{n+1}AX_n$, where M is an early transition metal, A is an element from the IIIA-VIA groups, X is carbon or nitrogen, and $n = 1, 2$, or 3. They consist of layered hexagonal crystal structure, of the space group P63/mmc, with two formulas per unit cell. In each case, there are two types of alternating layers. The first layer unit is a near close-packed layer of M-atoms with X-atoms filling octahedral sites, comprising a formula which is identical to those found in the rock salt structure of MX binaries. These octahedral layers alternate with layers of pure A-group elements which are located at the center of trigonal prisms. These sites are larger than the octahedral sites, and thus better able to accommodate the larger A-atoms. A schematic of three types of stoichiometric unit cells, along with a depiction of the M, A, and X elements, can be seen in Fig. 1.2. When $n = 1$, the A-layers are separated by two M-layers (Fig. 1.2(a)). When $n=2$, they are separated by three layers (Fig. 1.2(b)). When $n = 3$, they are separated by four layers (Fig. 1.2 (c)). MAX phases with more complex stacking sequences, such as M_5AX_4 , M_6AX_5 , and M_7AX_6 have also been reported.

In addition to the “pure” MAX phases that contain one of each of the M, A, and X elements, there are solid solutions that can replace individual atom sites. These include M site substitutions such as $(Nb,Zr)_2AlC$ and $(Ti,V)_2AlC$, A-site substitutions such as $Ti_3(Si,Ge)C_2$ and $Ti_3(Sn,Al)C_2$, and X-site substitutions such as $Ti_2Al(C,N)$ and $Ti_3Al(C,N)_2$. In addition, some of the solid solutions exist even when one of the end members do not. The number of MAX phases and their solid solution continues to expand through experimental and theoretical density functional theory (DFT) approaches. These approaches have revealed several useful trends about MAX phase materials that have led to a better understanding of their unique features. They have shown that (a) the bonding in MAX phases is a combination of metallic, covalent, and ionic bonding, (b) M and

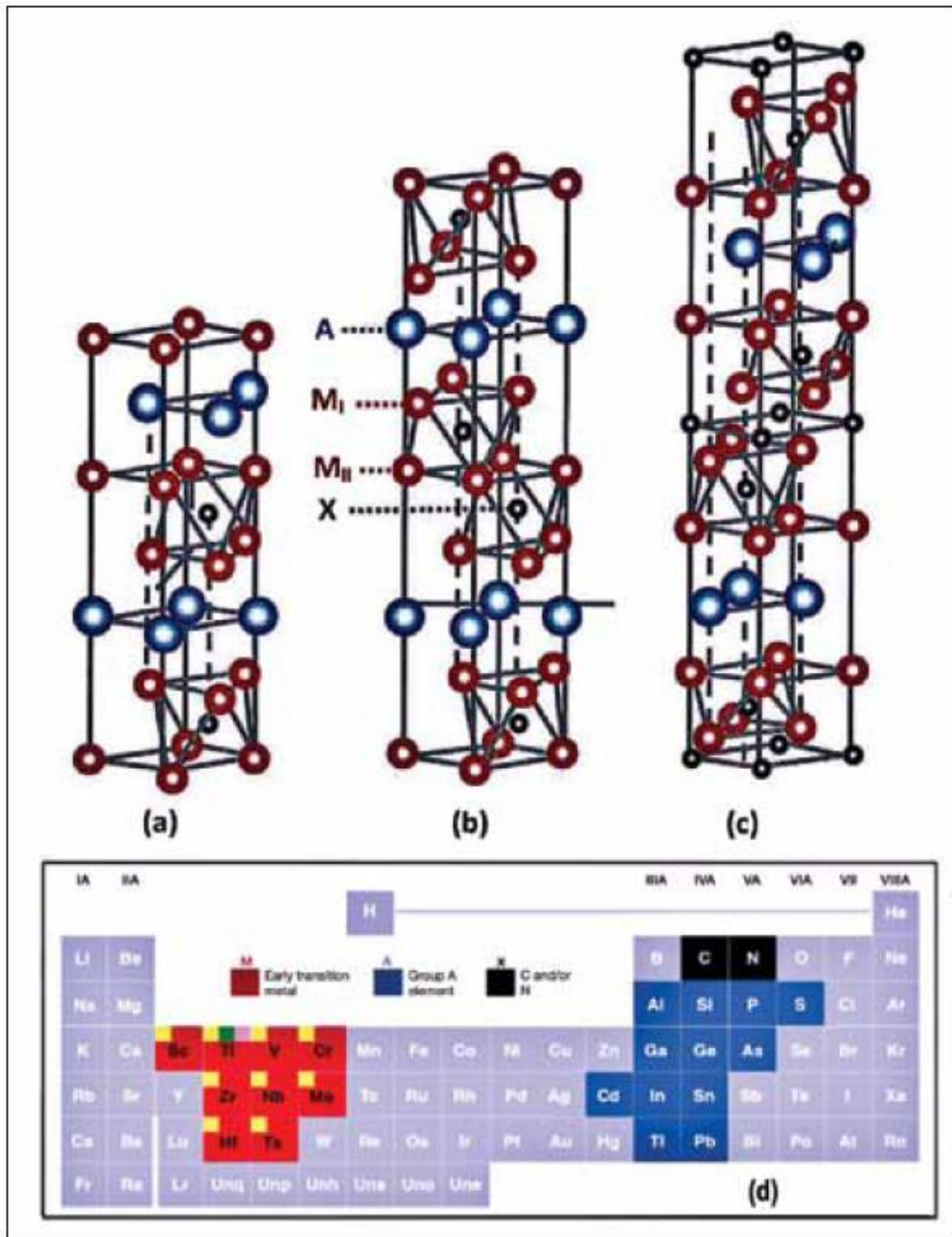


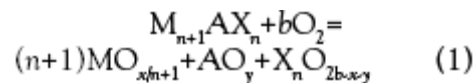
Figure 1.2 Unit cells of the MAX phases for (a) $n=1$, (b) $n=2$, and (c) $n=3$, and (d) M, A, and X elements that form the MAX phases [4].

X atoms form strong direction covalent bonds in the M-X layers that are comparable to those in the MX binaries, (c) M-d-M-d metallic bonding dominates the electronic density of states at the Fermi level, and (d) in most MAX phases, the M-A bonds are relatively weaker than the M-X bonds. Given the similarities in bonding between the MAX phases, and subsequently both the MX phases and traditional metals, it is not surprising that they combine many favorable properties into a single material [2-4].

1.3 Properties

Chemically, electrically, and thermally, MAX phases share many of the advantageous attributes of their respective stoichiometric binary metal carbides or nitrides: they are chemically stable up to high temperatures, and exhibit relatively high electrical and thermal conductivity.

Like traditional ceramics, many MAX phases are thermodynamically stable in inert atmospheres up to at least 1500° C, with some, such as Ti₃SiC₂, having decomposition temperatures upwards of 2300° C. At temperatures high enough for decomposition, phases do not melt congruently, but decompose peritectically into A-rich liquids, higher *n*-containing MAX phases and/or M_{n+1}X_n carbides or nitrides. However, as expected, the MAX phases' stability in corrosive environment depends on many variables. For instance, when exposed to oxidizing environments at high temperatures, the MAX phases oxidize according to Eq. (1) [4, 5].



Consequently, their oxidation resistance depends on the nature of the oxides formed, which is inherently dependent on the chemistry of the MAX phase itself. For example, the most oxidation-resistant MAX phase is Ti₂AlC because it forms a stable protective Al₂O₃ layer that can withstand thermal cycling up to 1350° C for 10,000 cycles without spallation or cracking. In addition, other MAX phases

(such as Ti_3SiC_2 , Ti_2AlC , and Ti_3AlC_2) have been found to have excellent corrosion resistance in acids, alkali liquids, and molten lead.

Electrically, most of the MAX phases are excellent conductors, with the majority of the electrical resistivities falling in the range of $0.2\text{--}0.7\ \mu\Omega\cdot\text{m}$ at room temperature. Like other metallic conductors, the resistivities of the MAX phases tend to increase with increasing temperature (Fig. 1.3(a)). Some MAX phases, such as Ti_3SiC_2 and Ti_3AlC_2 are actually better conductors than the M-atom metal alone (in this case titanium).

Thermally, the MAX phases behave similarly to their MX counterparts, namely they are good thermal conductors, due to their being good electrical conductors. At room temperatures their thermal conductivities fall in the range of $12\text{--}60\ \text{W}/(\text{m}\cdot\text{K})$ (Fig. 1.3(b)). The typical MAX phase coefficient of thermal expansion falls in the range of $5\text{--}10\ \mu\text{K}^{-1}$, a relatively low value that is typical for a refractory solid.

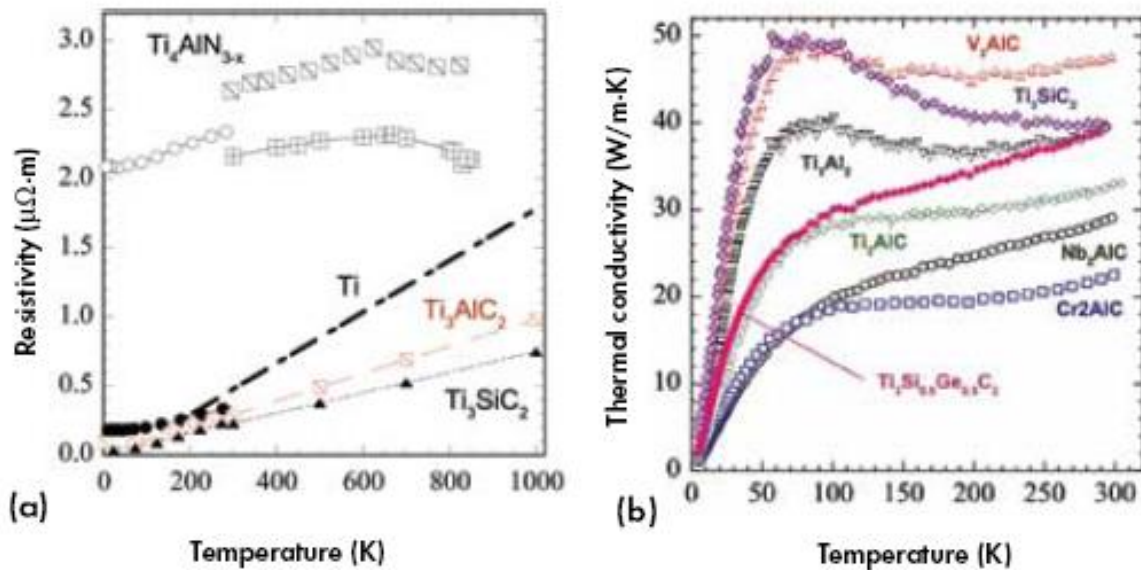


Figure 1.3 Temperature dependence of (a) electrical resistivity and (b) thermal conductivity of select MAX phases [4].

Despite the similarities in physical properties stated above, the MX and MAX phases are strikingly different with regards to mechanical properties. While the MX phases are generally regarded as some of the hardest solids known, they have a few key weaknesses. They are brittle, non-machinable, damage intolerant, and susceptible to thermal shock. In sharp contrast, the MAX phases are able to retain the majority of the MX's stiffness while also being relatively soft, exceedingly damage tolerant and thermal shock resistant, and most are readily machinable. The Vickers hardness of polycrystalline MAX phases fall in the range of 2-8 GPa, making them softer than most structural ceramics yet harder than most metals. The room temperature fracture toughness values range from 5 to 20 MPa·m^{1/2} and are similar to those of relatively tough ceramics but well below typical values for metals. The MAX phase also exhibit *R*-curve behavior, in which the fracture toughness increases with crack length, due to the formation of plastically deformable bridging ligaments and the crack-arresting properties of kink bands (mechanisms unique to MAX phases). Additionally, unlike ceramics, MAX phases do not shatter after quenching. Finally, one of the MAX phases' best characteristic traits setting them apart from the MX phases or other high-temperature alloys is the ease with which they can be machined. The MAX phases can be machined using high-speed tool bits with little to no lubrication or cooling required. In addition, thick films can also be produced through traditional thermal spray methods.

The stark difference between the MX and MAX phases comes down to the MAX phases' ability to facilitate mobile dislocations. Dislocations multiply and are mobile at room temperature, but glide exclusively on the basal planes, which results in a fewer number of slip systems than is needed for polycrystalline ductility (which requires five). For this reason, the MAX phases are pseudo-ductile under confined deformations/high temperature, but are brittle at room temperature, thus representing a compromise between metals and ceramics [2-4, 6].

1.4 Potential Application

Due to the MAX phases' unique combination of high temperature stability, stiffness, conductivity, corrosion resistance, machinability, and possible radiation tolerance, they are currently being considered as a possible advanced nuclear material for a variety of applications, including current generation fission light water reactors (LWRs), future generation (Gen. IV) fission, and proposed fusion reactors. Proposed applications include; oxidation-resistant spray-on coating for cladding, piping, and steam generator tubes in current LWR systems, structural material piping and core internals in advanced fission reactors due to high chemical compatibility with select coolants such as molten lead and sodium, high temperature, high dose cladding material for future generation fission reactors, and high temperature, high dose structural materials for future generation fission and fusion reactor systems. These are but a few of the numerous application possibilities for this highly versatile family of materials in an industry that is continually pressing the limits of material science [7, 8].

1.5 Research Goals

The purpose of this thesis was to characterize the radiation resistance of several leading-candidate MAX Phase materials using modern ion beam irradiation techniques. The experiment focused on three MAX Phase materials, Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC , which are three of the most characterized and readily available MAX Phase materials to date. The experimental set up and procedure were designed to ensure that the temperatures and doses were highly reliable, thus ensuring the authenticity of the results. The experiment was conducted at multiple temperatures and doses so as to better help quantify the damage tolerance of the three specific MAX Phase materials as well as establish trends of the MAX Phase material type. These trends include the effects of varying A atoms and stoichiometry (varying n) on radiation tolerance and the effect of temperature on self-healing/ damage resistance, both of which are

paramount in helping identify other MAX Phase material candidates and shape the path for future research. It is hoped that this thesis has helped to fill an important void and to gain a better fundamental understanding of MAX Phase damage tolerance in nuclear reactor environments.

1.6 Thesis Outline

This thesis consists of eight chapters including necessary background and motivation in Chapter 1. Chapter 2 provides a brief introduction to the theory and mechanisms of radiation effects in materials. Chapter 3 introduces prior work conducted on radiation response in MAX phase ceramics. Chapter 4 discusses the experimental design of the ion irradiations completed for this thesis. Chapter 5 provides a brief summary of the analytical techniques used on irradiated samples. The results of these analytical techniques are provided in Chapter 6. Chapter 7 provides discussion and conclusions of these research efforts, and finally, Chapter 8 provides recommendations for future research interests.

2 Radiation Effects in Materials

The purpose of this chapter is to provide a brief background for understanding the theory and mechanisms discussed in this thesis as they pertain to the effects of radiation on materials. Some of the most profound effects of irradiation on materials occur in the core of nuclear power reactors, arguably the most extreme irradiation environments that exist on earth. These effects stem from the numerous atomic displacements suffered by components during their engineering lifetimes in radiation environments. As reactor lifetimes continue to increase and proposed fission/fusion reactor designs push the limit in material requirements, a firm understanding of the effects of radiation on materials is required now, more than ever, to create new, more radiation-tolerant materials. This chapter will briefly discuss the creation and quantification of radiation damage, the effects radiation has on microstructure, and the physical and mechanical effects of radiation damage as they pertain to this thesis.

2.1 Creation and Quantification of Radiation Damage

2.1.1 The Radiation Damage Event

On an atomistic level, radiation damage is defined as the transfer of energy from an incident projectile into a solid and the resulting distribution of target atoms following the loss of energy. The result of radiation damage is the creation of a collection of point defects (vacancies and interstitials) and the defect clusters they form in the crystalline lattice. Subsequent events involving the migration and clustering or dissolution of the point defects and defect clusters are classified as radiation damage processes. These atomistic changes in turn can exert pronounced effects on macroscopic physical and mechanical properties. However, before the response of a material to radiation can be examined, it is important to understand and quantify radiation damage, or how an energetic

particle interacts with a solid and produces said defects. The sequential process by which radiation damages a crystalline material is as follows:

1. The interaction of an energetic incident particle with lattice atoms.
2. The transfer of kinetic energy to the lattice atom, giving birth to a primary knock-on atom (PKA).
3. The displacement of the atom from its lattice site (creating a vacancy).
4. The passage of the displaced atom through the lattice and the accompanying creation of additional knock-on atoms.
5. The production of a displacement cascade (collection of point defects created by the PKA).
6. The termination of the PKA as an interstitial, i.e. the atom comes to rest in the interstices between normal lattice sites.

Though all radiation types can impart nuclear damage as described above, it is important to note that the consistency in which that damage is imparted differs significantly between irradiation types. When developing irradiation resistant materials for use in nuclear reactor environments, the key focus is the interaction of energetic neutrons in solids, and by virtue of that process as described above, the interaction of energetic ions in solids, therefore those will be the focus of this discussion. Due to their electrical neutrality, energetic neutrons have relatively large ranges in solids, with a finite probability that they will undergo elastic collisions with nuclei in the solid, leading to the creation of a PKA. In stark contrast, energetic ions, such as PKA's, lose energy via electronic excitation in addition to relatively frequent elastic collisions when traveling through a solid. This, in conjunction with the increased elastic interaction probability, results in a relatively short range in solid materials for ions when compared to neutrons. For the same energy, ions with heavier masses deposit their energy over shorter distances, resulting in higher damage rates while neutrons have low damage rates constant over a large distance. A visual representation of damage rates versus penetration depth for energetic neutrons and ions can be seen in Fig. 2.1 [9, 10].

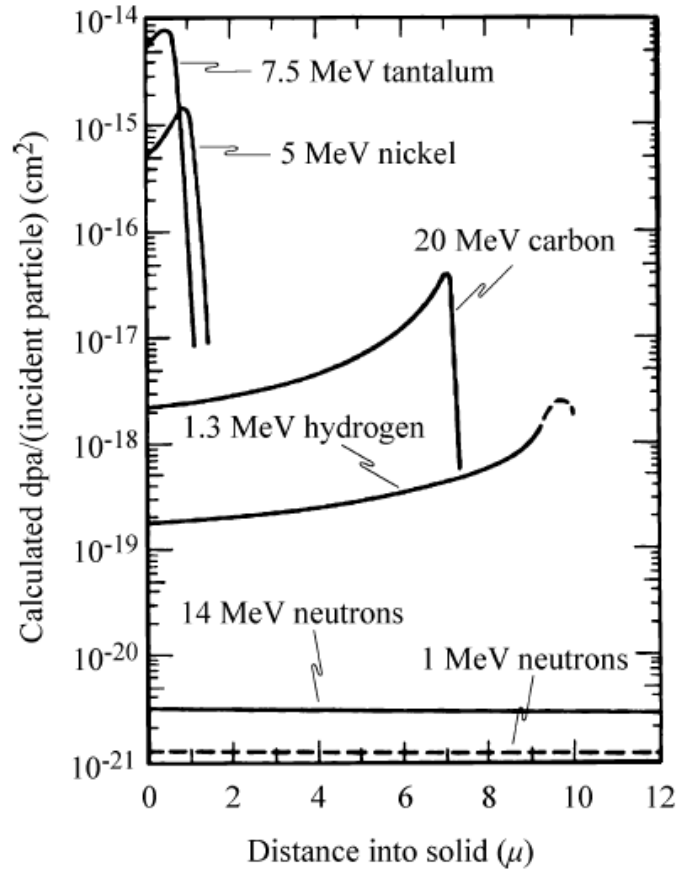


Figure 2.1 Displacement-damage effectiveness for various energetic particles in nickel [9].

2.1.2 Quantification of Radiation Damage

When quantifying radiation damage, the ultimate goal is to be able to accurately correlate and predict material response properties to specific amounts of damage. In doing this, it is often useful to determine the number of vacancies and interstitials produced by an incoming projectile. This quantitative number is termed displacements per atom, or dpa, and is typically a complicated function dependent on the irradiation interaction cross-sections, energy, and flux. Due to the fact that it incorporates many parameters of the irradiation, the calculated number of displaced atoms is often an improvement over other comparative units, such as neutron or ion fluence.

Various models have been proposed to compute the total number of atomic displacements by a given irradiation type as a function of PKA energy. The most widely cited model is that based on a model proposed by Kinchin and Pease, which assumed that between a specified threshold energy and an upper energy cut-off, there was a linear relationship between the number of Frenkel pairs produced and the PKA energy. Below the threshold, no new displacements would be produced, and above the high energy cut-off, it was assumed that the additional energy was dissipated in electronic excitation and ionization [11]. Later, Lindhard and co-workers developed a detailed theory for energy partitioning that could be used to compute the fraction of the PKA energy that was dissipated in the nuclear system in elastic collisions and in electronic losses [12]. This work was used by Norgett, Robinson, and Torrens (NRT) to develop a secondary displacement model that is still used as a standard in the nuclear industry and elsewhere to compute atomic displacements [13]. The number of displacements per atom, ν_{NRT} , is proportional to the damage energy, T_{dam} , or the fraction of PKA energy that is deposited in elastic collisions and the displacement threshold energy, E_d , or the energy required to create a stable Frenkel pair. This can be seen in Eq. (2).

$$\nu_{NRT} = 0.8 \cdot T_{dam} / 2 \cdot E_d \quad (2)$$

It is important to note that the Norgett, Robinson, and Torrens model has some significant limitation, the most important of which is that it does not account for anything other than total initial atomic displacements (e.g. no information on in cascade formation of point defect clusters and recombination or subsequent microstructural evolution). Additionally, it does not take into account transmutation production or synergistic effects due to ionization.

As with most physical processes, radiation damage cannot be treated as a black box, concluding with the calculation of total number of displacements per atom. Rather, to fully understand the effect of damage on the properties, the evolution of the defects after they are formed must be understood, and is the subject of the next section [9, 10].

2.2 Evolution of Radiation Defects

Even in the absence of irradiation, a crystal cannot exist in a state of absolute perfection. Statistically, there is a finite probability that sufficient energy will be concentrated, by local fluctuations, to form a defect in the crystal lattice. And even as there are point defects inherent in crystalline materials, both atoms in a lattice and defects in the material are in a constant state of motion due to thermal vibration. The random nature of this thermal vibration gives rise to random walk of the atoms via the defects that are in thermal equilibrium with their surroundings. This is known as self-diffusion.

When considering radiation damage, it is the actual number of defects that survive the displacement cascade and their spatial distribution in the solid that will determine the effect of irradiation on the microstructure. Shortly following the initial energetic displacement cascades due to irradiation, there are a number of time dependent defect annihilation stages, including spontaneous recombination, close-pair recombination, and intracascade recombination. Spontaneous and close pair recombination occur when vacancies and interstitials are created in close vicinity to each other in the displacement cascade and are responsible for defect production saturation at increasing doses due to cascade overlap. These effects are relatively temperature independent and do not play a large role in radiation response differences between materials. Following these short order events multiple thermally activated processes can occur, including intracascade (correlated) recombination, intercascade (uncorrelated) recombination, and self-clustering of vacancy and interstitial defects, together providing the basis for radiation response in materials. These long-order defect evolution processes, based on self-diffusion, form the foundation for all observed effects of irradiation on the physical and mechanical properties of materials.

Once created, defects can either be annihilated or react to form larger clusters. They will either grow by absorption of defects of the same type, or shrink/disappear by absorption of defects of the opposite type. The

concentrations of these defects (vacancies and interstitials) in solids are determined by equating the rates of defect production and removal by all mechanisms, providing the basis for radiation response. There are five major, temperature dependent defect recovery states observed in materials following irradiation near absolute zero [9, 10]. They play the dominant role in determining defect concentrations and properties in materials and are as follows.

Self-interstitial atom (SIA) migration.

Migration of SIA-impurity complexes and SIA clusters.

Monovacancy migration.

Migration of vacancy-impurity complexes.

Thermal dissociation of vacancy clusters.

The two most pronounced and physically important recovery stages are Stage I (onset for interstitial migration) and Stage III (onset for vacancy migration). A graphic representation of these recovery stages can be seen in Fig. 2.2.

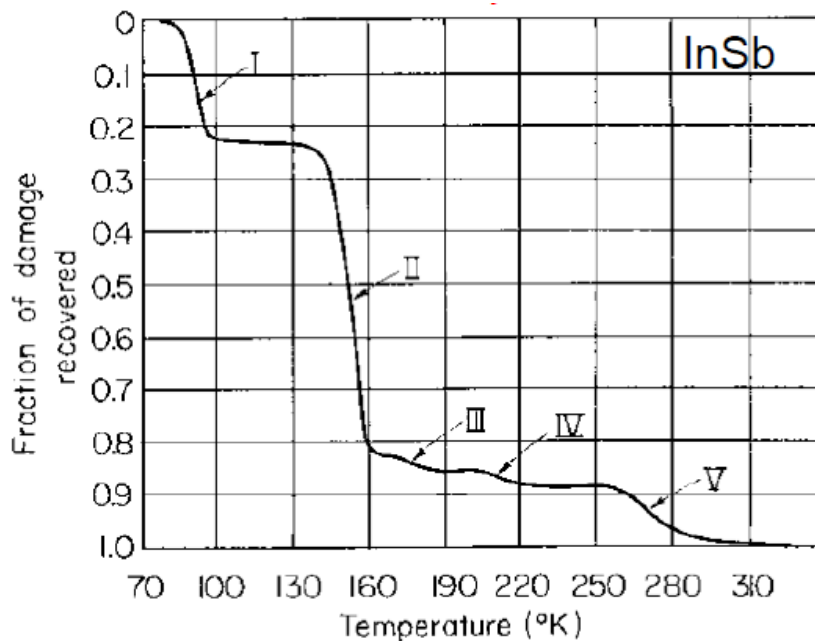


Figure 2.2 Defect recovery stages in InSb following electron irradiation at 4 K [14].

In low temperature regimes (above recovery Stage I, but below recovery Stage V), the irradiated microstructure is typically characterized by a high density of “black dots” (defects clusters that are too small to clearly resolve in the transmission electron microscope, $<2\text{nm}$) and the defect density increases rapidly with dose to a saturation volumetric concentration within $\sim 0.1\text{-}1\text{ dpa}$ [10]. As temperature is increased (near and above recovery Stage V), the radiation induced microstructure changes from one dominated by a high density of small dislocation loops to one containing fewer, larger dislocation loops and network dislocations. The dislocation loop density is expected to increase rapidly with dose (although less rapid than for “black spot” defects) and then saturate and remain constant after a few dpa. The loop density would be expected to decrease with increasing temperatures above recovery Stage V due to reduced point defect supersaturation levels. The dislocation network density is expected to decrease in proportion to the faulted loop density as temperature is increased above recovery Stage V. At high Stage III-V and higher temperature regimes, the population generally consists of a low density of faulted loops and large dislocation networks.

For clusters of vacancies to grow into a void, there must be a net increase in the number of vacancies absorbed over the number of interstitials absorbed. Below recovery Stage III temperatures, void growth is impossible due to vacancy immobility. It is possible under irradiation to produce a supersaturation concentration of vacancies, but they cannot self-cluster due to insufficient mobility, and vacancies tend to be lost via recombination with mobile interstitials, prohibiting growth of any nascent vacancy clusters. As temperature is increased above Stage III, the mobile vacancies are capable of self-clustering to form voids. The maximum void swelling level is typically reached at temperatures above recovery Stage V as both the vacancy concentration and mobility increase to the point that loss due to mutual recombination is minimal. There tends to be a linear increase in void swelling with dose as it is typically a sink-dominated process. At very high temperatures (much greater than recovery Stage V), the

emission of vacancies from voids counterbalances the net vacancy influx driven by irradiation, and void growth is suppressed. The processes by which defect loops and voids evolve are intimately linked and form the basis for radiation-induced changes in mechanical properties as well as physical properties such as volumetric swelling due to void formation [9, 10].

2.3 Physical and Mechanical Effects of Radiation Defects

Irradiation-induced physical and mechanical changes can greatly alter structural integrity of materials and can make them behave significantly differently from their unirradiated counterparts. Some of the most common examples include radiation hardening and embrittlement, volumetric and void swelling, solute segregation and phase instability, irradiation creep, and helium bubble formation. All of these effects are grounded in the defect formation and evolution discussed previously. The primary focus of this chapter will be the discussion of phase instability, volumetric swelling, and hardness and embrittlement as they pertain to MAX phases.

2.3.1 Radiation Induced Phase Instability

As mentioned, irradiation can have profound effects on the formation or dissolution of phases by alteration of the stability of those phases. The most direct way in which irradiation can alter phase stability is by causing localized enrichment or depletion of atoms, such that solubility limits or phase boundaries are crossed. Irradiation can also dissolve phases by recoil dissolution, cause disordering by creating anti-site defects, and lead to nucleation and growth of distinct phases. Under specific conditions, irradiation can also lead to the formation of metastable phases including amorphization.

Due to its complex bonding and crystal structure, the potential effect of radiation induced phase change on MAX phases is a significant concern with regard to radiation tolerance, especially when regarding secondary phases. Complexities during synthesis, in which secondary phases such as MX and

higher order MAX phases tend to compete with the target MAX phase if conditions are not closely monitored, and with its peritectic dissociation at high temperatures, in which the material does not melt congruently but instead dissociates into different phases, suggests there may be problems with phase stabilities in an extreme radiation environment, and is something that should be specifically investigated [9, 10].

2.3.2 Radiation Induced Volumetric Swelling

In addition to phase instability, volumetric expansion through point defect and void swelling/ bubble formation plays a critical role when designing materials for nuclear environments as substantial dimensional changes are unacceptable for typical engineering designs. The temperature intervals of these swelling regimes are defined by the defect recovery stages mentioned in the last section and within a given swelling regime the magnitude of swelling can be highly temperature dependent, providing the basis for defining possible temperature application regimes or “operational temperature windows”. A graphic showing the swelling regimes for a typical ceramic (Al_2O_3) can be seen in Fig. 2.3. It is important to note that amorphization is typically relevant only at low temperatures where interstitials are immobile (usually room temperature or below; too low for nuclear reactor application). Since amorphization is not anticipated to arise in irradiated MAX phase ceramics at the irradiation conditions investigated in this thesis, this phenomenon will not be discussed here (although for other materials this could be an issue).

The “point defect swelling” stage of volumetric swelling is induced through the addition of radiation defects and is prominent between recovery Stage I and Stage III, typically between ~ 0.1 and $\sim 0.3 T_M$ [10]. “Point defect swelling” typically reaches a saturation value after doses of 0.1-1 dpa, corresponding to the saturation in point defect and defect cluster density for this temperature regime mentioned earlier in this chapter. Lattice dilatation around an interstitial produces a volume change that is typically between one and two atomic

volumes, while lattice relaxation around a vacancy produces a slight volume contraction that is typically less than one atomic volume. This leads to slight volumetric expansion for a Frenkel pair, and forms the physical basis for “point defect swelling” in irradiated materials (along with the analogous lattice expansion from small defect clusters and dislocation loops). The magnitude of the point defect swelling is typically about an order of magnitude larger in ceramics compared to metals: linear swelling levels may be on the order of 1% or larger for irradiated ceramics, as shown in Fig. 2.3 at intermediate temperatures.

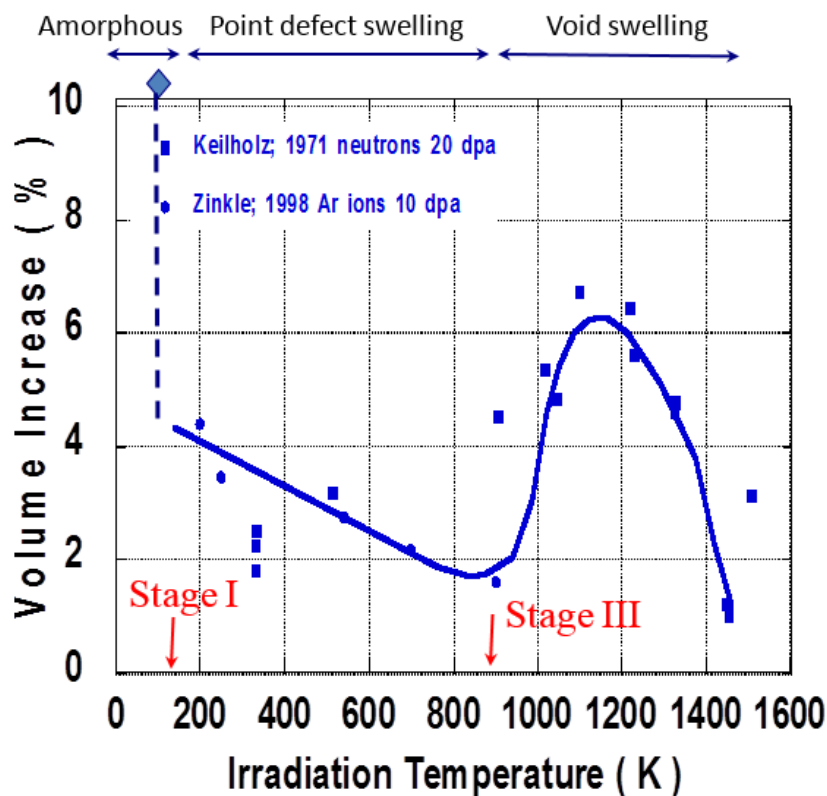


Figure 2.3 Volumetric swelling regimes for irradiated Al_2O_3 [15].

In hexagonal close packed (HCP) materials, interstitial defects typically tend to preferentially agglomerate on the basal plane, resulting in significant swelling of the c-lattice parameter (c-LP) with smaller deviation in the a-lattice parameter (a-LP). This anisotropic swelling can induce pronounced strain at grain boundaries

in HCP ceramics with random grain orientations, leading to grain boundary cracking and loss of mechanical strength, making it a major limiting factor for application of HCP ceramics in nuclear environments. The radiation-induced lattice parameter changes for two well-known HCP ceramics irradiated near RT, Al_2O_3 and BeO , can be seen in Fig. 2.4.

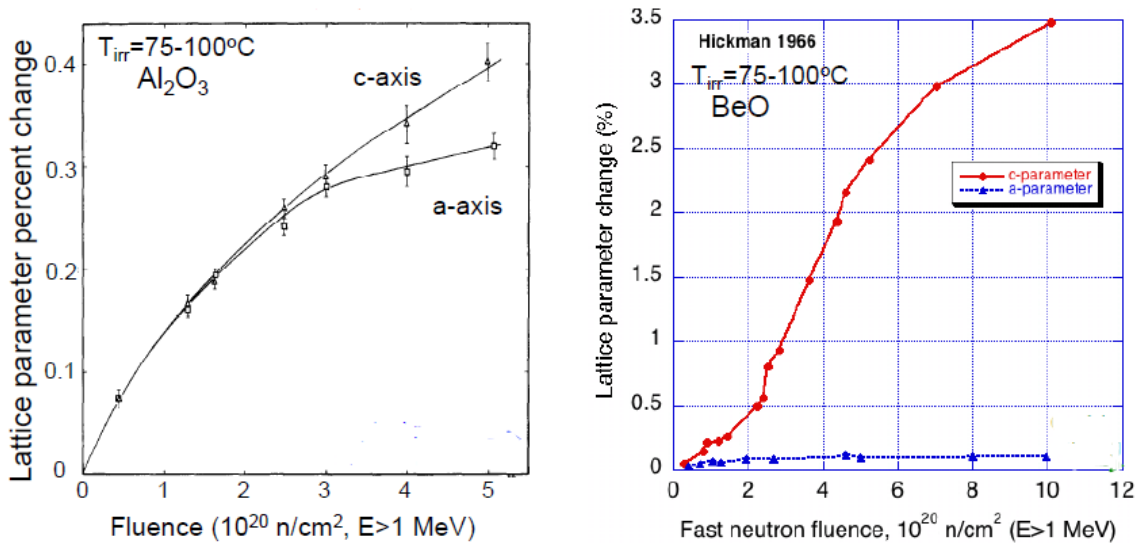


Figure 2.4 Effects of neutron irradiation on lattice parameters for (a) Al_2O_3 and (b) BeO irradiated near RT [16, 17].

As previously discussed, as the temperature increases, the mobility of interstitials increases and a lower volumetric concentration of larger loops/dislocation networks are formed. The lower concentrations of larger defects reduces the magnitude of volumetric swelling due to the rapid decrease in cluster density, along with more efficient collapse of defect clusters into dislocation loops that have relatively low swelling per defect (compared to uncollapsed defect clusters).

For irradiation temperatures above Stage III recovery regime, volumetric swelling associated with interstitial defects becomes eclipsed by void swelling. Void swelling is typically of concern for irradiation temperatures between ~ 0.3 and $\sim 0.6 T_M$. Unlike point defect swelling, void swelling typically increases with

increasing dose without saturation. In some materials, a prolonged low-swelling transient regime occurs at relatively low doses before the onset of steady-state void swelling. Typical steady state volumetric swelling rates are in the range of 0.1-1 percent per dpa. With increasing temperature, the void density decreases logarithmically and the size increases, which is the typical behavior for a process that is dominated by nucleation at low temperatures where the void growth is slow, and by growth at high temperatures where the free energy difference driving void growth is small. A schematic graphic showing void density and size as a function of irradiation temperature above in the Stage III regime can be seen in Fig. 2.5.

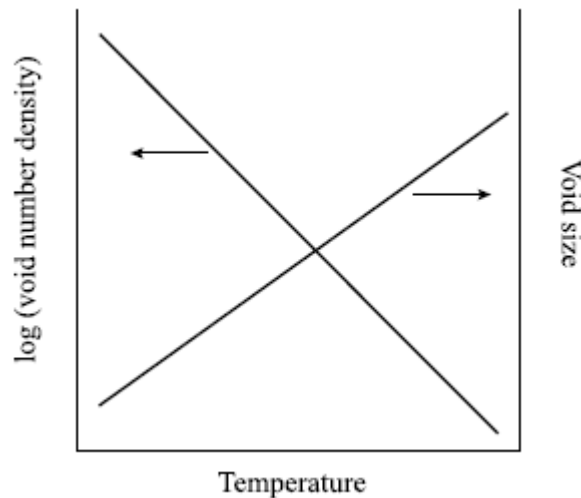


Figure 2.5 Schematic of the temperature dependence of void density and void size [9].

At very high temperatures, void growth ceases due to pronounced vacancy emissions by voids and void swelling is reduced. This results in a local maximum for void swelling at intermediate temperatures (~ 0.4 to $\sim 0.5 T_M$).

It is important to note that He produced by (n, α) reactions (along with other radiation-produced gases such as H from (n,p) reactions) forms directly within the lattice materials and can become trapped by vacancies and vacancy

clusters. Unlike vacancies and self-interstitials, gaseous atoms such as He cannot annihilate (recombine) and they must therefore maintain its identity. The gas atoms can react with vacancies to form gas-vacancy clusters complexes and bubbles, which can enhance cavity growth beyond that of a true void, making it a significant concern for many engineering materials exposed to neutron irradiation environments at elevated temperatures. This is a particularly significant concern in reactors with very energetic neutron energy spectra such as fusion reactors, due to the higher (n,α) cross-sections for many elements at high energies.

For the relatively new class of materials known as MAX phase, the effects of irradiation damage on swelling are not known. At a more fundamental level, important physical parameters such as interstitial and vacancy migration energies (which establish the important Stage I and Stage III defect migration temperatures) are not yet known. As such, an important step in determining radiation tolerances for these materials revolves around determining the approximate Stage I and Stage III recovery stage temperatures of the different atom species present [9, 10].

2.3.3 Radiation Induced Hardening and Embrittlement

The last relevant physical effect of irradiation damage on materials is that pertaining to radiation hardening and embrittlement. As discussed in the previous chapters, radiation creates defects in the crystalline lattice, which provide obstacles to dislocation motion, resulting in an increase in strength and a decrease in tensile elongation. Radiation hardening also tends to increase the ductile-brittle transition temperature and reduce the fracture toughness for BCC/FCC metals. A schematic demonstrating the effect of irradiation on stress-strain curves of FCC and BCC metals can be seen in Fig. 2.6.

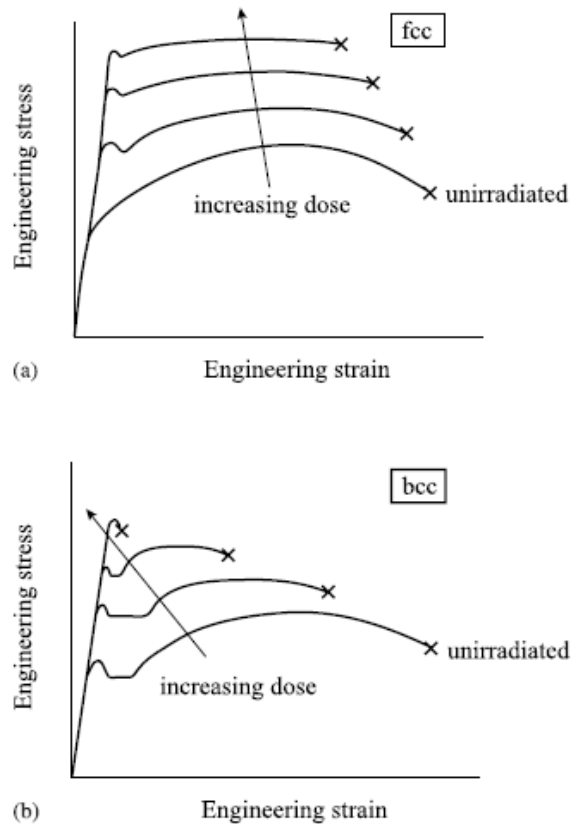


Figure 2.6 Effects of irradiation on the stress-strain behavior in (a) an austenitic (fcc) stainless steel and (b) ferritic (bcc) steel [9].

In typical ductile metals, radiation hardening and embrittlement is most pronounced for low irradiation temperatures ($T_{irr.} < 0.4 T_M$) and tends to “saturate” at low doses (~ 0.1 dpa) due to the aforementioned saturation in defect cluster density after 0.1-1 dpa in this temperature regime. This general behavior occurs in both fission and fusion reactor environments, and the mechanical hardening data obtained in different irradiation spectra can be correlated with each other on the basis of dpa. An example of this equivalency for fission and fusion neutron irradiated copper can be seen in Fig. 2.7.

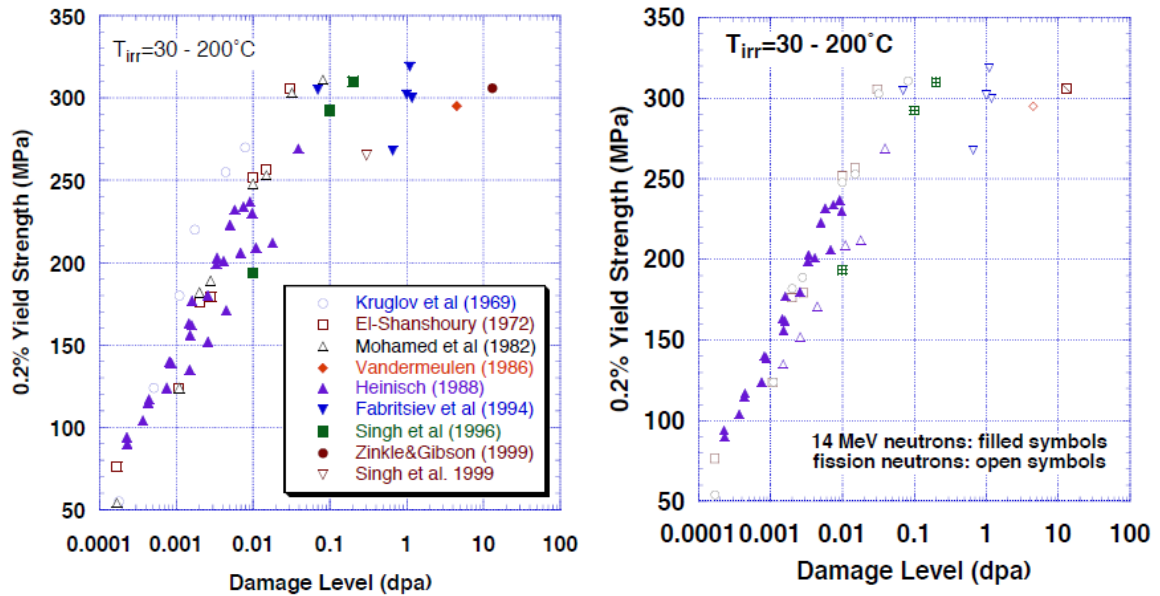


Figure 2.7 Hardness saturation effect in neutron irradiated copper [18].

For a complex, pseudo-ductile material such as the MAX phase, it is possible that hardness and embrittlement evolution is not as straight forward as for typical, well-known metals, and as such is a major area of ongoing investigation. However, since dislocations are claimed to be mobile in the MAX phase ceramics and their strength is purported to be controlled by dislocation interactions, then dislocation pinning by radiation-induced defect clusters is anticipated to produce radiation hardening in irradiated MAX phase ceramics. The possible impact of radiation hardening is that more conservative structural design rules may be required due to the accompanying reduction in uniform elongation and ductile-brittle transition temperatures as they pertain to thermal shock and other safety scenarios, and can greatly affect application of materials in nuclear reactor environments [9, 10].

2.4 Simulation of Neutron Irradiation Effects with Ions

When determining radiation response properties of materials, the irradiation damage produced by energetic neutrons in reactor environments can be simulated using heavy ions to allow for characterization of irradiated samples

without requiring special handling precautions that are necessary for neutron irradiated (radioactive) samples. This is possible due to the fact that the kinetic energy of a neutron is predominantly transferred to a medium through elastic collisions with primary knock-on atoms (PKA's) of the target material. These PKA's subsequently become a projectile and cause additional nuclear interactions with other target atoms as discussed in Chapter 2.1.1. There is significant incentive to use ion irradiation to study fundamental aspects of radiation damage as this technique has the potential for yielding answers on basic processes while being significantly more time and cost effective [9].

2.4.1 Comparison of Neutron and Ion Beam Irradiations

Neutron irradiations typically require months to years of in-core exposure to reach appreciable fluence levels for accelerated post irradiation testing. This is typically accompanied by at least another year of capsule design and preparation as well as disassembly and cooling. Additionally, due to the long cycle time and complications associated with induced activity, there are typically requirements including special facilities, sample handling, and analysis, which tend to make the costs for neutron irradiation experiments very high.

In contrast, ion (heavy, light, or electron) irradiations have considerable advantages in required time and cost. Due to high achievable fluence levels, ion irradiations rarely require more than several tens of hours to reach damage levels in the 1-10 dpa range. Additionally, ions induce little to no radioactivity, and thus do not require special facilities or precaution during post-irradiation handling and examination. These features make ion irradiations an attractive alternative to neutron irradiation with regards to irradiation damage studies, specifically regarding new materials. This being said, ion irradiations have several drawbacks when being used as a surrogate for neutron irradiations, most notably with regard to the short penetration depth and varying damage profile in contrast with the homogeneous irradiations possible with neutrons. In general, the higher dose rates associated with ion irradiations causes differences in the

detailed microstructural evolution compared to lower dose rate neutron irradiations. Some of these differences can be accounted for by applying a “temperature shift”, i.e., performing the ion irradiation at a higher temperature to account for the high production rate of radiation defects relative to thermal annealing processes. When analyzing ion irradiation samples, one must use special techniques and be able to sample regions at well-defined depths from the surface in order to minimize dose variations.

When analyzing microstructural changes induced by ion irradiation, the effects of surfaces and the peak ion implantation region must be kept in mind when determining the correct region to sample radiation damage, as both can have profound effects on defect formation. A graphic of damage rate and ion deposition rate as a function of ion depth can be seen in Fig. 2.8(b). As can be seen, the peak ion implantation region is very close to the peak damage region and can have profound effects on void swelling and radiation induced segregation. An example of this can be seen in Fig. 2.8(a) for Ni⁺ ion irradiation of Fe-15Cr-35Ni. Due to the fact that each Ni ion creates an additional interstitial when it comes to stop in the lattice, the void swelling is significantly suppressed at the peak implantation region due to the increase in vacancy-interstitial recombination, even though the damage is 3 X that of the surface region. Additionally, the surface can act as a sink for interstitials and vacancies, resulting in a skew in void formation in the near surface regions. Due to effects such as these, it is imperative that the midrange ion region be chosen for sampling and determining radiation response while minimizing artifacts.

2.4.2 Calculation of Ion Beam Displacements per Atom Using SRIM

The most popular worldwide approach for calculating quantitative ion beam damage is the computer program known as the Stopping and Range of Ions in Matter or SRIM [19]. The program is based on a Monte Carlo simulation method that uses the binary collision approximation with a random selection of impact

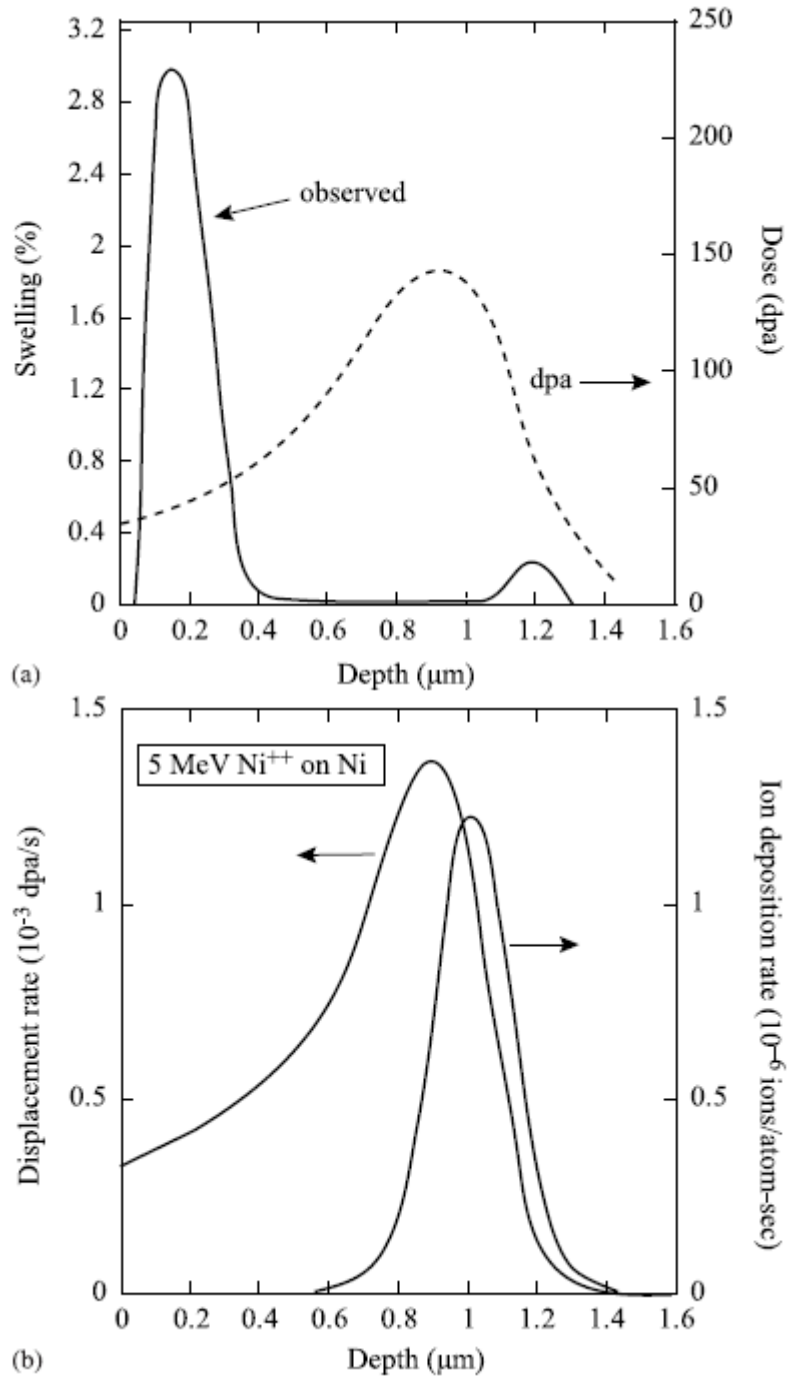


Figure 2.8 (a) Subsurface swelling resulting from 5 MeV Ni⁺ ion irradiation of Fe-15Cr-35Ni at 625 °C. (b) Displacement and ion deposition rate calculated for 5 MeV Ni⁺⁺ on nickel [9].

parameters for each colliding ion. Recommendations were taken from Stoller [20] to accurately calculate the displacements per atom, ν_{NRT} , as a function of depth while minimizing error. The general process is as follows.

1. Run SRIM 2013 using the “Quick” Kinchin Pease option with a minimum of 10,000 ions.
2. Set the displacement threshold energy values as appropriate for the material.
3. Set the lattice binding energy to zero.
4. Compute the damage energy according to Eq. (3).
5. Use the computed value of the damage energy to calculate the number of displacements according to Eq. (2)

The damage energy is given by

$$T_{dam} = E_{recoil} - E_{ionization} \quad (3)$$

Where E_{recoil} is the energy given to recoil ions and $E_{ionization}$ is the energy lost due to ionization, as calculated by SRIM 2013. Calculation results for this experiment can be seen in Chapter 4.

3 Literature Review

Due to the MAX Phases' unique combination of MX ceramic and metallic characteristics, it is speculated that MAX phases could be a promising candidate for application under extreme radiation conditions in both current generation fission, and proposed future fission and fusion programs. Specifically, it is suggested that both the high radiation damage tolerance of the MX compounds and the rapid damage recovery inherent in metallic MA compounds might be present in the MAX phases. However, numerous scientific questions need to be addressed before the MAX phases' potential is solidified; chief among them being the MAX phases' resistance to displacement damage. It is possible that microstructure evolution induced by irradiation may lead to changes in mechanical properties, and could prove to be a major obstacle in the application of MAX phases for structural applications in extreme irradiation environments. This section will briefly discuss previous heavy ion irradiation, helium ion irradiation, and preliminary neutron irradiation studies that explore the radiation response properties of MAX phase ceramics.

It must be noted that establishing the utility of MAX phases for the in-core nuclear applications first requires a thorough evaluation of un-irradiated MAX phase properties important to structural components and fuel pellet coatings. Of the 60 plus MAX phases currently known, the largest collection of knowledge resides with the families of titanium silicon carbides and titanium aluminum carbides due in part to their early discovery compared to other MAX phases. In 1996, Ti_3SiC_2 became the first reported bulk phase-pure MAX phase synthesized [21], and sparked an explosion in MAX phase research. Consequently, a large number of excellent articles regarding the synthesis, structure, and properties of the MAX phases were published in the following decade, many revolving around the aforementioned Ti_3SiC_2 , as well as the titanium aluminum carbides Ti_2AlC and Ti_3AlC_2 [6, 21, 22]. A general summary of some physical and mechanical

properties of these three MAX phases at room temperature can be seen in Table 1.

Table 1 Room temperature density, shear modulus G , Young's modulus E , Poisson's ratio ν , fracture toughness K_{Ic} , and flexural strength σ of select MAX phases [6, 23].

Material	Density (g cm ⁻³)	G (GPa)	E (GPa)	ν	K_{Ic} (MPa m ^{1/2})	Flexural σ (MPa)
Ti ₃ SiC ₂	4.52	139	341	0.20	7	720
Ti ₃ AlC ₂	4.5	124	297	0.20	6.9	340
Ti ₂ AlC	4.1	118	277	0.19	6.5	275

Additionally, these materials exhibit many of the beneficial MAX phase properties as mentioned in Chapter 1, such as oxidation resistance and stable crack growth/R-curve behavior [5, 24]. Due to the large amount of studies involving the basic structural and physical properties of Ti₃SiC₂, Ti₂AlC, and Ti₃AlC₂, the majority of irradiation studies to date have used a combination of these materials, with but a few studies including titanium aluminum nitrides.

An overview of irradiation conditions examined in previous studies on MAX phases can be seen in Fig. 3.1 [2, 7, 8, 26-40]. The majority of prior irradiation studies have been performed at room temperature. Although this provides some useful initial information on the general stability of a material to displacement damage, it is generally not applicable for assessing suitability for fission or fusion reactor applications operating at 300-800 °C due to the typically strong temperature dependence of radiation effects phenomena. Therefore, the present study was designed to focus on relatively high dose, high temperature response of irradiated MAX phase materials, which is most relevant for potential future nuclear energy applications. It should be noted that due to discrepancies in methods used in calculating displacements per atom (in particular recently discovered errors when the SRIM “full cascades” option is used to calculate dpa

[20]), the initially reported dpa values have been adjusted in this figure to provide a better quantitative comparison with the dpa calculation method used in this thesis research. Finally, this chapter briefly discusses only conclusions and trends drawn from previously conducted experiments, but does not make any statements on merit, which will be held until the discussion chapter.

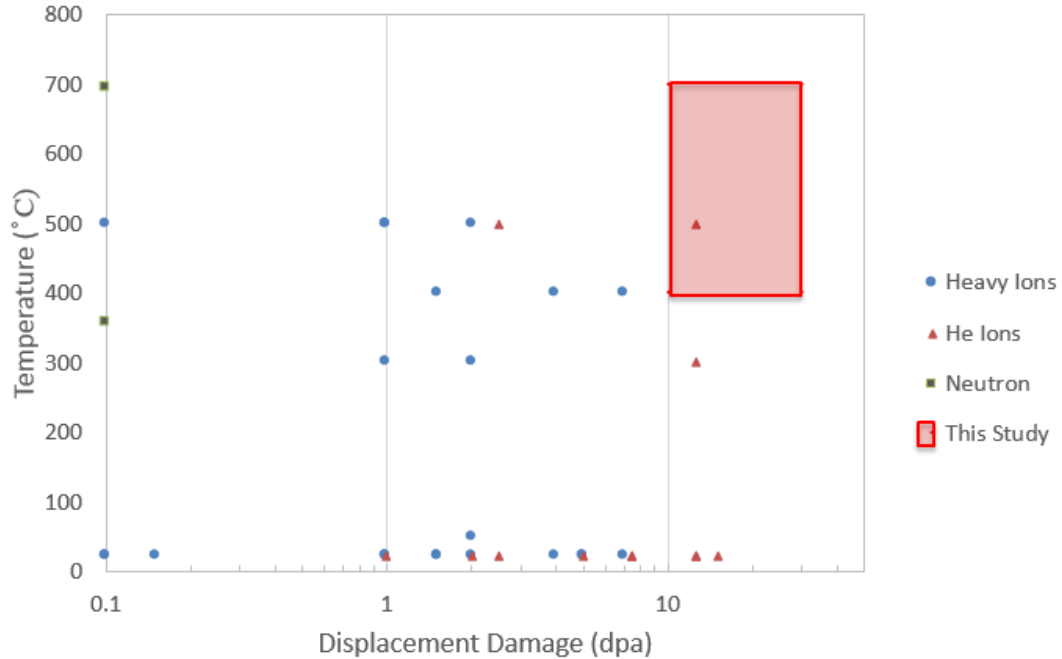


Figure 3.1 Overview of irradiation doses and temperatures investigated in prior published studies of irradiated MAX phase ceramics. The shaded red box indicates the high-dose, high-temperature regime selected for the present study.

3.1 Heavy Ion Irradiation Experiments

While neutron irradiations will always be required to qualify materials for reactor application, ion irradiation experiments provide a low cost and rapid means of evaluating and screening materials for important radiation response mechanism, and are typically the focus of early stage research. Therefore, ion

irradiation studies compose the majority of MAX damage experiments to date, with neutron irradiation results only recently beginning to emerge in publications.

In 2009 Nappe' et al. studied the effect of 90 MeV Xe ions on Ti_3SiC_2 at room temperature up to fluences of 10^{15} cm^{-2} , showing the differences in electronic and nuclear interactions in the MAX phases, leading to possible surface layer amorphization through electronic interactions, and selective grain boundary sputtering due to nuclear interactions [30]. In 2010, Liu et al. characterized Al-doped Ti_3SiC_2 irradiated with 74 MeV Kr and 92 MeV Xe at room temperature, 300 °C and 500 °C up to a maximum dose of 3.25 dpa. Using X-ray diffraction and Rietveld refinement, they showed a steadily increasing expansion in the c-lattice parameter (c-LP), without any evidence of saturation up to the maximum investigated fluence (with only a slight increase in the a-lattice parameter, a-LP), and micro-strain, as well as reported the possible existence of a new, disordered β - phase to explain the presence of new peaks found in the post-irradiated XRD patterns. They also reported the disappearance of lattice peaks with increasing dose, believed to be due to lattice disturbances. Finally, they showed that the diffraction patterns were less disturbed at higher irradiation temperatures, suggesting a positive correlation between irradiation temperature and radiation resistance. A plot showing the relative increase in the c-LP with increasing fluence for aluminum doped Ti_3SiC_2 (or $\text{Ti}_3\text{Si}_{0.90}\text{Al}_{0.10}\text{C}_2$) irradiated with Xe and Kr at various temperatures can be seen in Fig. 3.2 [29].

Using nanoindentation, Liu et al. then observed temperature dependent radiation induced hardness, with less pronounced increase in hardness at higher temperatures, which was confirmed with 800 °C annealing, confirming the improvement in radiation resistance at increased temperatures. A graphic depicting relative hardness increase at RT and 500 °C as a function of dose for 74 MeV Kr ion irradiated $\text{Ti}_3\text{Si}_{0.90}\text{Al}_{0.10}\text{C}_2$ samples up to a maximum midrange dose of 1 dpa, and subsequent post-irradiation annealing are presented in Fig. 3.3(a) and Fig. 3.3(b) respectively [8]. Furthermore, Both X-ray diffraction and

nanoindentation confirmed the retention of crystallinity at RT irradiation conditions up to a maximum dose of 3.25 dpa [8, 29].

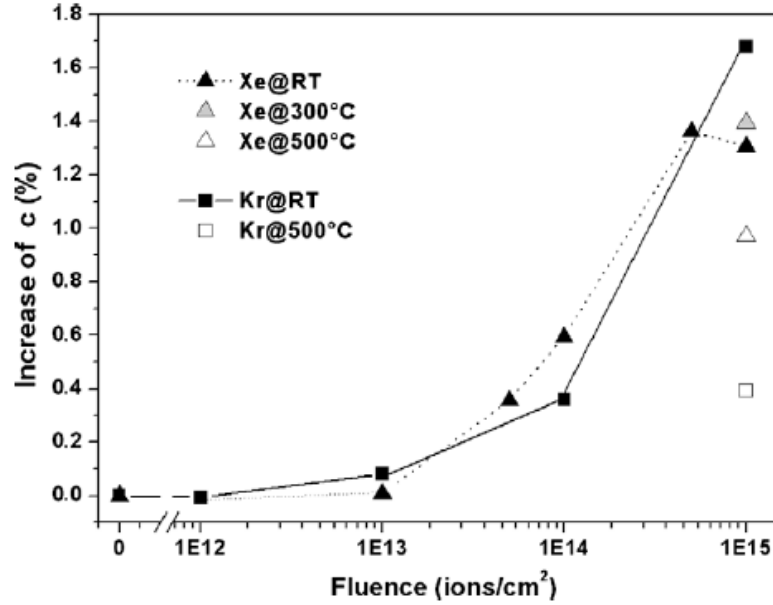


Figure 3.2 Dose dependent relative increase in lattice parameter c of $\text{Ti}_3(\text{Si}_{0.90}\text{Al}_{0.10})\text{C}_2$ for samples irradiated with 92 MeV Xe and 74 MeV Kr at RT, 300 °C, and 500 °C, with an ion flux of 1×10^5 corresponding to approximately 0.2 dpa [29].

Also in 2010, Whittle et al. studied the radiation tolerance of Ti_3SiC_2 and Ti_3AlC_2 up to very high dpa (~25-30 dpa) using 1 MeV Kr and Xe ions at 50 and 300 K. Using Selected Area Electron Diffraction (SAED) and TEM imaging, they found only minor evidence of amorphization, suggesting that the MAX phases remain crystalline up to much higher doses than many other ceramics (e.g., SiC), with only small differences between MAX phase systems. Additionally, SAED results suggested significantly more disorder in Ti_3SiC_2 than Ti_3AlC_2 at these irradiation conditions [37].

In 2011, Nappe et al. reported that nuclear collisions with 4 MeV Au ions up to a peak dose of 4.3 dpa resulted in anisotropic swelling (up to 2.2%) in Ti_3SiC_2

at room temperature, with a significant decreases in swelling at a higher irradiation temperature of 500 °C [31]. They went on to investigate the structural changes of Ti_3SiC_2 under a large variety of ions, fluences, and energies, concluding that it is not sensitive to electronic interactions (i.e., ionization processes), but that nuclear interactions greatly damage the structure of Ti_3SiC_2 , though they did not lead to amorphization even up to the highest studied dose of 4.3 dpa. Furthermore, through TEM analysis, they determined that the retention of defects was the reason for the anisotropic changes in lattice parameters (an increase in c-LP and a decrease in the a-LP) which lead to an increase in lattice micro-strain. Figure 3.4 shows change in lattice parameters and unit cell volume as a function of ion fluences for various ion and temperature irradiation conditions [32].

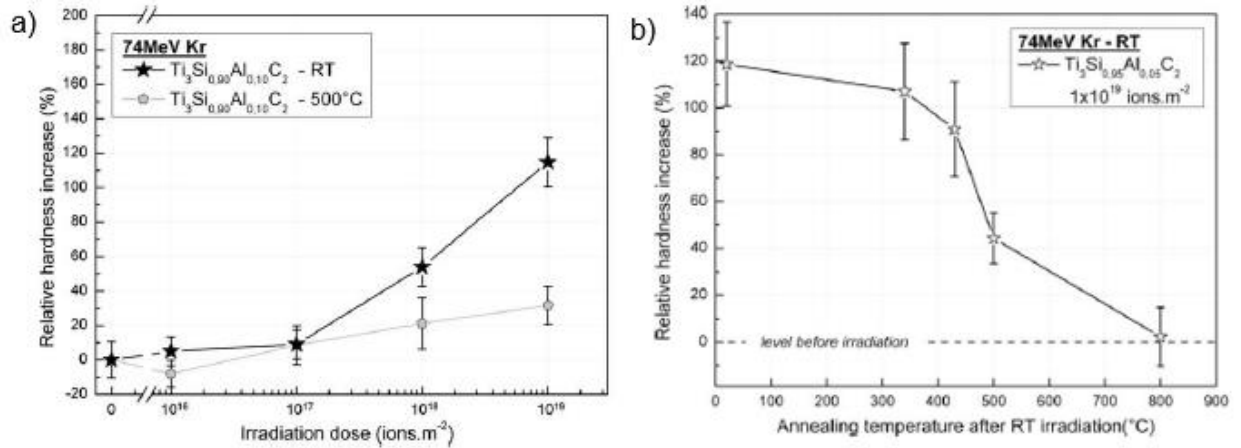


Figure 3.3 (a) Dose dependence of the relative hardness increase at two irradiation temperatures and (b) effect of post-irradiation annealing after RT irradiation on the relative hardness of 74 MeV Kr ion irradiated $\text{Ti}_3\text{Si}_{0.90}\text{Al}_{0.10}\text{C}_2$ to approximately 1 dpa or $1 \times 10^{19} \text{ m}^{-2}$ [8].

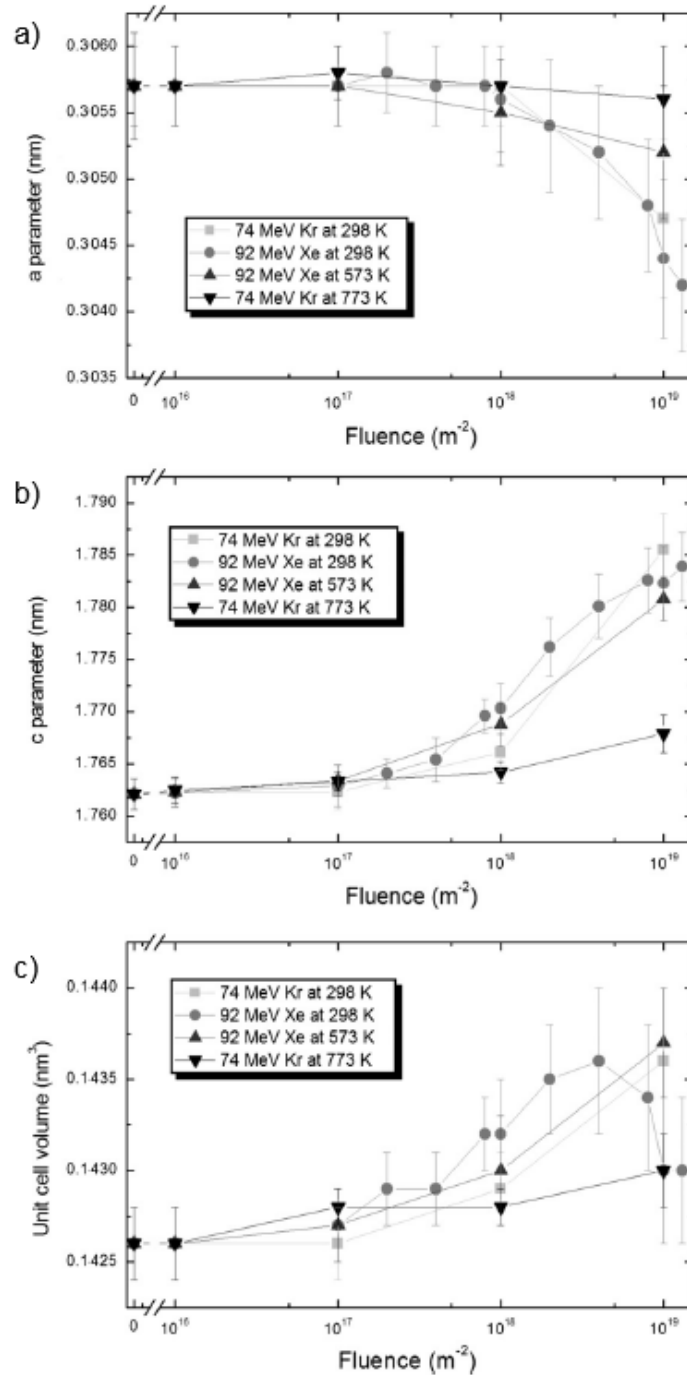


Figure 3.4 Changes in (a) a-LP, (b) c-LP, and (c) unit cell volume in Ti_3SiC_2 as a function of ion fluences for various ion and temperature irradiation conditions [32].

In 2012, Zhang et al. irradiated Ti_3SiC_2 with 2 MeV I ions at room temperature, finding evidence of the formation of TiC and/or 3C-SiC phases using X-ray diffraction, though the material did not fully decompose and remained crystalline up to 10.3 dpa [27]. In 2013, Le Flem and Monnet irradiated $\text{Ti}_3(\text{Si}_{0.95}\text{Al}_{0.05})\text{C}_2$ using 92 MeV Xe ions at room temperature up to a maximum dose of 16.6 dpa. Using nanoindentation, they observed a significant increase in hardness with increasing dose up to 3.2 dpa, whereas at higher damage levels there was a plateau in the measured radiation hardening, suggesting damage saturation [41]. Also in 2013, Bugnet et al. irradiated Ti_3AlC_2 thin films using 150 keV Ar ions at room temperature, followed by careful analysis by EELS, XRD, and TEM. They confirmed no signs of amorphization but showed significant loss of chemical order along the *c* axis. Their analysis demonstrated that the Ti_6C octahedra layers remained unperturbed while there was significant disordering of the aluminum layers [25].

3.2 Helium Ion Irradiation Experiments

While radiation-induced deterioration of fission reactor materials is dominated by displacement damage, it is important to note that in fusion reactors, the influence of (n, α) produced helium upon material deterioration is regarded to be of equal importance due to the high (n, α) nuclear reaction rate caused by the high-energy fusion neutrons and the current understanding that transmutant He generally leads to an enhancement of a variety of radiation damage phenomena. Therefore, as a proposed fusion structural material, there has been significant interest in using helium ion bombardments in order to observe both induced displacement damage and possible helium bubble formation in the most well established (“front-running”) MAX phases.

In 2013, Wang et al. irradiated Ti_3AlC_2 with 50 keV He ions at room temperature with fluences ranging from $8 \times 10^{16} \text{ cm}^{-2}$ to $1 \times 10^{18} \text{ cm}^{-2}$. Using grazing incidence XRD analysis, they observed a pronounced decrease of intensity and broadening of specific peaks, suggesting disruption in the

crystalline lattice without amorphization, which was further confirmed using selected area electron diffraction (SAED). Additionally, using TEM analysis, they observed several distinct stages of helium bubble development starting with spherical bubbles forming once He concentrations reached $\sim 1.1 \times 10^5$ appm, which then coalesced into string-like bubbles and subsequently formed “faulting zones” with increasing fluence up to a peak He concentration of 3.3×10^5 appm [36]. Also in 2013, Patel et al. irradiated Ti_3AlC_2 samples with 200 keV He ions to a maximum dose of 5.5 dpa at 500 °C. By carefully analyzing XRD patterns, they showed that the Ti_3AlC_2 crystal structure was maintained, but with an increase in c-LP and a decrease in a-LP along with significant disordering of the Al layers. Further examination by TEM analysis showed no He bubble agglomeration at the peak implantation region (He concentration ~ 12 atomic percent) and suggested that if He bubbles did exist, they were <1 nm in diameter, in stark contrast to the helium bubble formation observed by Wang et al. at room temperature [33].

In 2014, Yang et al. reported on structural changes induced in Ti_3AlC_2 by 50 keV He ion irradiations over a wide range of fluences from $5 \times 10^{16} \text{ cm}^{-2}$ to $6 \times 10^{17} \text{ cm}^{-2}$ at room temperature. Careful TEM observations showed no amorphization up to high fluences, though significant amounts of anti-site defects were produced starting at low fluences, which then formed extended defects, including stacking faults and Frank loops, as fluence increased. They also observed significant disruption of the nanolamellar structure and the formation of a disordered β -phase structure starting at low fluences [39]. Most recently, Song et al. irradiated Ti_3AlC_2 using 500 keV He ion at fluences ranging from $5.0 \times 10^{16} \text{ cm}^{-2}$ to $1.0 \times 10^{18} \text{ cm}^{-2}$ and temperatures including room temperature, 300 °C, and 500 °C. Using TEM and XRD analysis, they again confirmed no amorphization up to ~ 25 dpa at room temperature and showed significant crystal structure recovery with increasing irradiation temperature. Moreover, they showed that He only formed small spherical and platelet-like bubbles, and did not agglomerate into large bubbles even at the highest irradiation temperature of 500 °C and maximum He concentration of $\sim 6.4 \times 10^5$ appm. The authors

hypothesized the cavity growth was constrained by the nanolamellar structure of Ti_3AlC_2 [34].

3.3 Neutron Irradiation Experiments

In addition to heavy ion and helium irradiation studies, a small number of neutron irradiation studies have begun to emerge in the literature. In 2012, Hoffman et al. compared three of the front running MAX phases, Ti_3SiC_2 , Ti_3AlC_2 , and Ti_2AlC , to SiC and Alloy 617, two leading structural material candidates for next generation power reactors, in an analysis of calculated neutron activation for exposures to a neutron flux in hypothetical fast and thermal reactors for periods of 10, 30, and 60 years. It was shown that the specific radioactivities of these MAX phases were similar to SiC and three orders of magnitudes less than Alloy 617 after 10-60 years decay for all three exposure times in both the fast and thermal reactor spectra. As with SiC, the main radioisotopes after a decay period of 10 years for all three activation times in the MAX phases are tritium and carbon [7].

Much more recently, in 2015, Tallman et al. reported on the first bulk neutron irradiation of a number of different MAX phases including Ti_3SiC_2 , Ti_3AlC_2 , Ti_2AlC , and Ti_2AlN , showing the retention of crystallinity up to a dose of 0.1 dpa at temperatures of 360 °C and 695 °C. Using X-ray diffraction analysis methods, they showed significant increase in the c-LP and a slight decrease in the a-LP, while also showing significant reduction in lattice parameter distortion with increasing irradiation temperature. In all cases the aluminum based MAX phase exhibited significantly worse distortions than the silicon based MAX phase, with Ti_2AlC exhibiting the largest change from pristine. A graphic representation of the exhibited change in (a) c-LP and (b) a-LP as a function of irradiation temperature for various neutron irradiated MAX phase can be seen in Fig 3.5. Additionally, using Rietveld refinement, they were able to obtain the best fit for each material by assuming the partial dissociation of MAX phases into their corresponding MX counterpart. The results of this analysis indicated that the

aluminum based MAX phases dissociate more rapidly during irradiation than the silicon based MAX phases, with Ti_3AlC_2 , being the least radiation resistant material, supposedly dissociating 50 w.t.% into TiC . Finally, microstructural analysis observed a difference in formation of dislocation loops as irradiation temperature increased, showing a high density of small dislocation loops at low temperatures and fully formed basal defect loops at high temperatures for all materials. This, in conjunction with resistivity measurements, suggested dynamic damage recovery as irradiation temperature increases from 365 to 695 °C [35].

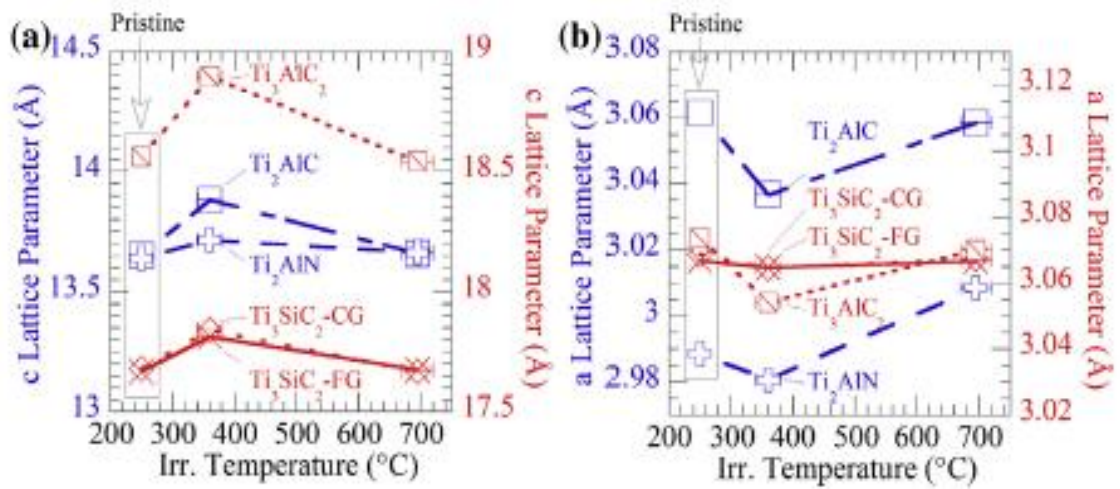


Figure 3.5 Plots comparing (a) c-LP and (b) a-LP Ti_3SiC_2 as a function of irradiation temperature for $\text{Ti}_3\text{SiC}_2\text{-FG}$ (fine grain), $\text{Ti}_3\text{SiC}_2\text{-CG}$ (coarse grain), Ti_3AlC_2 , Ti_2AlC , and Ti_2AlN , showing a significant temperature dependence on irradiation-induced lattice deformation after low dose neutron irradiation (0.1 dpa) [35].

3.4 Synopsis of Prior Irradiation Studies

While radiation response mechanisms of the MAX phase ceramics at relevant advanced reactor operating conditions are still widely undocumented, some useful trends can be drawn from the experiments completed to date as much of

the information is relevant for determining radiation response trends. They also provides some preliminary knowledge regarding radiation response differences in various MAX phase based on composition.

The first and most basic conclusion that can be drawn from these experiments is that, similar to both traditional metals and ceramics, the MAX phase are susceptible to atomic displacement through nuclear collisions, through which modification of the underlying crystal structure results in changes in both physical and mechanical properties. Due to this fact, the MAX phases are expected to follow physical and mechanical property change trends similar to those seen in traditional HCP ceramics and will be compared accordingly.

Secondly, previous experiments suggest that the MAX phases are generally resistant to amorphization up to relatively high doses (~25 dpa) between temperatures of 25 °C and 500 °C. This has been confirmed using SAED and TEM imaging techniques in the popular Ti_3SiC_2 and Ti_3AlC_2 at ~25 dpa [37], and using SAED, TEM, XRD, and nanoindentation at lower damage levels (~5 dpa) for multiple irradiation conditions between RT and 500 °C. Based on these studies, amorphization is not expected to be an issue at the relevant advanced reactor operating conditions which would operate at temperatures between 300 and 1000 C [8, 25, 27, 29, 31-33, 41]. Additionally, there is no evidence of void formation in Ti_3SiC_2 and Ti_3AlC_2 up to 500 °C and ~25 dpa [37], suggesting that vacancies are immobile below 500 °C (or else that void nucleation and growth is extraordinarily difficult). These two factors hint that the temperatures of 25 °C and 500 °C in MAX phases correspond to temperatures above recovery Stage I (onset for interstitial motion) and below recovery Stage III (onset for vacancy motion), as discussed in Chapter 2.

Finally, according to X-ray diffraction, TEM analysis techniques, and nanoindentation results, these prior studies suggest that the MAX phases have a positive correlation between temperature and radiation damage recovery. This is manifest in the decrease in crystalline lattice disorder and defects observed at higher irradiation temperature conditions by XRD and TEM [25, 29, 31-33], as

well as the pronounced decrease in hardness observed at higher irradiation temperature during nanoindentation [8, 25]. Due to this, it is hypothesized that the MAX phases will have substantial radiation resistance up to relatively high damage levels at advanced reactor operating temperatures.

4 Experimental Design

As discussed in the previous chapter, experiments have begun to show promising radiation response features of MAX phase ceramics. However, there are still numerous unresolved scientific questions that require additional research at nuclear energy relevant temperatures and doses before any potential reactor applications can be considered. Upon seeing the lack of high temperature/damage studies, this thesis chose to explore three leading-candidate MAX phases, Ti_2AlC , Ti_3AlC_2 , and Ti_3SiC_2 , at a combination of 400 °C and 700 °C and 10 dpa and 30 dpa. Post irradiation, several specialized analytical techniques were used to characterize ion irradiated samples and are discussed further in Chapter 5.

When performing the ion irradiations, a key focus was to maintain accurate and consistent measurements of experimental conditions (temperature, ion fluence, etc.), so as to ensure the validity of any results and conclusions drawn from the analysis of the irradiated samples. This section discusses sample preparation, the design and creation of a new sample holder whose purpose was to ensure the accuracy of the experimental conditions, specifically the irradiation temperature, and the methods used to calculate the corresponding fluence to nominal displacements per atom.

4.1 Sample Synthesis and Preparation

The MAX phase bulk samples used in this experiment were synthesized and provided by our collaborator, Darin Tallman, at Drexel University. As such, a detailed explanation of the synthesis and processing conditions is discussed elsewhere [21, 42], but an abbreviated description is as follows. The Ti_2AlC samples were prepared by pouring pre-reacted Ti_2AlC powders (Kanthal, Hallstahammar, Sweden) into graphite dies, which were loaded into a vacuum hot press and hot pressed for 4 h under a load corresponding to a stress of ~40 MPa and a vacuum pressure of 10^{-1} Pa at a temperature of 1300 °C. The

Ti₃AlC₂ samples were fabricated by ball milling stoichiometric mixtures of pre-reacted Ti₂AlC and TiC powders (Alfa Aesar, Ward Hill, MA, USA) for 24h and in turn, hot pressed at 1400 °C for 4 h. Finally, the Ti₃SiC₂ samples were prepared by ball milling stoichiometric mixtures of Ti, Si, and C powders (Alfa Aesar, Ward Hill, MA, USA) for 24 h, which were then hot pressed at 1450 °C for 4 h.

In preparation for this experiment, the bulk samples received from Drexel were sectioned into ~1 mm thick wafers and subsequently cut into ~3 mm TEM diameter disks using an Allied diamond blade low speed sectioning saw and a Gatan ultrasonic disk cutter. Once in disk form, the samples were divided into batches and ground down to approximately a 0.6 mm thickness using a Gatan precision grinder and 60 grit SiC paper, making sure that all roughened edges were removed. Following the grinding, the samples were polished using an Allied multi-prep polisher and diamond lapping film starting from 30 µm and going down to 0.25 µm. Following the lapping film mechanical polishing, the surfaces of the samples were further polished using a 0.05 µm colloidal silica suspension on polishing cloth. After the final polishing, the 3 mm diameter disk samples had a nominal final thickness of 0.55 mm.

4.2 UTK IBML Sample Holder Design

This thesis project was the first in what is hoped to be a series of ion beam irradiations at high temperatures using the UTK ion accelerator. Therefore, a large portion of this initial work was devoted to the design and creation of a new sample holder that would be robust and can be reused to provide consistent ion beam irradiation conditions. When conducting the ion irradiations, the main design criteria was the capability to perform multiple sample, high temperature irradiations under identical beam irradiation conditions, with the irradiation temperature being accurately measured. The reasoning behind this approach was three fold. (1) When comparing the radiation response of materials, it is imperative that all of the materials in question are subjected to the same irradiation environment. Thus it follows that the easiest way to ensure

environment equality would be to irradiate samples simultaneously. (2) Conducting multiple sample irradiations significantly reduces the amount of required irradiation time in the ion beam facility. This ensured that the irradiations were cost efficient and did not unduly monopolize a facility in high demand. (3) Accurate temperature measurements are critical in accounting for beam heating and temperature variations, ensuring the authenticity of results.

Considering that the planned irradiations would be completed at the University of Tennessee's Ion Beam Materials Laboratory (IBML), a sample platen that was compatible with the existing IBML vacuum chamber/stage was obtained from the company Thermionics Vacuum Products, and provided the foundation for a new sample holder design. A visual of the purchased sample platen can be seen in Fig. 4.1.



Figure 4.1 Thermionics molybdenum sample platen.

The commercially produced sample platen uses three thin, spring-loaded clips to hold samples on a heated molybdenum plate. This simple method proved insufficient in holding multiple small samples while also ensuring adequate thermal contact between the samples and the heated back plate. In lieu of this, the sample holder design was modified to ensure that the samples were held securely in place to provide the necessary thermal contact between heated plate and sample. To do this, a series of two plates/masks were designed and created using molybdenum, a refractory metal, so as to allow for high temperature

capabilities ($>800^{\circ}\text{C}$) and relative ease of machining. A schematic of these plates and how they are assembled can be seen in Fig. 4.2.

Although it is important to provide uniform irradiation fluxes in target regions, the traditional methods of beam flattening, such as electronic rastering (the scanning of the ion beam over the target area to ensure uniformity), are undesirable as they inevitably lead to pulsed beam conditions, resulting in radiation defect annealing and possible overestimation of radiation resistance. In order to avoid this issue, a relatively large, unfocused beam spot was used. This limited the target area to approximately $6\times 6\text{ mm}^2$ in dimensions for the UTK IBML facility and ultimately required the positioning and spacing of the TEM disks to be constricted to center of the sample holder with a tightly spaced geometric arrangement.

The middle plate was designed with three circular slots that were slightly larger than the samples and was used to position the samples laterally on the sample platen in said arrangement. The middle plate was machined to have a thickness comparable to, but slightly larger to those of the polished samples at around 0.6 mm. After positioning the samples in the middle plate, 0.125 mm diameter crushable annealed niobium wire rings were placed on the samples to account for any potential thickness variations in the samples and to ensure that the samples were held in good thermal contact with the base plate. The top plate/mask was designed with $\sim 2\text{ mm}$ holes centered directly over the samples. These holes, which are slightly smaller than the size of the samples, crush the Nb wire rings against the outside diameter of the sample face, firmly pushing the entirety of samples against the samples platen, while also allowing the ion beam to hit the center of the samples. The mask ensures that the pressure is evenly distributed around the outer edges of the samples and that good thermal contact is made between the sample backs and the heated surface of the platen. Once in position, the plates are held in place with six stainless steel screws that are threaded through the outer holes of the plates.

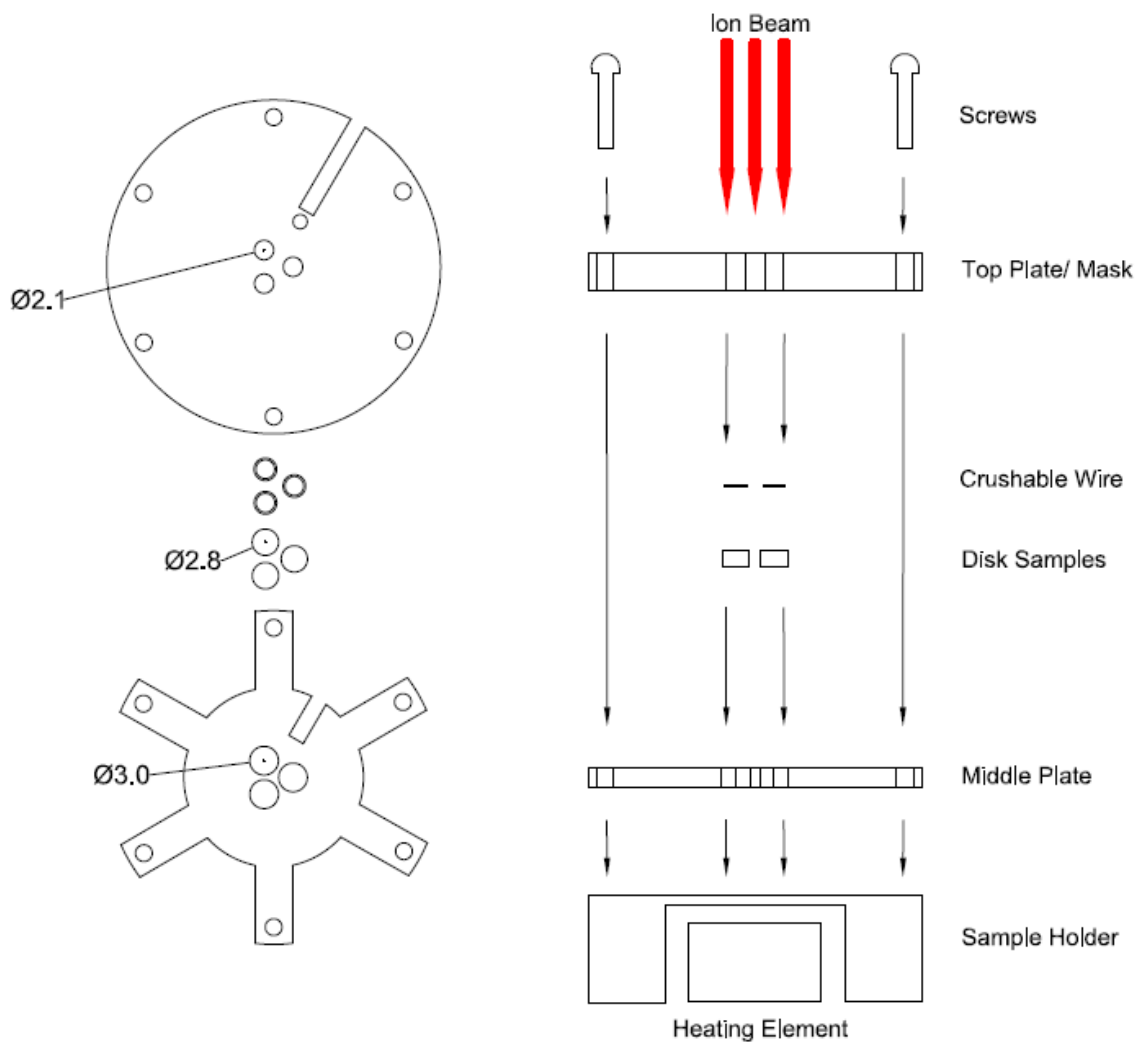


Figure 4.2 Modified sample holder schematic.

In order to ensure the accuracy of the experimental conditions, four type-K thermocouples were used to measure the temperature of the sample holder at different positions. Two thermocouples were built into the system, and as such, there was little control over their positioning and possible error. The first, termed Auxiliary, was positioned in the back of the sample holder near the heating element, and provided a nominal reading of its thermal output. The second, termed Main, was attached to the sample platen, and utilizing the machined trenches in the middle and Mo top plates, was positioned near where the samples made contact with the sample platen's heated plate. The tip of this thermocouple was mechanically held against the sample using a molybdenum screw. This thermocouple provided a nominal temperature reading of the heated surface. In addition to the built-in thermocouples, two additional thermocouples were added to ensure accuracy of readings. The first, termed Sample, was spot welded to the surface of one of the samples and was used measure the sample's nominal temperature to help account for any beam heating during irradiation. The second, termed Surface, was attached to the surface of the top plate outside the beam spot using a molybdenum clip, and was used to provide a base line measurement of temperature that would be unaffected by beam heating.

4.3 Temperature Calibration

Prior to performing the initial UTK IBML ion irradiations, a temperature calibration experiment in a non-irradiation environment was conducted to verify the sample holder's high temperature capabilities and determine the electrical currents that needed to be supplied by the heating element in order reach desired temperatures. A temperature calibration curve for the four thermocouples during a sequential ramp up in temperature (heating current) can be seen in Fig. 4.3. Due to thermocouple positioning and heat transfer through the plates, one would expect to have a thermocouple temperature distribution of Aux>Main>Sam>Sur. However, as can be seen, the Main thermocouple read significantly lower than expected, suggesting a malfunction in the wiring of the

built in thermocouple. For this reason, the Main thermocouple reading was not used as a reliable source of temperature measurement.

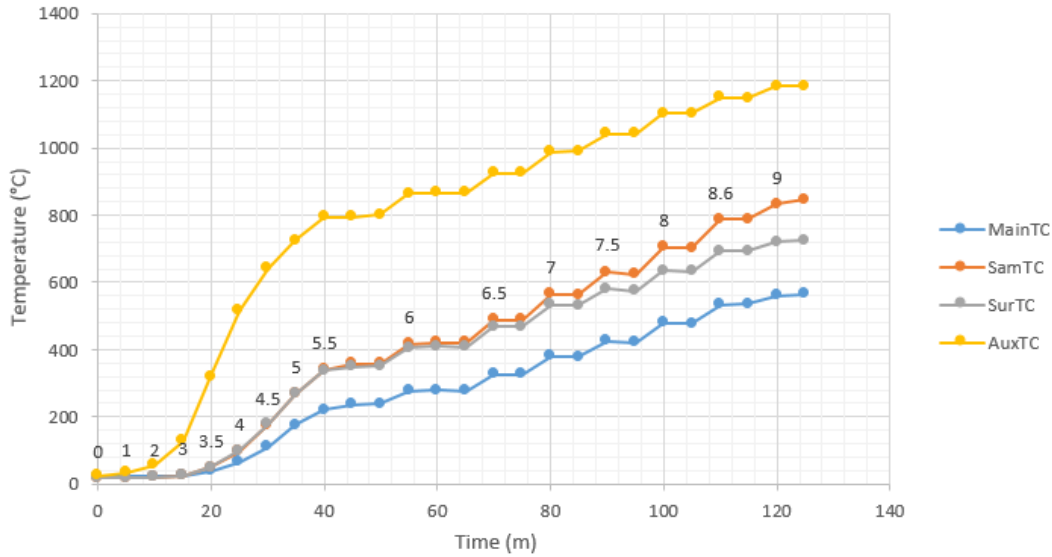


Figure 4.3 Sample holder temperature calibration curve. The numbers along the sample thermocouple denote heating element currents in milliamps.

In addition to the thermocouples, an infrared camera was also used during the temperature calibration experiment to verify the achievement of an even temperature distribution. Infrared image captures at nominal Sample thermocouple temperature readings of 400 °C and 800 °C can be seen in Fig. 4.4.

4.4 Ion Beam Facilities and Fluence Calculations

Due to time constraints and scheduling conflict, the ion irradiations were completed at a combination of the Ion Beam Materials Laboratory located at the University of Tennessee and the Texas A&M University Accelerator Laboratory.

The Ion Beam Materials Laboratory (IBML) on the University of Tennessee (UT) campus is a research partnership between UT and Oak Ridge National Laboratory (ORNL) that provides unique capabilities to the UT and ORNL

scientific community. The IBML is equipped with a 3 MV tandem accelerator, two ion sources, three beam lines, and four end stations that provide state-of-the-art capabilities for ion beam analysis, materials modification, fundamental research on ion-solid interactions, and applied research on radiation effects in materials for nuclear and space applications. Features include availability of ions of most elements (except rare gases) from hydrogen to gold, energies from 500 keV up to about 30 MeV (depending on ion and current needed), and controlled irradiation temperatures from 140 to 1475 K [43].

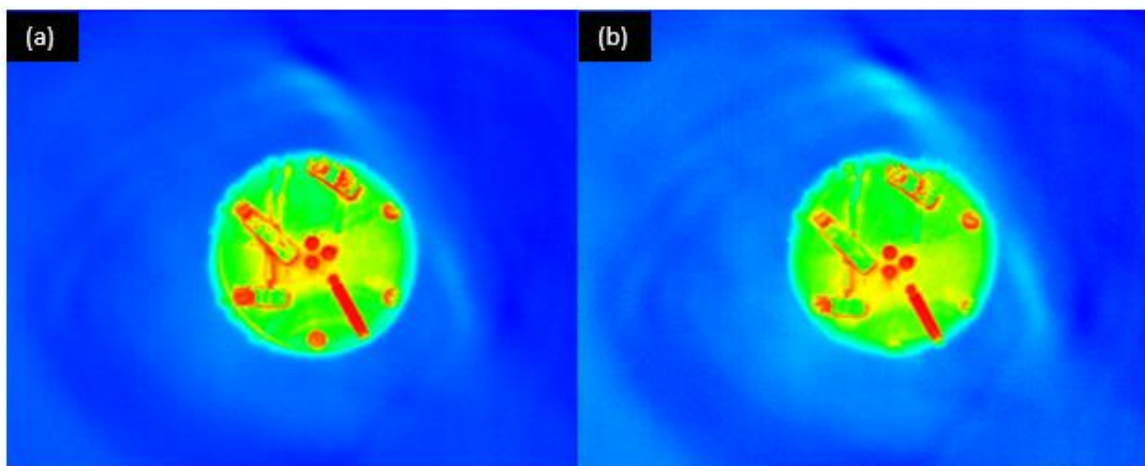


Figure 4.4 Infrared camera images at sample thermocouple readings of (a) 400 °C and (b) 800 °C. The three red dots near the center of the images correspond to the exposed 2 mm diameter surface regions of the three TEM disk samples.

The Accelerator Laboratory located at Texas A&M University (TAMU) is one of the largest university ion irradiation facilities in the United States with a total of five accelerators. The large number of accelerators enable the delivery of virtually any ion in the periodic table with energies ranging from a few hundred eV to a few MeVs. The lab provides unique capabilities to perform accelerator based irradiation studies on various nuclear materials and other multidisciplinary research, including fundamental ion solid interactions, accelerator based ion beam mixing, ion beam assisted film deposition, ion doping, Rutherford backscattering spectrometry, elastic recoil detection analysis, nuclear reaction

analysis, and particle induced X-ray emission analysis. The key ion irradiation facility used for this experiment in the TAMU laboratory was the 1.7 MV Ionex Tandetron Accelerator (with a RF Plasma Source and a SNICS source). Various heating and cooling systems are available that enable ion irradiations to be performed at different temperatures from cryogenic to $>700^{\circ}\text{C}$ [44].

When selecting the heavy ion type to be used in the irradiation, there were a number of considerations to take into account. Ideally, the best ion type would be a one that allowed for self-implantation while also allowing for a high ion beam current to minimize beam time. Due to the chemical compositions of the MAX phase materials, the only heavy ion that would allow for self-implantation of all three materials would be titanium. However, a high current titanium ion beam was not readily available/ feasible. Therefore, the next step was to find an ion that was relatively similar in weight to titanium but that could produce reliably high ion beam currents. The natural choice was nickel, which is used frequently for ion beam studies, making it a readily available and reliable ion source.

When selecting ion energy, it was imperative that the heavy ions had sufficiently large energy to penetrate a relatively large distance into the MAX phases' surfaces. This was necessary to ensure that there is a large portion of the ion beam track for analysis that is not compromised by proximity either the surface of the material or the ion implantation region. In order to calculate the penetration depth, the stopping power simulation program SRIM 2013 was used. These calculations lead to the choice of 10 and 5.8 MeV Ni^{4+} ion beam, which was the highest energy nickel beam available while maintaining a relatively large ion beam current at the UTK IBML and TAMU ion irradiation facilities respectively. Due to scheduling conflicts, only one irradiation, 10 dpa- 400°C , was conducted at the UTK IBML, and was never characterized due to time constraints. In order to get a more direct quantitative analysis, this irradiation condition was re-done, along with the three additional conditions using the 5.8 MeV beam using the TAMU ion irradiation facilities.

Using the SRIM calculations and Stoller recommendations [20] as mentioned previously, the NRT damage function, ν_{NRT} , was calculated as a function of depth in units of *dpa/angstrom-ion*. Knowing the target midrange dose values, the corresponding ion beam fluences were then calculated through simple unit conversion. A graphic of normalized displacements per atom versus depth for all three materials can be seen in Fig. 4.5, with the selected area for post-irradiation analysis defined by the red box. A list of irradiation conditions and corresponding doses for the four batches can be seen in Table 2. The batch names listed in the table are an abbreviation of the nominal irradiation conditions, namely low dose (10 dpa), high dose (30 dpa), low temperature (400 °C), and high temperature (700 °C). The midrange doses listed in the table were produced at a depth of $\sim 1.5 \mu\text{m}$.

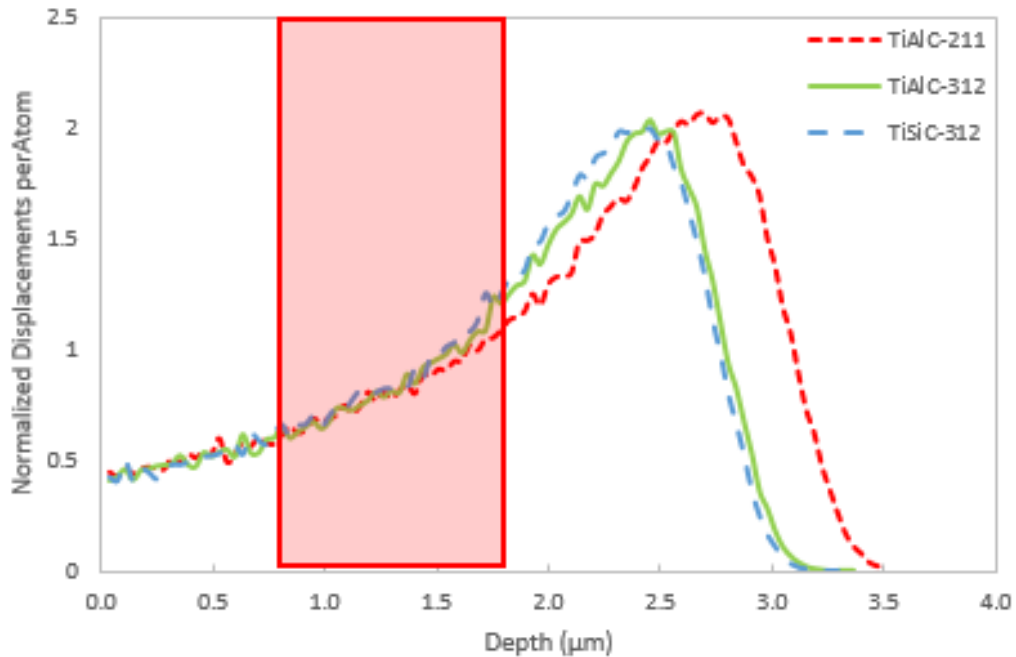


Figure 4.5 Damage versus depth profiles for 5.8 MeV Ni^{4+} ion irradiated MAX phase ceramics.

Table 2. Comprehensive list of irradiation conditions and corresponding fluences.

Batch	Ion Beam Condition	Midrange Dose (dpa)	Fluence (ion/cm ²)	Temp. (°C)
LD-LT	10 MeV, 5.8 MeV	10	2.43E+16	400
LD-HT	5.8 MeV	10	2.43E+16	700
HD-LT	5.8 MeV	30	7.30E+16	400
HD-HT	5.8 MeV	30	7.30E+16	700

5 Analytical Techniques

As seen in the previous chapters, the ion irradiated samples in this study consist of thin films ($\sim 3 \mu\text{m}$) of irradiated region on the surface of unirradiated substrates. In contrast, samples produced via neutron irradiations are homogeneously irradiated bulk samples. In view of this, it is not possible or practical to perform bulk sample tests, such as tensile and conductivity tests, to determine post-irradiation property changes. Instead, small scale analytical techniques must be used. This chapter discusses the application of grazing incidence X-ray diffraction, nanoindentation, scanning electron microscopy, and transmission electron microscopy for examining the thin film surface regions of ion irradiated samples.

5.1 X-Ray Diffraction

X-ray diffraction (XRD) is an analytical technique used to characterize crystalline materials and can provide useful information regarding phase composition, unit cell dimensions, disorder, etc. In XRD, crystalline atoms cause a beam of incident X-rays to diffract into many specific directions, and by subsequently measuring the angles and intensities of these diffracted beams, information regarding the composition of the material can be obtained. Typical XRD utilizes the large penetration depth of X-rays to analyze relatively large volumes of bulk, homogeneous material, typically in powder form. However, due to the small diffracting volumes of the irradiated thin film with respect to the substrate and background, a more specialized technique known as grazing incidence X-ray diffraction (GIXRD) is needed.

A brief description of GIXRD is as follows. Starting on the incident beam side, a combination of narrow slits and/or mirrors are used to make the incident beam nearly parallel. The stationary incident beam makes a very small angle with the sample surface termed omega, ω , which is typically between 0.3° and 3° , allowing for only very small penetration depths in the material and increasing the

path length in the film. This helps increase the film diffraction intensity while simultaneously decreasing the substrate and background intensities. The x-rays then pass through a Soller slit and on to the detector, only allowing those beams that are nearly parallel to arrive. During the collection of the diffraction spectrum, only the detector rotates through the angular range, thus keeping the incident angle, the beam path length, and the irradiated area constant. A schematic comparison of traditional XRD and GXRD can be seen in Fig. 5.1 [45].

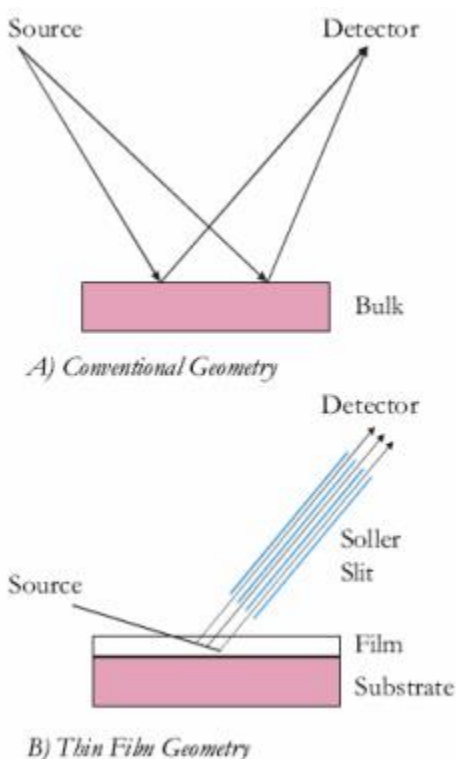


Figure 5.1 Schematic of (a) conventional X-ray diffraction geometry and (b) glancing incident X-ray diffraction used to analyze thin films [45].

For this experiment, a GXRD capable X'Pert/PANalytical XRD machine was used to analyze the irradiated MAX phase samples. Due to the small irradiated sample size and aperture constraints, samples were mounted on single crystal silicon to provide a nearly zero background plate test environment. The incident beam angle, ω , was calculated using the computer program HighScore Plus [46]

to achieve an approximate maximum beam depth of 1.5 μm , which corresponds to the depth for the nominal midrange dose. The calculated incident beam angles were 2.25° for Ti_2AlC and 2.5° for both Ti_3AlC_2 and Ti_3AlC_2 . The scans were performed using a 2Θ range of 8-80° with step sizes of 0.02° and 6 s count times at each step.

To analyze the diffraction patterns, the computer programs CMPR and Highscore Plus were used. CMPR is a multipurpose program developed by Argonne National Laboratory that can be used for displaying diffraction data, manual- and auto-indexing of diffraction peaks, and peak fitting and refinement [47]. It was used to accurately determine peak positions of the GXRD scans since irradiation caused some lattice parameter changes that shifted the diffraction peak positions of the materials. Highscore Plus is a full-pattern diffraction pattern analysis tool that unites phase identification, crystallographic analysis, unlimited cluster analysis, profile fits and Rietveld/structure fits under one common user interface [46]. Highscore plus was used to match the diffraction peak positions determined from CMPR to ICSD crystal data in order to determine lattice parameters of the irradiated samples.

5.2 Nanoindentation

Since its conception in the late 1970's, nanoindentation, or indentation load and depth sensing at nanometer to micrometer depth scales, has been established as one of the main techniques for determining the mechanical properties of small volumes of materials. In a traditional indentation test (macro or micro indentation), a hard tip with a well-defined geometry (typically made of a very hard material like diamond) is pressed into a specimen composed of softer material whose properties are unknown. The load placed on the indenter tip can either be set to a predefined value or systematically increased until the tip penetrates to a specific depth, where upon the load may be held constant for a period of time or removed immediately. Upon removal, the residual indentation in the sample is measured and the hardness, H , is calculated using Eq. (4).

$$H = \frac{P_{max}}{A_r} \quad (4)$$

Where P_{max} is the maximum measured load (or deadweight applied load) and A_r is the residual projected area of the indentation, which is determined optically.

In nanoindentation, very small loads and tip sizes are used, so the indentation area may be only a few square micrometers or even nanometers, which presents problems in accurately determining the residual indentation impression's area. Instead, an indenter with a geometry known to high precision at small scales (typically a Berkovich or three-sided pyramid geometry) is employed along with instrumentation to accurately record load and displacement during indentation. Using these recorded values, a number of methods can then be used to extract various mechanical properties of the indented material, most frequently the hardness, H , and elastic modulus, E [48].

A two dimensional cross-sectional schematic of nanoindentation on an ion irradiated surface can be seen in Fig. 5.2. It is crucial to recognize that during indentation, the region of material being measured does not simply correspond to the indentation depth, but is instead a culmination of all the material inside the strain field being affected by the indenter. This roughly hemispherical strain field has a radius that is typically 5-10 times the indentation depth. Therefore, the ideal maximum indent depth to obtain hardness data from the ion irradiated region with no effect from the underlying substrate was estimated to be between 300 and 600 nm (assuming a peak implantation depth of $\sim 3 \mu\text{m}$). In order to quantitatively verify the indenter depths where the hardness was unaffected by the substrate, data was obtained well past the estimated upper limit of 600 nm, to a depth of 1100 nm.

When processing the experimental nanoindentation data, it was crucial to determine the transition point between the irradiated and substrate regions. In order to determine this transition depth, the hardness curves were analyzed following the method recommended in the Nix-Gao Model [49], and the square of the measured hardness was plotted as a function of inverse indentation depth.

This allowed for two strain field regions to be distinguished: an irradiated-only near-surface region and an irradiated plus substrate strain field region.

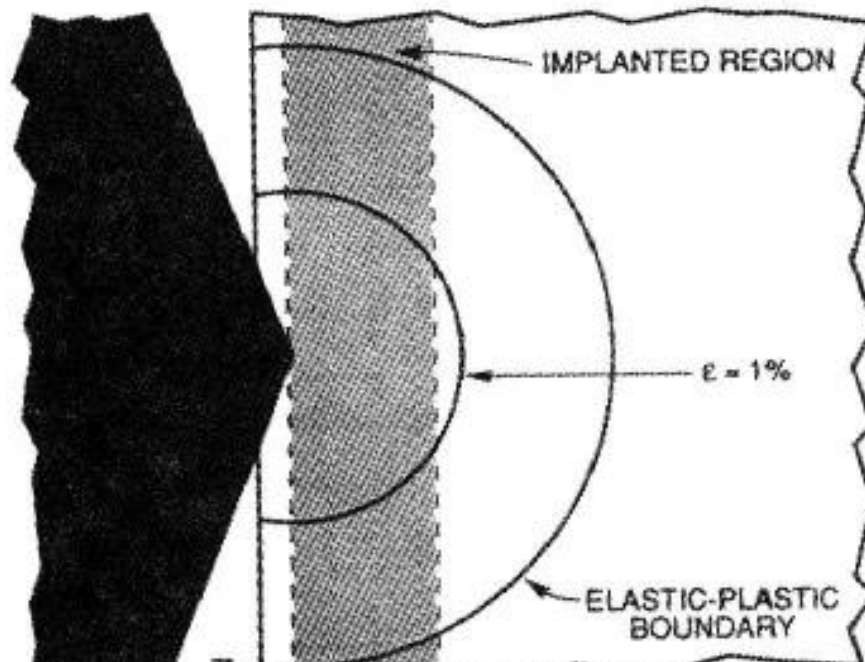


Figure 5.2 Schematic of nanoindentation and associated strain field for an ion implanted sample [50].

Finally, when analyzing the indentation data, the indentation size effect, wherein the hardness is observed to increase with decreasing indentation size, must be noted. Due to the small indentation sizes used in this experiment, the information presented in Chapter 6 cannot be extrapolated to bulk mechanical properties without complex analysis, and as such, typically has only been used in a relative comparison with other materials at similar indentation depths and irradiation conditions [49].

This thesis research utilized an Agilent nanoindenter with a Berkovich diamond indenter tip to examine the change of hardness and elastic modulus of the surface region post irradiation. Samples were loaded six hours before operation to allow for the dissipation of thermal drift and the machine was only

run during night hours to minimize disturbance from room vibrations. The indents were completed using a constant load rate of 500 $\mu\text{N/s}$ (continuous stiffness mode) and performed up to a depth 1100 nm. Optimized indentation positions were manually chosen using an optical microscope attached to the instrument. The areas considered optimized were those that appeared to be optically pristine and devoid of flaws, including scratches, pull-out, secondary phases, oxidation, etc. To avoid the effect of strain fields, the distance between indents, large scratches, and sample edges was at least 50 μm . Approximately twenty indents were made per sample to obtain a good statistical average. Hardness and elastic modulus were then determined as functions of indentation depth using the software associated with indenter [51].

5.3 Scanning Electron Microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of the surface of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography. SEM can achieve resolution better than 1 nanometer. A very common SEM operational mode is detection of secondary electrons emitted by atoms excited by the electron beam. By scanning the sample and collecting the secondary electrons with a special detector, an image displaying the topography of the surface is created. Using a Zeiss Gemini Scanning Electron Microscope, images were taken to view the effect of ion irradiation on sample surfaces. This process was also done following nanoindentation so as to view characteristic slip bands and cracking induced by the indentation.

5.4 Transmission Electron Microscopy

A transmission electron microscope (TEM) is an analytical tool allowing visualization and analysis of specimens in the realm of micrometers to nanometers. It allows detailed micro-structural examination through high-

resolution and high magnification imaging. It also enables the investigation of crystal structures, specimen orientations and chemical compositions of phases, precipitates and contaminants through diffraction patterns, via both energy-dispersive X-ray and electron-energy loss spectrometry. As such, TEM is a commonly-used and very powerful tool for investigating radiation-damage microstructures.

In order to investigate radiation damage in irradiated materials, one must first prepare a thin, cross-sectional foil, which is traditionally done using a Focused Ion Beam (FIB). This was completed with the help of Kiran Kumar at ORNL using a FEI V400ACE Focused Ion Beam. The samples produced were approximately 15 μm long by 10 μm deep with a viewing thickness of approximately 50-100 nm. Following the creation of thin, cross-sectional foils, samples can then be viewed in a TEM, which produces images from a sample by illuminating the sample with electrons (i.e. the electron beam) within a high vacuum, and detecting the electrons that are transmitted through the sample. Ultimately, using a TEM, it is possible to perform qualitative/quantitative analysis on a materials microstructure and even view individual columns of atoms along preferential oriented directions [52].

When examining radiation defects it is common-place to use a two-beam dynamical condition due to the weak lattice strain contrast sensitivity it provides and is generally set up by observation of the Kikuchi pattern in the diffraction mode. In this method, the foil is tilted so that one set of diffracting planes (corresponding to the diffraction vector g) is at, or very close to, the Bragg condition (as determined by Kikuchi patterns), allowing for the best possible strong-beam and weak-beam image contrasts. The image is formed by placing an objective aperture, situated in the back-focal plane of the objective lens, around either the forward-scattered beam or the diffracted beam g to form a bright-field or dark-field image respectively. Imaging of defect clusters, such as dislocation loops and stacking fault tetrahedra, can be completed reliably in this manner, and full characterization of the defect clusters can be completed using

various, more involved techniques (such as the inside-out method) [53-55]. A figure depicting standard two-beam conditions can be seen in Fig. 5.3.

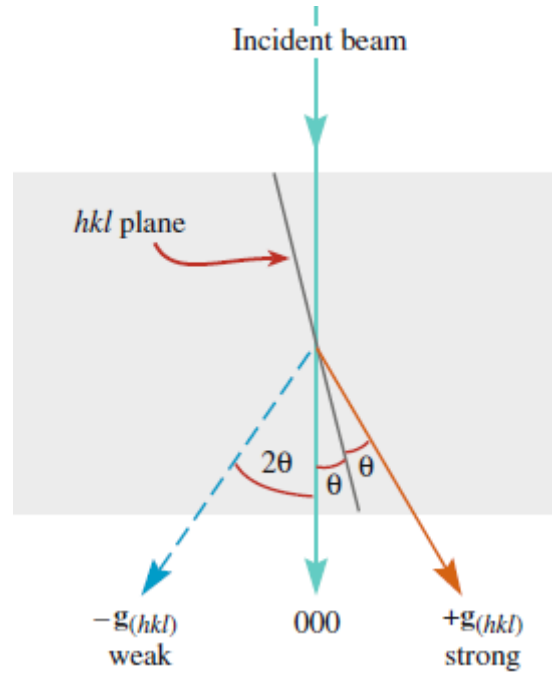


Figure 5.3 Schematic of the standard two-beam condition for use in transmission electron microscopy [52].

Though it is possible to due image large imperfections, such as voids, bubbles or amorphous zones due to the difference in structure factor using in-focus imaging, equilibrium voids generally do not have significant structure factor difference or long-range elastic stain fields to be imaged this way. When imaging small voids, the contrast arises from the change in mean inner potential between the void and the matrix, which causes a phase shift between electrons which traverse the void and those which pass through the adjacent perfect crystal. The effect is strongest for high-order reflections and depends sensitively on the degree of under- or over-focus of the objective lens. To image correctly, a bright-field through-focal series is recorded with the foil tilted well away from the

Bragg condition ($s_g > 0$) for the reflection of interest. Under such a two-beam kinematic condition, voids appear as white dots surrounded by a dark fringe in under-focus images, and as dark dots surrounded by a bright fringe in over-focus images [53-55].

When imaging for defects for this thesis research, a traditional two-beam condition was used with a beam direction of approximately $\langle 11\bar{2}0 \rangle$, as determined by electron diffraction and Kikuchi patterns. This allowed for imaging along the approximate diffraction vectors (g) of $\langle 0001 \rangle$ and $\langle 1\bar{1}00 \rangle / \langle 01\bar{1}0 \rangle$, the characteristic basal and prismatic directions of the HCP crystal structure. As no large voids were observed in the traditional two-beam imaging condition, under- and over-focus imaging at multi-beam weak kinematic conditions was used to search for the existence of any small voids in the materials.

6 Results

To serve as a convenient reference, the irradiation conditions for the 5.8 MeV Ni^{4+} ion irradiated MAX phase, Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 that were used for post irradiation examinations can be seen in Table 3. The conditions discussed will be low dose (10 dpa), high dose (30 dpa), low temperature (400 °C), and high temperature (700 °C). The midrange doses listed in the table were produced at a depth of $\sim 1.5 \mu\text{m}$. Generated graphics not directly relevant to the text, but that contain additional information may be seen in the attached appendix.

Table 3 List of irradiation conditions and corresponding fluences for specimens characterized in this study.

Batch	Midrange Dose (dpa)	Fluence (ion/cm ²)	Temp. (°C)
LD-LT	10	2.43E+16	400
LD-HT	10	2.43E+16	700
HD-LT	30	7.30E+16	400
HD-HT	30	7.30E+16	700

6.1 SEM Surface Analysis

SEM analysis was used to help gauge the influence of irradiation damage on the as-irradiated sample surfaces. Figures 6.1, 6.2, and 6.3 show as-irradiated sample surfaces at the four irradiation conditions for Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 respectively. From Figs. 6.1 and 6.2, it can be seen that both of the aluminum based MAX phases show significant surface cracking at both doses following irradiation at 400 °C, while no significant cracking was observed at both doses following irradiation at 700 °C. In contrast, the surface images of the silicon based MAX phase shown in Fig. 6.3 show no significant surface cracking at either the low or high temperature irradiation conditions for either dose.

Additionally, under SEM investigation, it can be seen that the Ti_3AlC_2 30 dpa -700 °C (Fig. 6.1(d)) sample has significant contamination build up on the surface

of the sample, believed to be hydrocarbon formation caused from outgassing of silver paste used to fasten the sample to the substrate for the Texas A&M ion irradiations. Cross section analysis showed that the contaminant film was 100-200 nm at its thickest. This surface contamination is believed to be responsible for slight difference between the Ti_3AlC_2 10 dpa -700 °C and 30 dpa -700 °C diffraction patterns and the unexpected decrease in hardness of the Ti_3AlC_2 30 dpa-700 °C data point as described later in this chapter.

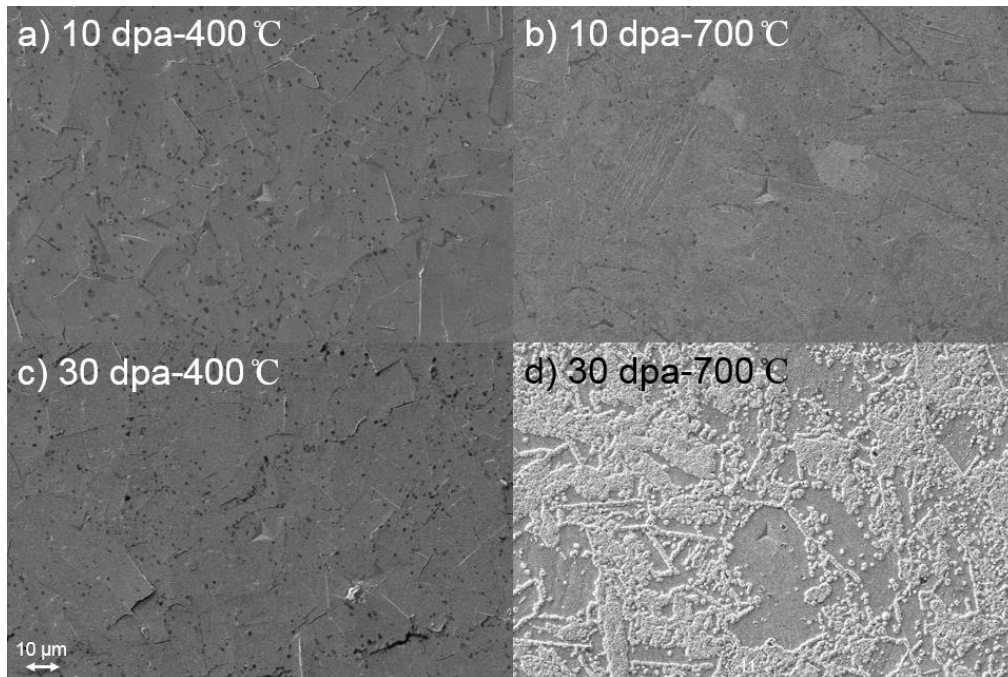


Figure 6.1 SEM surface images of Ni ion irradiated Ti_3AlC_2 for (a) 10 dpa-400 °C, (b) 10 dpa -700 °C, (c) 30 dpa-400 °C, and (d) 30 dpa-700 °C irradiation conditions.

Following the surface imaging, the degree of surface cracking was quantified for the irradiated MAX phase surfaces to determine if there was any discernable dependence of cracking on material composition, dose, or temperature. To do this, randomly oriented 50 μm long lines were drawn across surface images, and the number of crack intersections were counted. This number was counted for a large number of lines, and divided by the total line

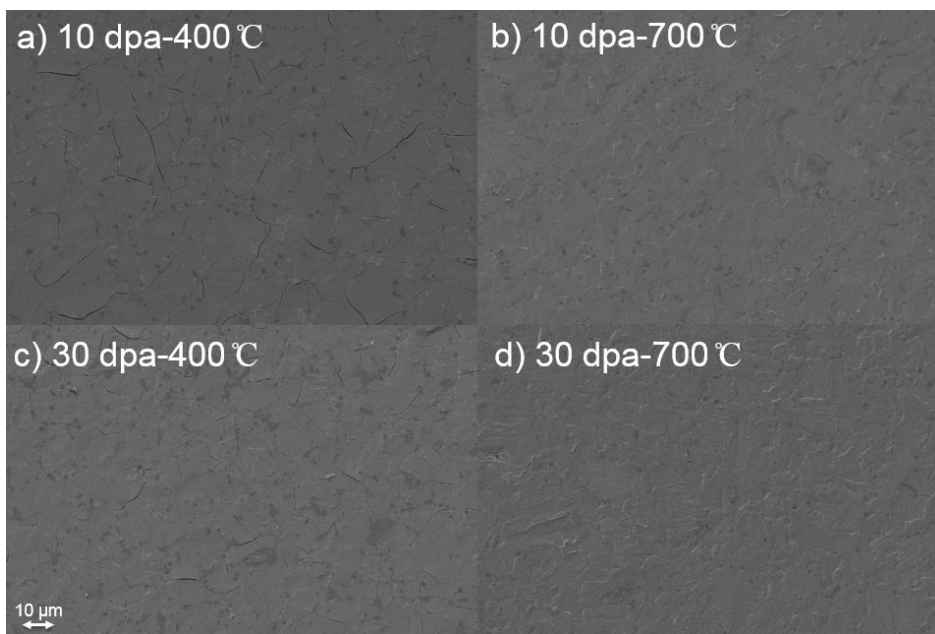


Figure 6.2 SEM surface images of Ni ion irradiated Ti_2AlC for (a) 10 dpa-400 °C, (b) 10 dpa-700 °C, (c) 30 dpa-400 °C, and (d) 30 dpa-700 °C irradiation conditions.

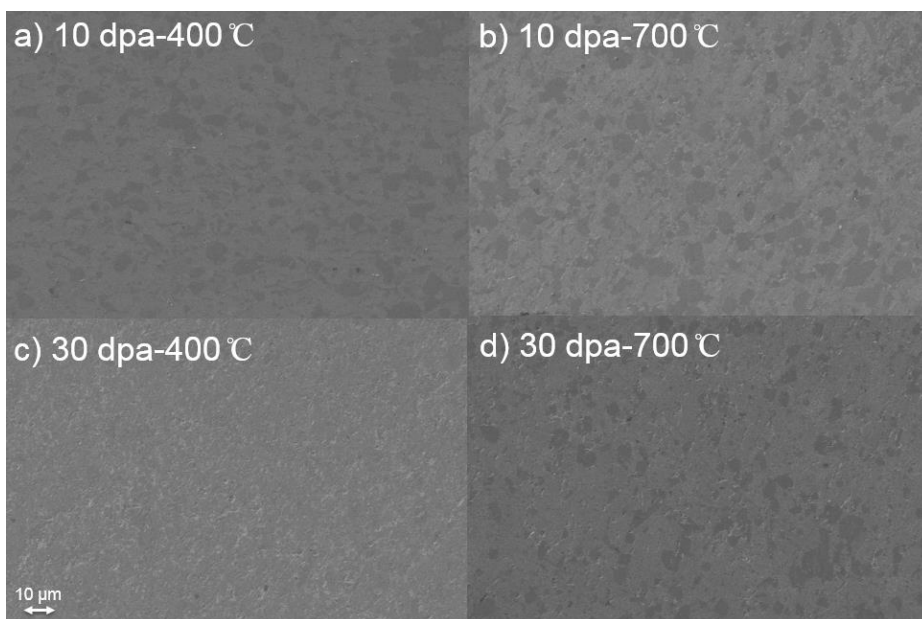


Figure 6.3 SEM surface images of Ni ion irradiated Ti_3SiC_2 for (a) 10 dpa-400 °C, (b) 10 dpa-700 °C, (c) 30 dpa-400 °C, and (d) 30 dpa-700 °C irradiation conditions.

length to provide a quantitative measure of the cracked grain boundary area per unit volume (S_v) using the formula $S_v=2N$ where N is the average number of cracked grain boundary intersections per unit length of randomly drawn surface lines [56]. This crack density parameter does not take into account other crack features that might have an impact on structural integrity, such as average crack length, but was used instead as a quantitative means for determining cracking severity. A summary of these measured values of grain boundary cracked surface per unit volume is given in Table 4. As can be seen, there is no discernable difference in the linear crack densities between the same aluminum MAX phase materials at different doses at 400 °C, though the Ti_2AlC does appear to have a slightly higher crack density than the Ti_3AlC_2 . As noted earlier, surface cracking was not observed in Ti_3SiC_2 for either dose at 400 °C, and no surface cracking was observed in any of the three materials irradiated at either dose at 700 °C.

Table 4 Irradiation-induced surface cracking per unit volume in Ti_3AlC_2 and Ti_2AlC irradiated at 400 °C.

Condition	S_v (1/ μ m)	Std. Dev.
Ti_3AlC_2 -10 dpa-400 °C	1.52E-01	9.72E-03
Ti_3AlC_2 -20 dpa-400 °C	1.49E-01	8.25E-03
Ti_2AlC -10 dpa-400 °C	2.13E-01	1.33E-02
Ti_2AlC -30 dpa-400 °C	1.97E-01	1.63E-02

6.2 XRD Results

The GXRD patterns collected from the Ti_3AlC_2 irradiation samples at low dose (10 dpa) and high dose (30 dpa) conditions can be seen in Fig. 6.4 and Fig. 6.5 respectively, where (a) denotes low temperature (400 °C), (b) high temperature (700 °C), and (c) pristine conditions. The graphics are presented in

such a way that, going from bottom to top, it can easily be seen that there is a significant temperature dependence on the disruption of the diffraction patterns. It can also be seen, that when comparing Fig. 6.4 to Fig. 6.5, there is very little variation in the irradiated diffraction patterns with increasing dose from 10 dpa to 30 dpa, with the sole exception of the high dose, high temperature (30 dpa-700 °C) sample, which was believed to have an artifact associated with the surface contamination accrued during the irradiation (as discussed in section 6.1). Additionally, determining lattice parameter changes for all four irradiation conditions yielded virtually identical results for samples irradiated at the same temperature but different doses. For these reasons, and in order to save time and cost, the following two materials, Ti_2AlC and Ti_3SiC_2 , were only analyzed using GXRd at the high dose irradiation conditions (30 dpa), with only the high dose Ti_3AlC_2 patterns being used for comparison. The GXRd patterns collected from the Ti_2AlC and Ti_3SiC_2 samples at (a) high dose, low temperature (30 dpa-700 °C), (b) high dose, high temperature (30 dpa-700 °C), and (c) pristine conditions are shown in Figs. 6.6 and 6.7 respectively.

In all cases, the ion irradiation resulted in augmentation of the diffraction pattern through reduction of the peak heights, broadening, and shifting of the peak locations. In all three materials, there is significantly less disruption of the diffraction pattern at the 30 dpa-700 °C condition than at the 30 dpa-400 °C condition. Consequently, there are only slight differences in the pristine and 30 dpa-700 °C diffraction patterns for all three materials, with the Ti_3AlC_2 30 dpa-700 °C sample exhibiting the most change. Further examinations of the diffraction patterns shows that the Ti_3SiC_2 irradiated samples appear to show the least disturbance due to irradiation, with very little peak shift and only slight peak reduction and broadening. Consequently, only minor diffraction peaks are lost for this material at the 30 dpa-400 °C condition. In stark contrast, both aluminum based MAX phases appear to have suffered significant damage at the 30 dpa-400 °C irradiation. Only the largest diffraction peaks are still visible in Ti_2AlC and

both the both aluminum MAX phases exhibit peaks that are not prevalent in the pristine samples, suggesting large shifts and/or emergence of new peaks.

Manipulation of the ICSD diffraction pattern peak positions to match the observed data using Highscore Plus yielded nominal lattice parameter changes for each material. A summary of these calculated values can be seen in Table 5.

In all three MAX phases, there was a pronounced increase in the c-LP at the 30 dpa-400 °C irradiation condition, with a less significant increase of the c-LP in the Ti₃AlC₂ and only minimal change for the Ti₂AlC, and Ti₃SiC₂ at the 30 dpa-700 °C irradiation condition. At the 30 dpa-400 °C condition, the Ti₂AlC exhibited the highest c-LP swelling, with an increase from 13.41(5) Å to 13.74(8) Å, an increase of approximately 2.46%. The Ti₃SiC₂ exhibited the least amount of c-LP swelling for irradiation at 400 °C, with an increase of 17.65(4) Å to 17.72(6) Å, corresponding to a relative increase of approximately 0.40%. For the 30 dpa-400 °C irradiation condition, Ti₃AlC₂ fell in between with an increase of 18.54(6) Å to 18.74(9) Å, or 1.08%. For the 30 dpa-700 °C condition, only the Ti₃AlC₂ exhibited lattice parameter swelling, which was limited to 0.38%, from 18.54(6) Å to 18.61(3) Å. Both the Ti₂AlC, and Ti₃SiC₂ exhibited slight contraction from pristine c-LP values at the 30 dpa-700 °C condition.

With respect to the a-LP, both aluminum MAX phases exhibit a slight a-LP reduction at the 30 dpa-400 °C condition with minimal change at the 30 dpa-700 °C condition, while the silicon based MAX phase exhibits a slight a-LP increase at both irradiation conditions. The Ti₂AlC shows the most a-LP contraction at the 30 dpa-400 °C irradiation condition, decreasing from 3.061(8) Å to 3.04(1) Å, a change of 0.69%. The Ti₃AlC₂ exhibits a less exaggerated reduction, going from 3.0735(7) Å to 3.065(5) Å, a 0.28% change at the 30 dpa-400 °C condition. Both aluminum MAX phases exhibit only slight change at the 30 dpa-700 °C irradiation condition (absolute change of 0.2% or less). The silicon base MAX phase exhibits a slight increase in the a-LP at both the 30 dpa-400 °C and 30 dpa-700 °C irradiation conditions, going from 3.059(4) Å to 3.069(3) Å and 3.067(3) Å, a 0.33% and 0.26% respective increase. A plot of both the relative (a) c-LP and (b)

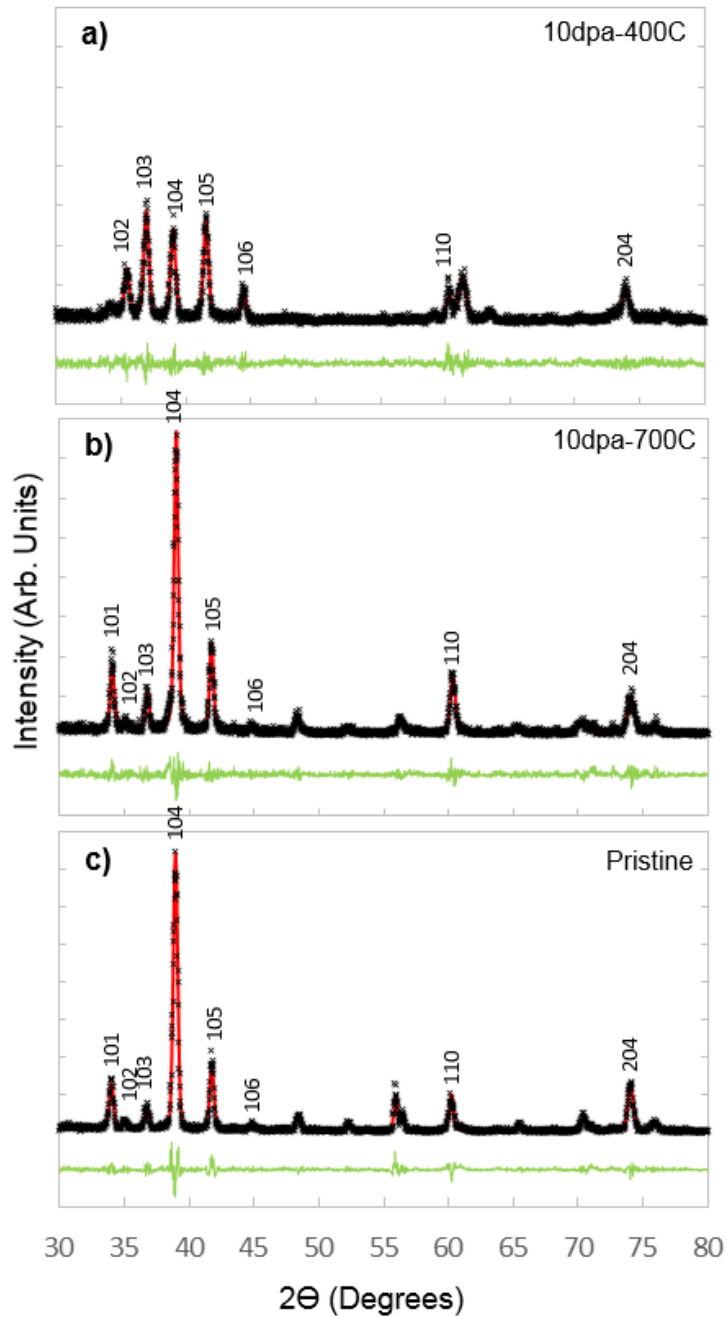


Figure 6.4 GXRD spectra of Ti_3AlC_2 irradiated to a midrange dose of 10 dpa using 5.8 MeV Ni ions at (a) 10 dpa-400 °C, (b) 10 dpa-700 °C, and (c) Pristine Ti_3AlC_2 . Black data points, solid red lines, and solid green lines represent the observed data, calculated model, and the difference between the two respectively.

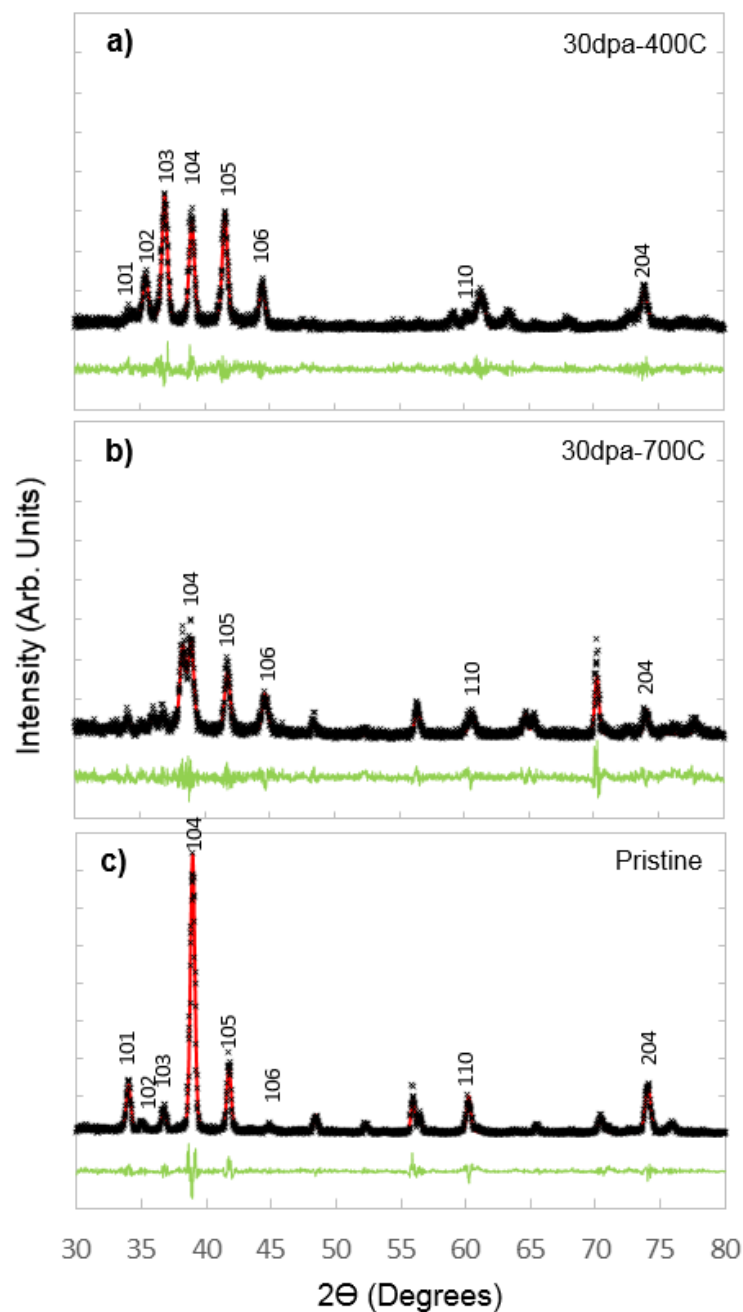


Figure 6.5 GXRD spectra of Ti_3AlC_2 irradiated to a midrange dose of 30 dpa using 5.8 MeV Ni ions at (a) 30 dpa-400 °C, (b) 30 dpa-700 °C, and (c) Pristine Ti_3AlC_2 . Black data points, solid red lines, and solid green lines represent the observed data, calculated model, and the difference between the two respectively.

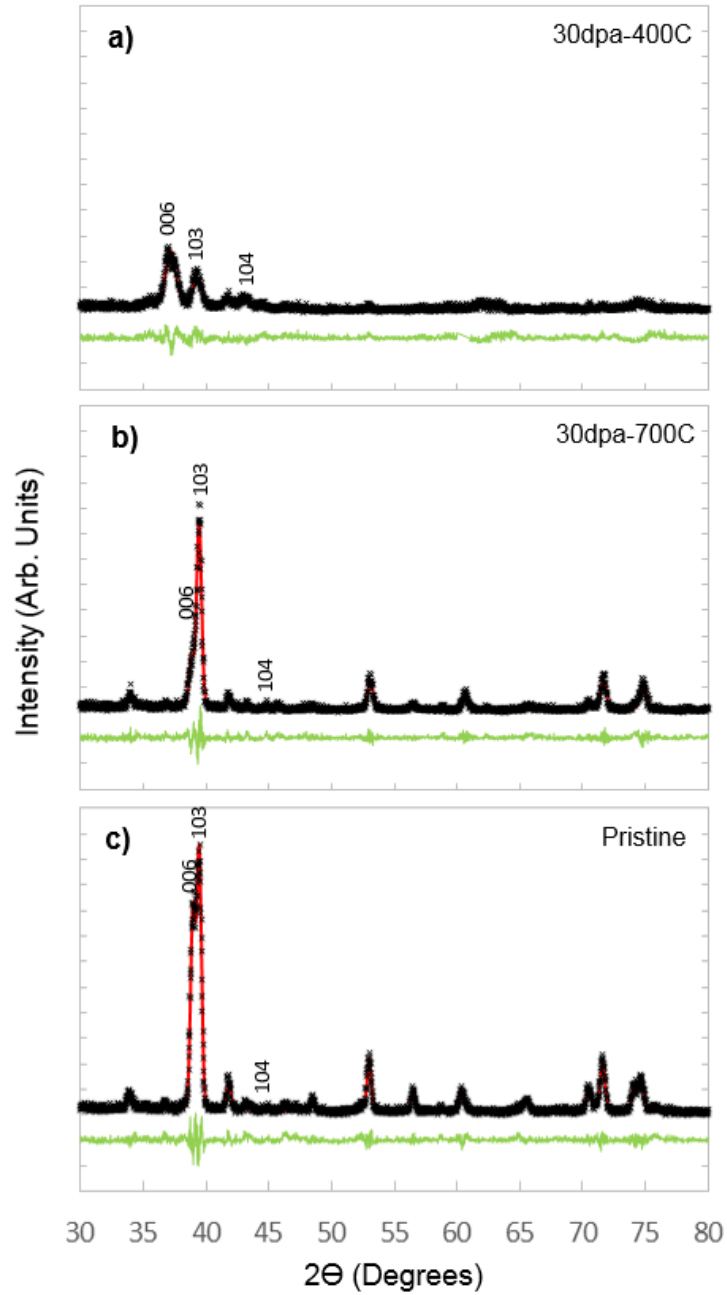


Figure 6.6 GXRD spectra of Ti_2AlC irradiated to a midrange dose of 30 dpa using 5.8 MeV Ni ions at (a) 30 dpa-400 °C, (b) 30 dpa-700 °C, and (c) Pristine Ti_2AlC . Black data points, solid red lines, and solid green lines represent the observed data, calculated model, and the difference between the two respectively.

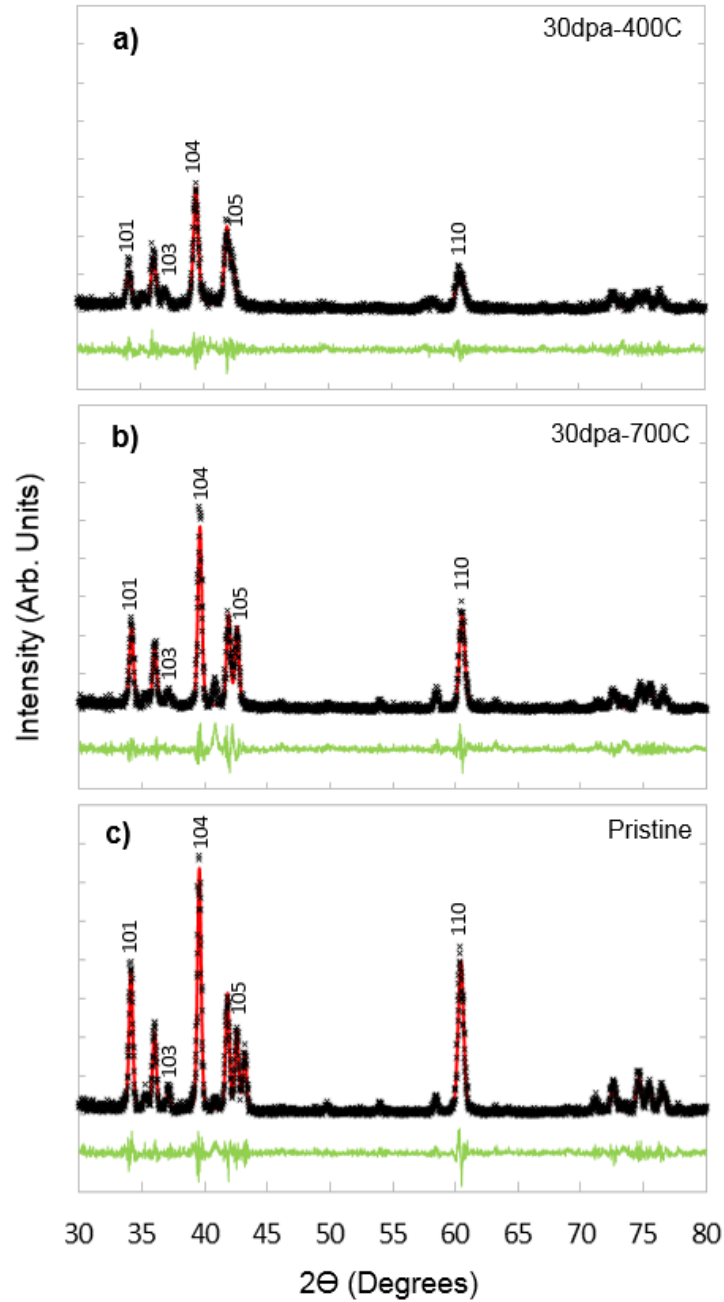


Figure 6.7 GXR D spectra of Ti_3SiC_2 irradiated to a midrange dose of 30 dpa using 5.8 MeV Ni ions at (a) 30 dpa-400 °C, (b) 30 dpa-700 °C, and (c) Pristine Ti_3SiC_2 . Black data points, solid red lines, and solid green lines represent the observed data, calculated model, and the difference between the two respectively.

Table 5 Irradiation-induced structural changes in Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 for irradiation up to 30 dpa at 400 °C and at 700 °C.

Condition	a-LP (Å)	Δ a-LP (%)	c-LP (Å)	Δ c-LP (%)
Ti_3AlC_2 -Pristine	3.0735(7)	-	18.54(6)	-
Ti_3AlC_2 -10 dpa-400 °				
C	3.068(6)	-0.18	18.74(7)	1.08
Ti_3AlC_2 -10 dpa-700 °				
C	3.070(1)	-0.11	18.60(1)	0.32
Ti_3AlC_2 -30 dpa-400 °				
C	3.065(5)	-0.28	18.74(9)	1.08
Ti_3AlC_2 -30 dpa-700 °				
C	3.076(3)	0.08	18.61(3)	0.38
Ti_2AlC -Pristine	3.061(8)	-	13.41(5)	-
Ti_2AlC -30 dpa-400 °				
C	3.04(1)	-0.69	13.74(8)	2.46
Ti_2AlC -30 dpa-700 °				
C	3.055(7)	-0.20	13.38(5)	-0.22
Ti_3SiC_2 -Pristine	3.059(4)	-	17.65(4)	-
Ti_3SiC_2 -30 dpa-400 °				
C	3.069(3)	0.33	17.72(6)	0.40
Ti_3SiC_2 -30 dpa-700 °				
C	3.067(3)	0.26	17.61(3)	-0.23

Numbers in parentheses represent one standard deviation of the last significant digit.

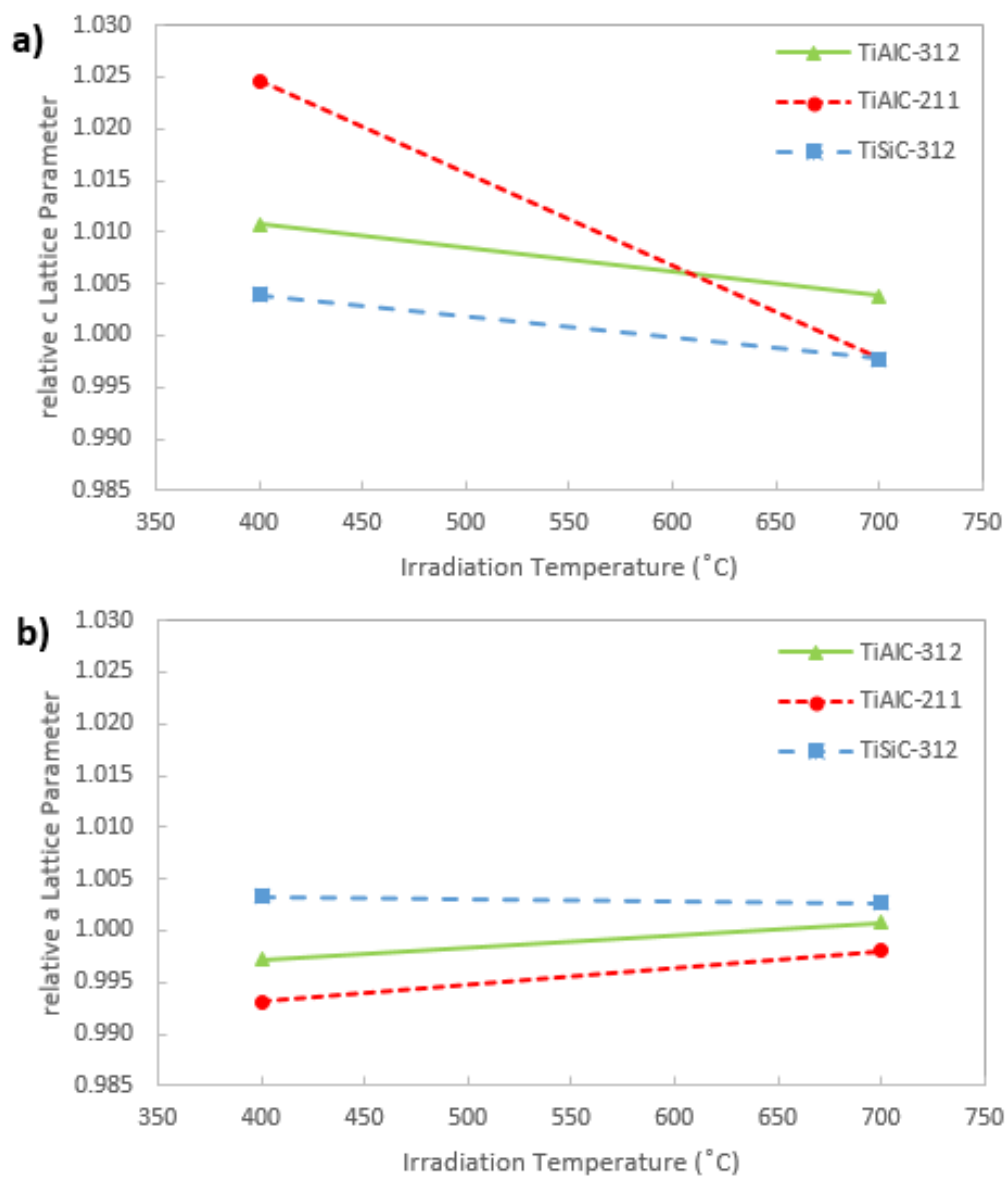


Figure 6.8 Temperature dependent relative lattice parameter shifts at 30 dpa midrange dose for (a) c-LP and (b) a-LP.

a-LP shifts post irradiation can be seen in Fig. 6.8. It should be noted that large differences in c-axis and a-axis swelling will produce pronounced strains at randomly oriented grain boundaries and can result in grain boundary cracking depending on the magnitude of anisotropic swelling and material parameters. The results obtained from GXRD support this anisotropic swelling as the underlying cause for grain boundary cracking in the 400 °C irradiated aluminum MAX phases.

6.3 Nanoindentation

Plots of relative hardness as function of indentation depth for all irradiations conditions and materials are shown in Fig. 6.9. These plots provide the raw data from which the information regarding radiation induced hardness was drawn. As previously discussed, the Nix-Gao methodology was used to determine the thin film transition depth for each irradiated material. Example plots can be seen in Fig. 6.10, showing (a) unirradiated Ti_2AlC and (b) Ti_2AlC irradiated at 400 °C to a midrange dose of 10dpa. It can be seen, that for an unirradiated material, the Nix-Gao plot results in a linear curve, indicating no depth-dependence of the intrinsic hardness. However, for the irradiated material, there are two distinct segments, the first being the irradiated only region for high values of $1/h$ (i.e. relatively shallow indent depths, h), and the second being the combined irradiated and bulk-unirradiated region. The indenter depth transition between these two regions was found to be approximately 400 nm in all of the 5.8 MeV Ni ion irradiated samples. Therefore the hardness value measured at a depth of 400 nm or shallower represents the hardness obtained entirely within the ion irradiated region, without contributions from the bulk substrate. The average hardness values over the range of 200-400 nm for different irradiation conditions were then compared to one another to determine relative radiation hardening for the three materials. The data collected below 200 nm indentation depth was removed due to large statistical scatter associated with surface imperfections from the mechanical polishing.

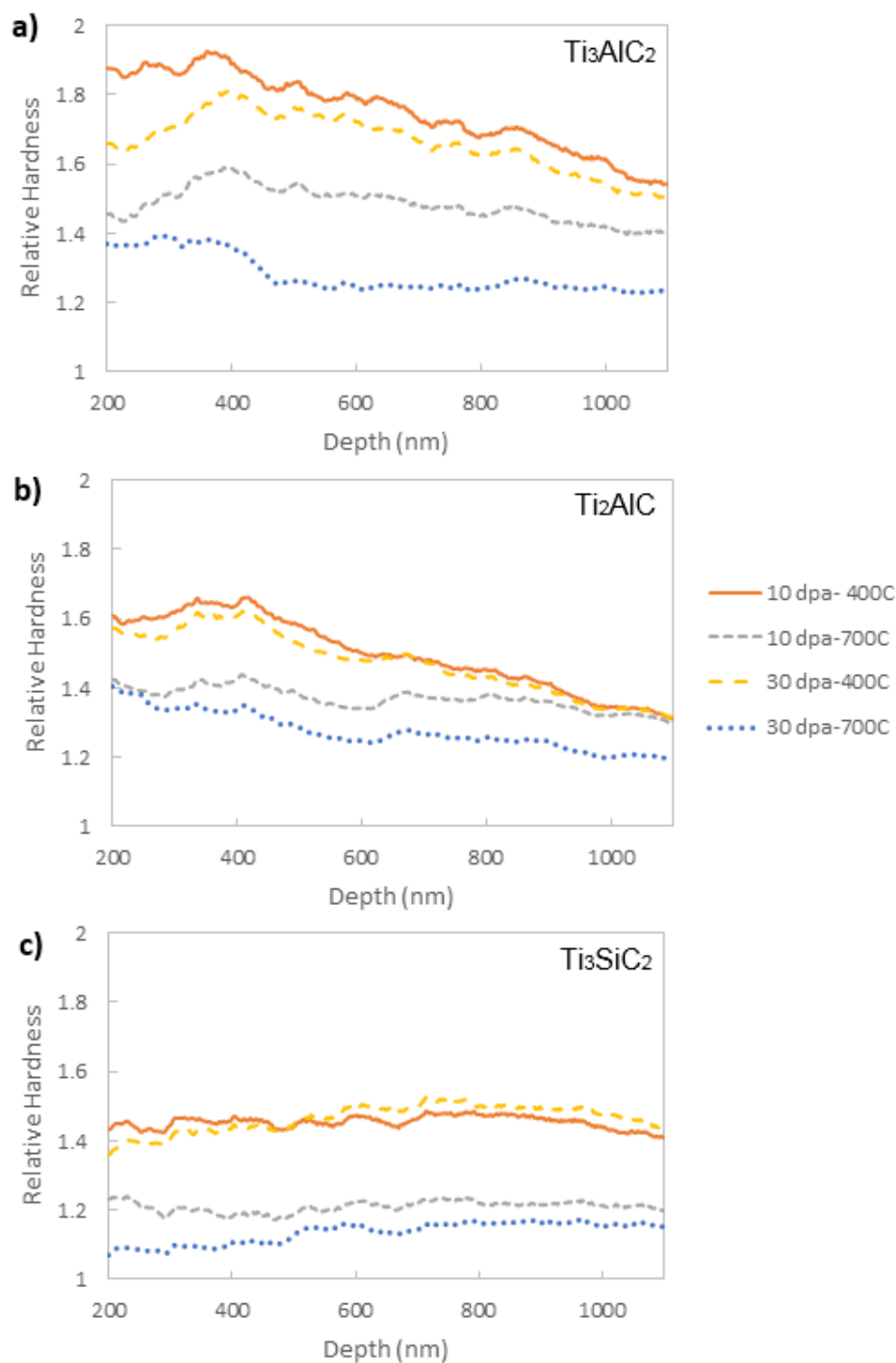


Figure 6.9 Normalized hardness as a function of indentation depth in irradiated (a) Ti_3AlC_2 , (b) Ti_2AlC , and (c) Ti_3SiC_2 by 5.8 MeV Ni ions at the four experimental irradiation conditions.

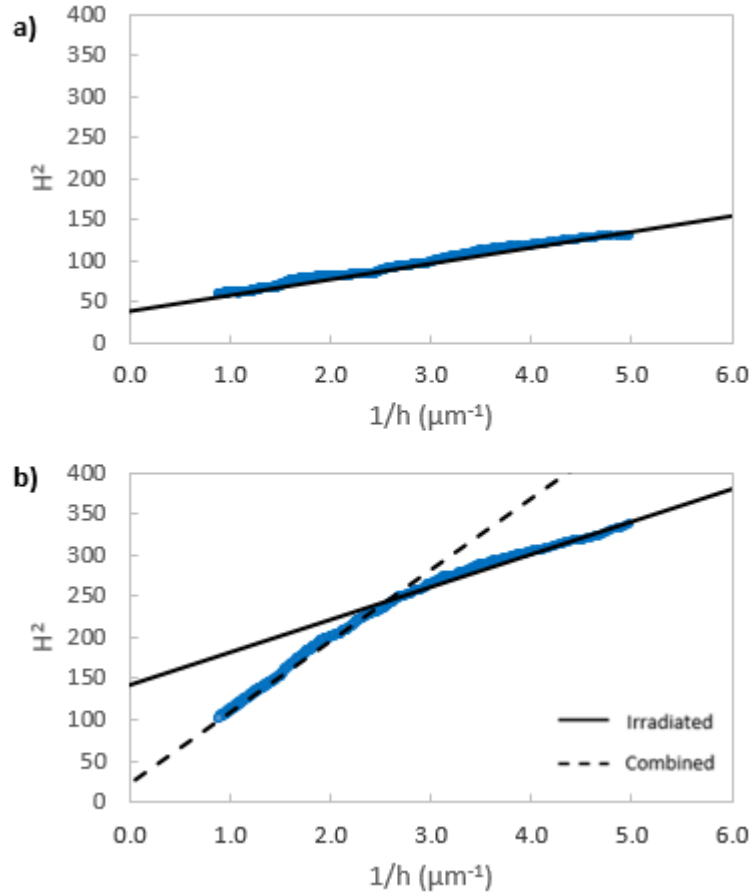


Figure 6.10 Nix-Gao plots of the hardness data for (a) unirradiated Ti_2AlC and (b) Ti_2AlC irradiated at 400°C to a midrange dose of 10 dpa.

The evolution of hardness as a function of irradiation dose averaged over 200-400 nm for the three MAX phase materials can be seen at (a) 400°C and (b) 700°C in Fig. 6.11. It can be seen that for all three materials at both 400°C and 700°C , there is significant increase in hardness from the pristine samples to the irradiated samples, due to radiation induced defects, as discussed in Chapter 2. Of the three materials, Ti_3AlC_2 exhibits the most radiation hardening up to a maximum of approximately 1.9x for the low temperature irradiations and 1.6x for high temperature irradiations. In comparison, Ti_3SiC_2 exhibits the least amount of hardening at both the low and high temperature irradiation conditions with a

maximum of approximately 1.4x and 1.2x respectively. The Ti_2AlC falls in between the other materials with a maximum relative hardening of approximately 1.6x at the low temperature condition and 1.4x at the high temperature condition. Additionally, it can be seen that there is little variation in hardness from samples irradiated at to a midrange dose of 10 dpa and those irradiated to a midrange dose of 30 dpa, for both irradiation temperatures. This suggests a saturation effect in the radiation induced hardening has occurred for a dose of 10 dpa and higher. As noted for the GXRD results in the previous section, the surface contamination of the 30 dpa- 700 °C was believed to have induced significant error on the nanoindentation results associated with this sample. As such, as dose increases from 10 to 30 dpa for Ti_3AlC_2 at the 700 °C irradiation temperature, the relative hardness of an uncontaminated sample is expected to stay constant, as is consistent with radiation hardness saturation, rather than the significant decrease as observed in the measured results.

The effect of irradiation temperature on hardness for all three materials at a midrange dose of (a) 10 dpa and (b) 30 dpa can be seen in Fig. 6.12. From this figure, it becomes apparent that there is a significantly less hardening at an irradiation temperature of 700 °C than at an irradiation temperature of 400 °C for all three materials. This suggest a positive correlation between irradiation temperature and radiation induced hardness.

Plots of relative elastic modulus (ratio of irradiated to unirradiated) as function of indentation depth for all irradiations conditions and materials are shown in Fig. 6.13. These plots provide the raw data from which the information regarding elastic modulus was drawn.

The evolution of the relative elastic modulus of the three materials as a function of irradiation dose averaged over 200-400 nm can be seen in Fig. 6.14 for (a) 400 °C and (b) 700 °C, and as a function of irradiation temperature in Fig. 6.15 for (a) 10 dpa midrange dose and (b) 30 dpa midrange dose. For irradiated

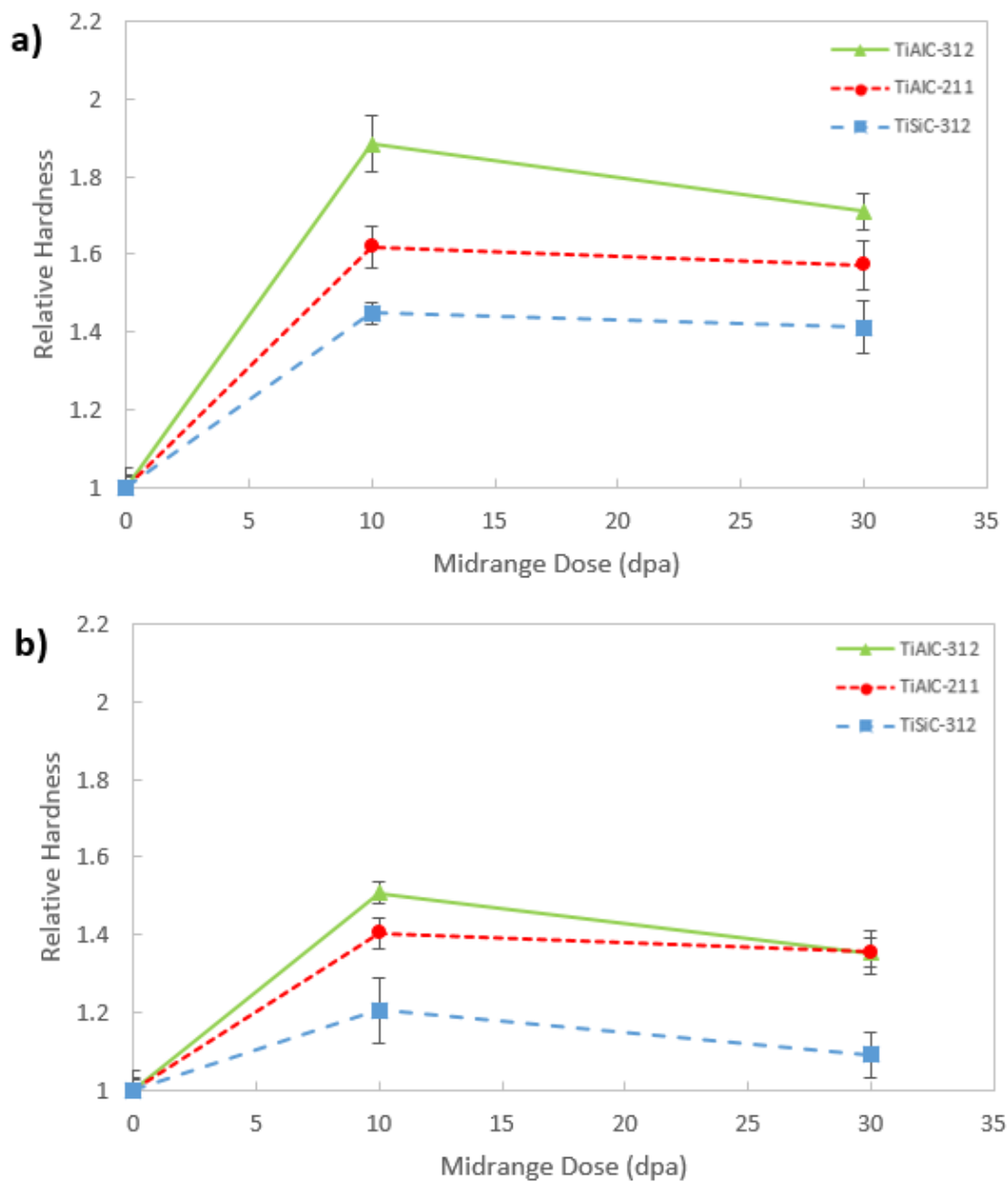


Figure 6.11 Normalized hardness dose dependence in irradiated Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 by 5.8 MeV Ni ions at (a) 400 °C and (b) 700 °C.

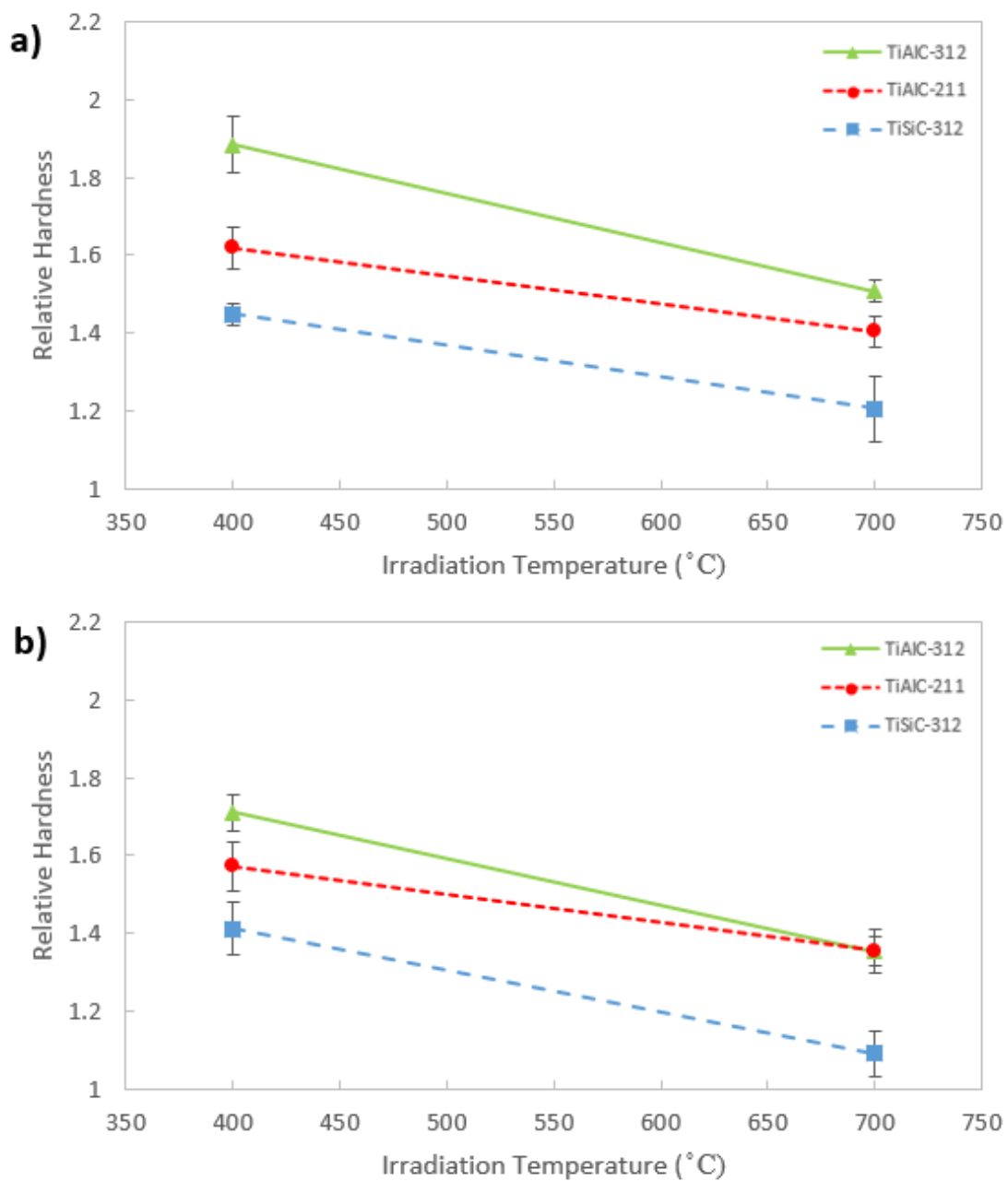


Figure 6.12 Normalized hardness temperature dependence in irradiated Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 by 5.8 MeV Ni ions at midrange doses of (a) 10 dpa and (b) 30 dpa.

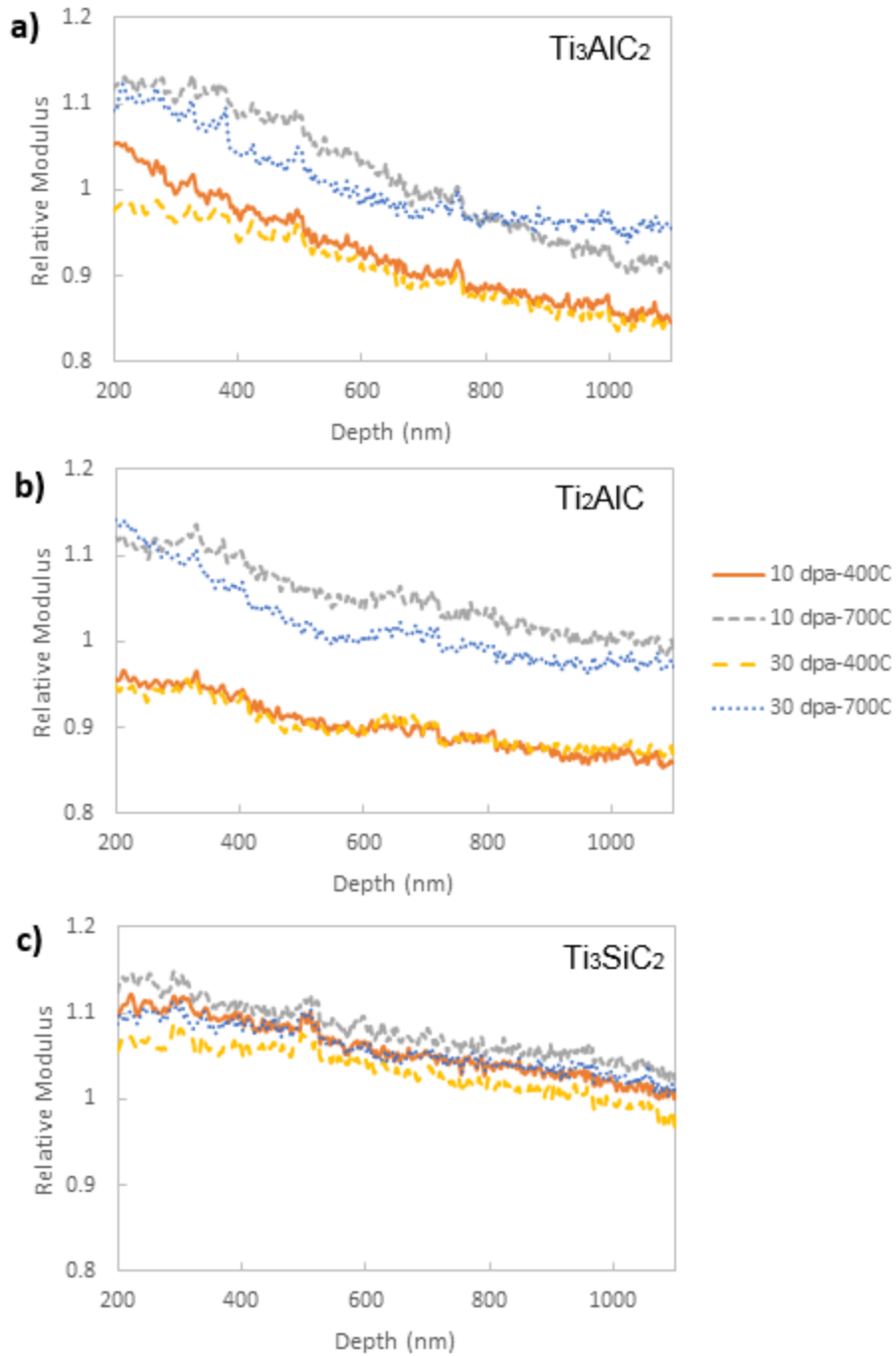


Figure 6.13 Normalized elastic modulus as a function of indentation depth in irradiated (a) Ti_3AlC_2 , (b) Ti_2AlC , and (c) Ti_3SiC_2 by 5.8 MeV Ni ions at the four experimental irradiation conditions.

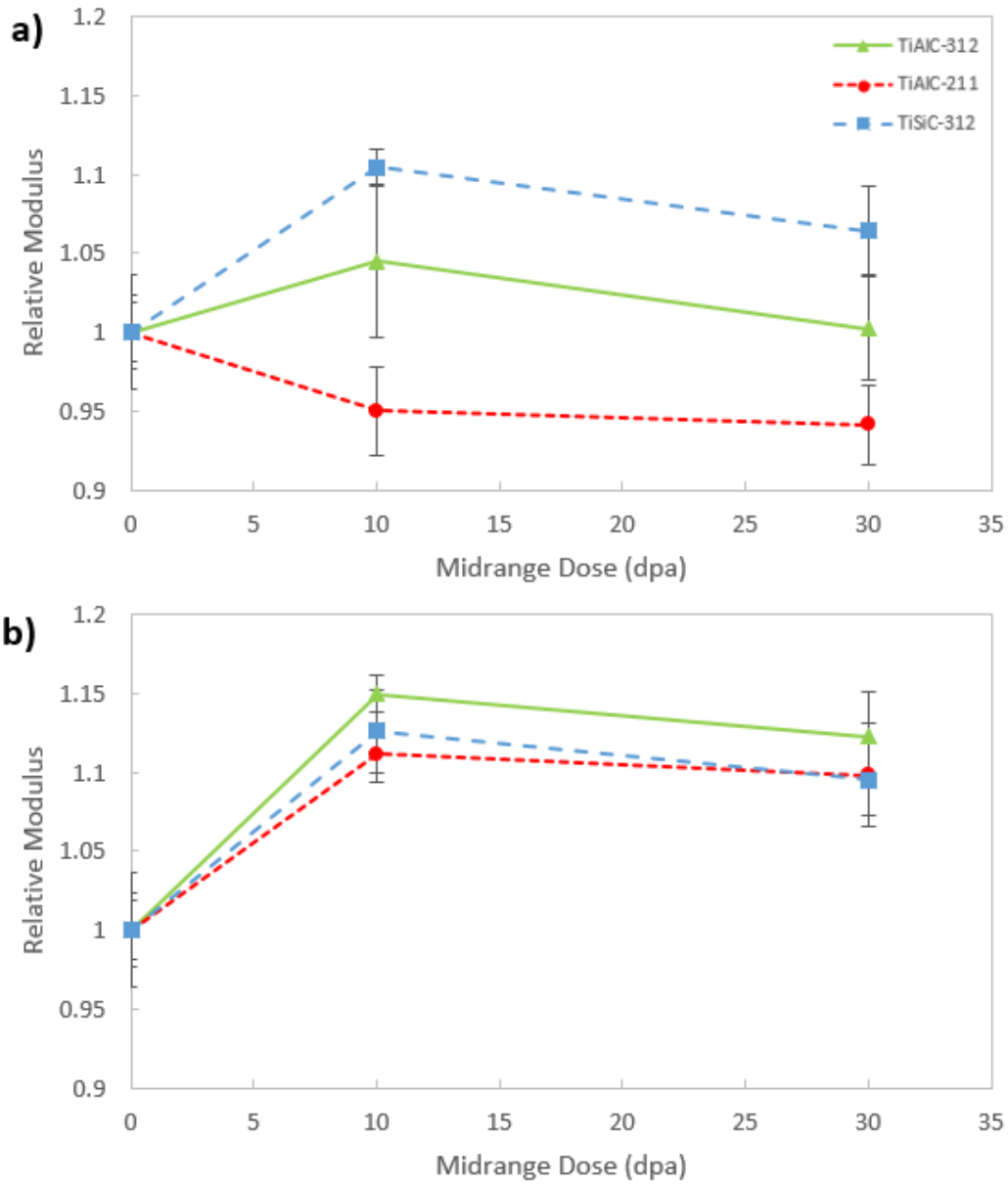


Figure 6.14 Normalized elastic modulus dose dependence in irradiated Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 by 5.8 MeV Ni ions at (a) 400 °C and (b) 700 °C.

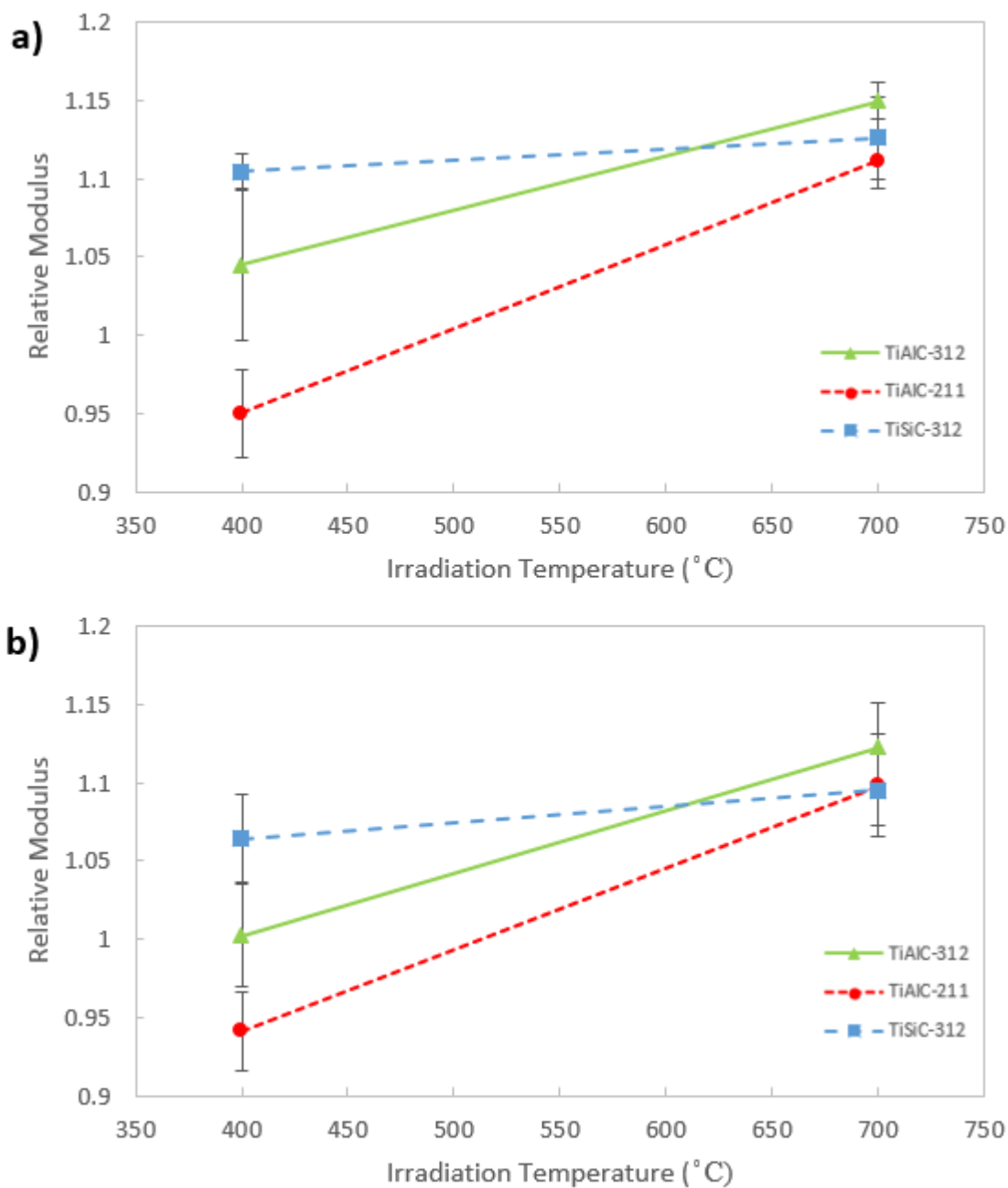


Figure 6.15 Normalized elastic modulus temperature dependence in irradiated Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 by 5.8 MeV Ni ions at midrange doses of (a) 10 dpa and (b) 30 dpa.

materials there is expected to be a slight change in the elastic modulus that saturates after relatively small amounts of damage, similar to irradiation induced hardness. Upon examination, it appears that all of the irradiated samples follow this trend, with the majority of samples experiencing a slight elastic modulus increase of approximately 10%. The exception to this trend are the low temperature irradiations of the aluminum MAX phases, in which Ti_3AlC_2 exhibited little to no change in elastic modulus and Ti_2AlC exhibited a slight decrease in elastic modulus of about 6%. This behavior is indicative of a radiation induced effect not found in other samples.

SEM examination was used following indentation hardness testing to observe the surface features associated with nanoindentation. Imaging the surface indents, it was seen that for the 400 °C irradiated aluminum MAX phase surfaces (those that experienced cracking), the indenter produced significant corner cracking. For the un-cracked aluminum and all the silicon based MAX phase surfaces, the indentation did not induce corner cracking and features analogous to that of indentation on pristine MAX phase, such as slip bands/delamination and push-out, are observed. Figures 6.16, 6.17 and 6.18 show indents in surfaces irradiated at the (a) 10 dpa-400 °C and (b) 10 dpa-700 °C conditions in Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 respectively.

6.4 TEM Cross Section Analysis

Following SEM, GXR, and nanoindentation, TEM cross section analysis was used to quantify microstructural defects in several ion irradiated MAX phase materials. Due to machine usage and time constraints, only a limited number of samples were able to be analyzed. Therefore, the samples chosen were those that were thought to be most relevant to the questions raised by the previous SEM surface, XRD, and nanoindentation analysis, the most important of which are why are the aluminum based MAX phase sample cracking at the 400 °C irradiation conditions and not cracking following 700 °C irradiation, as well as are

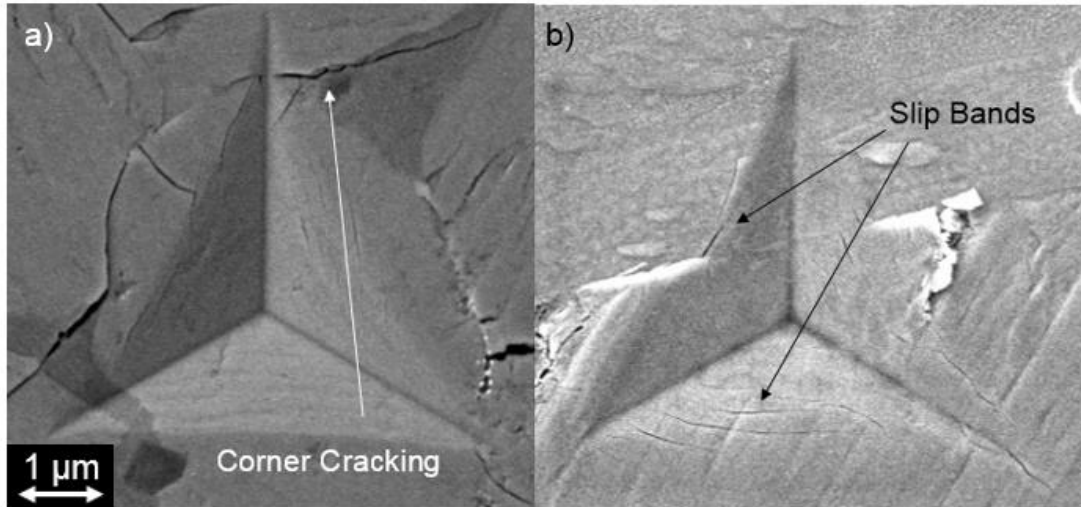


Figure 6.16 SEM morphology of indents on (a) 10 dpa-400 °C, and (b) 10 dpa-700 °C Ni ion irradiated Ti_3AlC_2 .

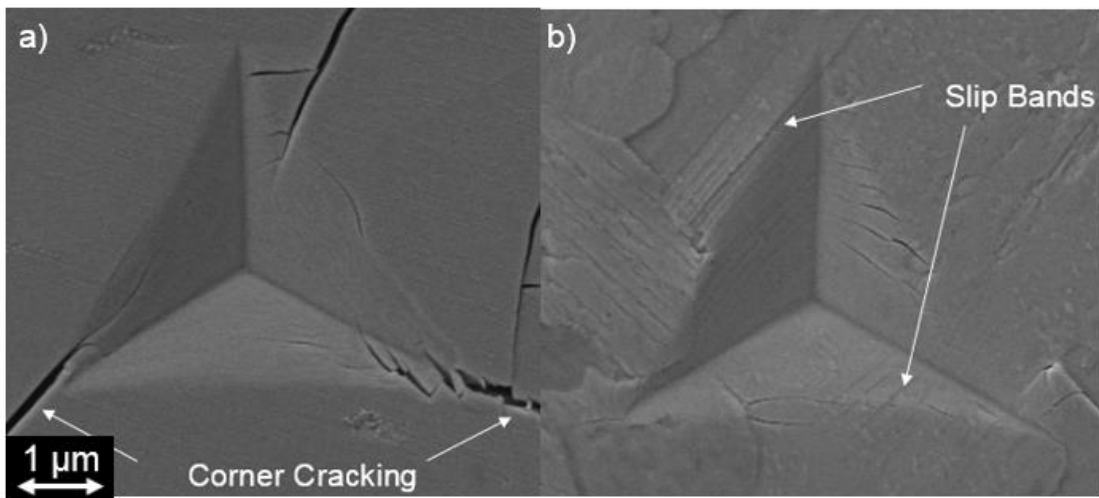


Figure 6.17 SEM morphology of indents on (a) 10 dpa-400 °C, and (b) 10 dpa-700 °C Ni ion irradiated Ti_2AlC .

vacancies sufficiently mobile to produce observable cavity formation in either the aluminum or silicon based MAX phase at 700 °C. Assuming that both the aluminum MAX phases would exhibit qualitatively similar microstructural evolution under irradiation (due to their qualitatively similar response in terms of lattice parameter changes, hardening, and surface cracking propensity), the samples deemed as highest priority for TEM analysis were Ti_3AlC_2 30 dpa-400 °C, Ti_3AlC_2 30 dpa-700 °C, and Ti_3SiC_2 30 dpa-700 °C.

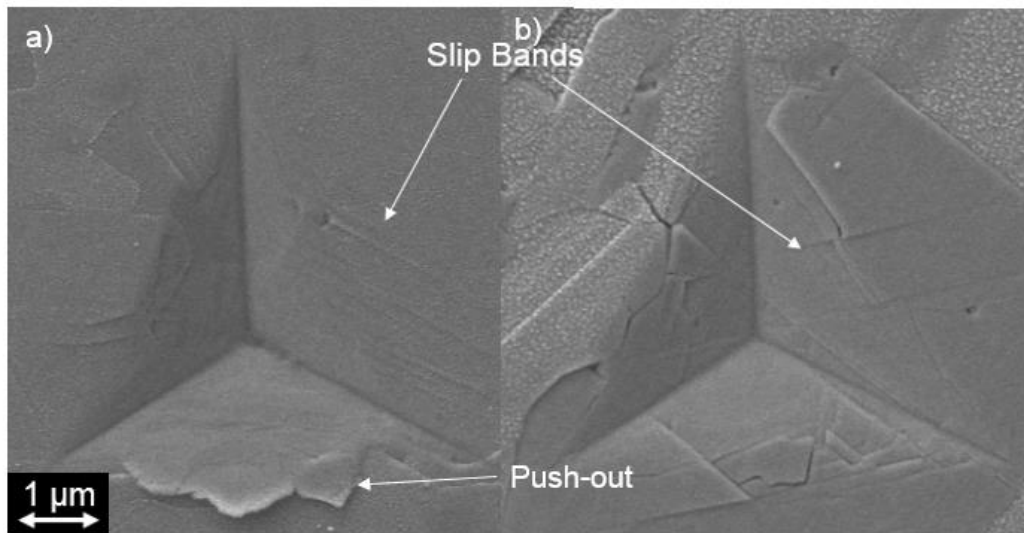


Figure 6.18 SEM morphology of indents on (a) 10 dpa-400 °C, and (b) 10 dpa-700 °C Ni ion irradiated Ti_3SiC_2 .

A low-magnification TEM micrograph of the Ti_3AlC_2 30 dpa-400 °C cross-section foil and SAED results for the underlying unirradiated region (2) can be seen in Fig. 6.19. The green arrow represents the direction of ion irradiation, which penetrated to a depth of approximately 3 μm, as displayed by the white line denoting the separation of the irradiated area and non-irradiated bulk. This is consistent with SRIM ion penetration depth calculations provided in Chapter 4. Before micrographs of the irradiated region were taken, SAED was used on the unirradiated region, well beyond the range of the ions (2) (displayed in the upper right hand corner), in order to determine both the phase and orientation of the

grain. Comparing experimental and ICSD diffraction pattern spacing, the grain was confirmed to be the nominal Ti_3AlC_2 phase and the beam direction for this tilt condition was determined to be the $\langle 11\bar{2}0 \rangle$ prismatic direction.

Following this confirmation of phase and beam direction, standard two-beam conditions were used to obtain bright field and dark field images along the $\langle 0001 \rangle$ (basal) and $\langle 1\bar{1}00 \rangle$ (prism) zone axis for both the unirradiated (2) and irradiated (1) regions of Ti_3AlC_2 irradiated to 30 dpa at 400°C , as shown in Figs. 6.20 and 6.21 respectively. It is important to note that the irradiated region (1) was chosen at a depth of $\sim 1.5\ \mu\text{m}$, corresponding to the nominal midrange dose of 30 dpa. As can be seen in both the basal and prism zone axis in Figs. 6.20, in the pristine region, there is only a low density of dislocations or large defect clusters, which is typical of unirradiated materials. On the contrary, for both the basal and prismatic zone axis in the 400°C irradiated materials shown in Fig. 6.21, there is a large density of “black spots” or small defect clusters, with a distinct lack of voids, which was confirmed using under- and over-focusing techniques. The very high density of defect clusters visible in these images suggest a saturation of interstitial point defects in the irradiated area induced through nuclear displacements.

A TEM micrograph of the entire Ti_3AlC_2 30 dpa- 700°C cross-section foil and SAED results for the underlying unirradiated region (2) can be seen in Fig. 6.22. As can be seen, the ion irradiated region extended to a depth of approximately $2.6\ \mu\text{m}$ and is consistent with SRIM ion penetration depth calculations when taking into consideration the sample surface contamination discovered during SEM analysis. Again, before any micrographs of the irradiated region were taken, SAED was performed on the unirradiated region, well beyond the range of the ions (2) (displayed in the upper right hand corner), in order to determine both the phase and orientation of the grain. Comparing experimental and ICSD diffraction pattern spacing, the grain was confirmed to be the nominal

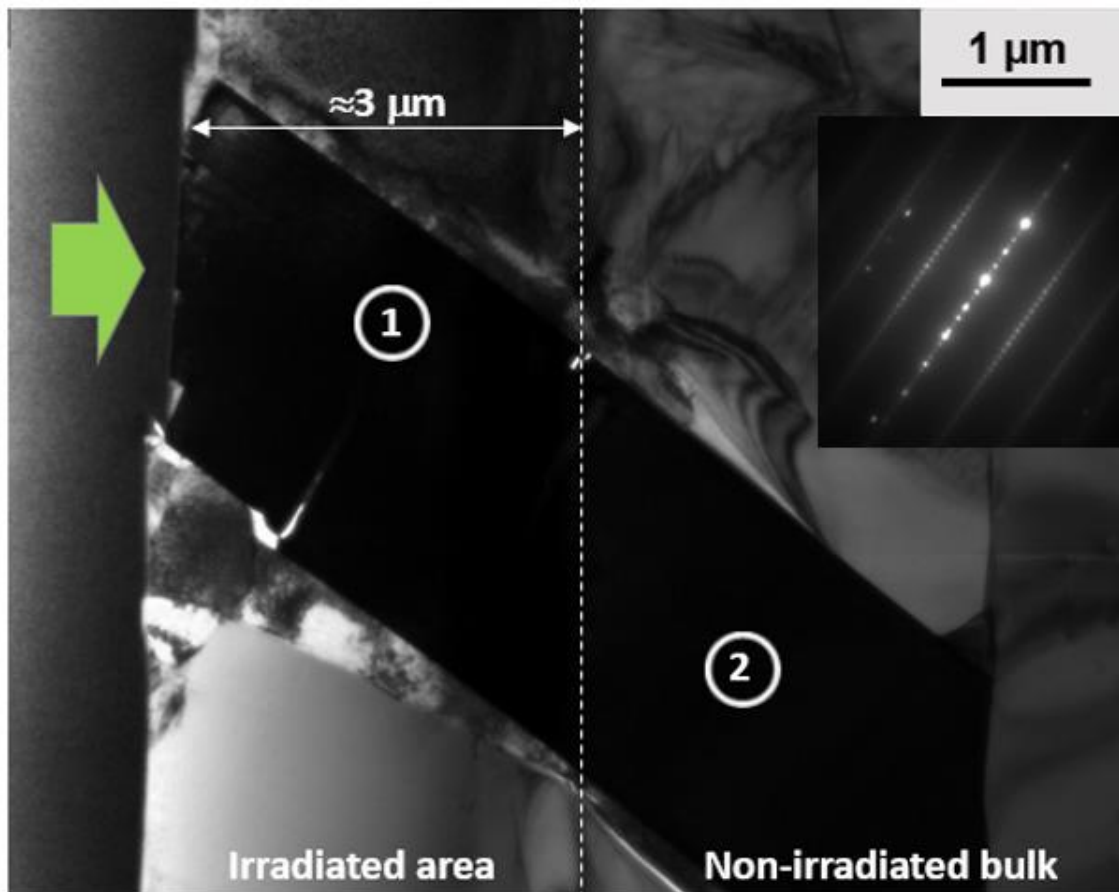


Figure 6.19 Cross-sectional TEM micrograph of the full Ti_3AlC_2 foil irradiated to 30 dpa at 400 °C using 5.8 MeV Ni ions, with ion direction denoted by the green arrow. The dashed white line denotes the transition depth between the ion irradiated area and the non-irradiated bulk. Region 1 denotes the selected area for ion radiation damage characterization and Region 2 denotes the selected area for pristine crystal characterization. SAED pattern for the pristine crystal can be seen in the upper right-hand corner.

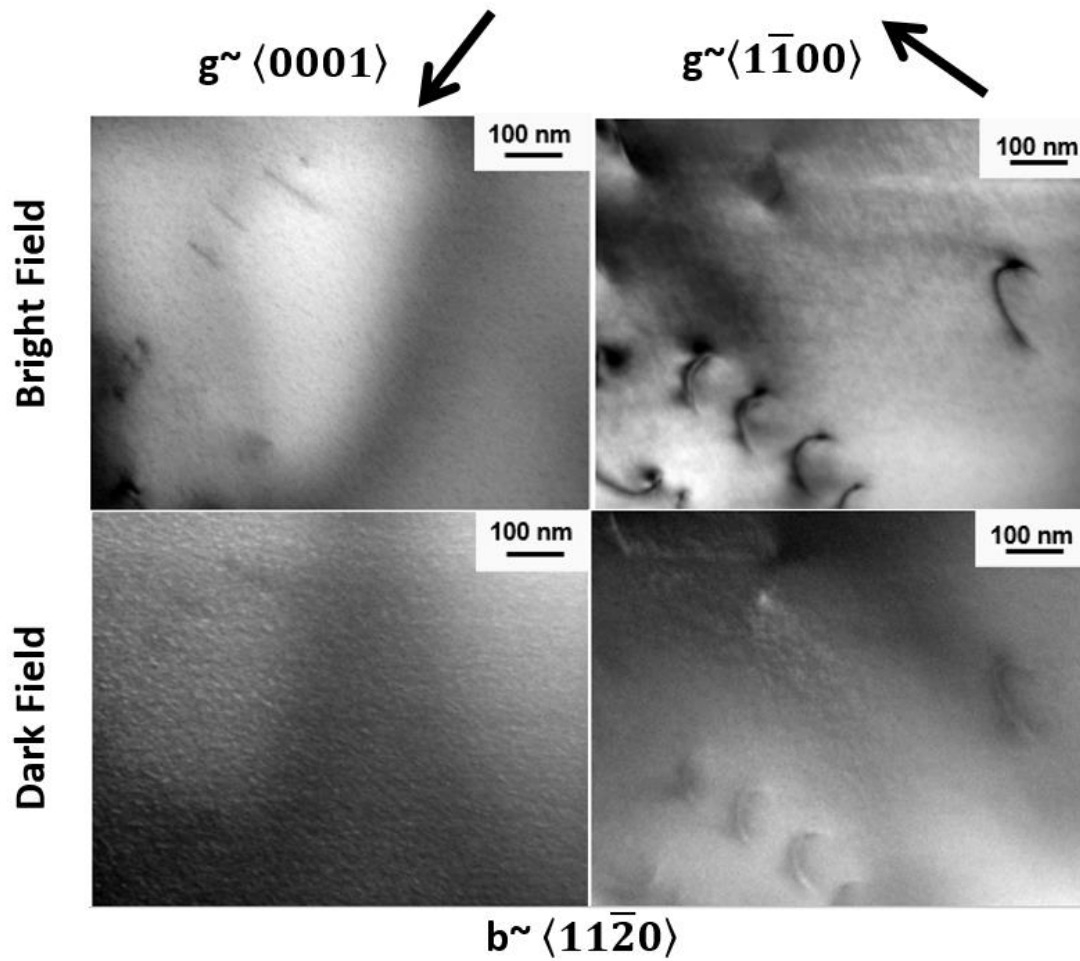


Figure 6.20 High magnification bright field and dark field cross-sectional TEM micrographs of pristine Ti_3AlC_2 (region 2). The basal and prism zone axis directions are indicated by $\langle 0001 \rangle$ and $\langle 1\bar{1}00 \rangle$ diffraction vectors respectively.

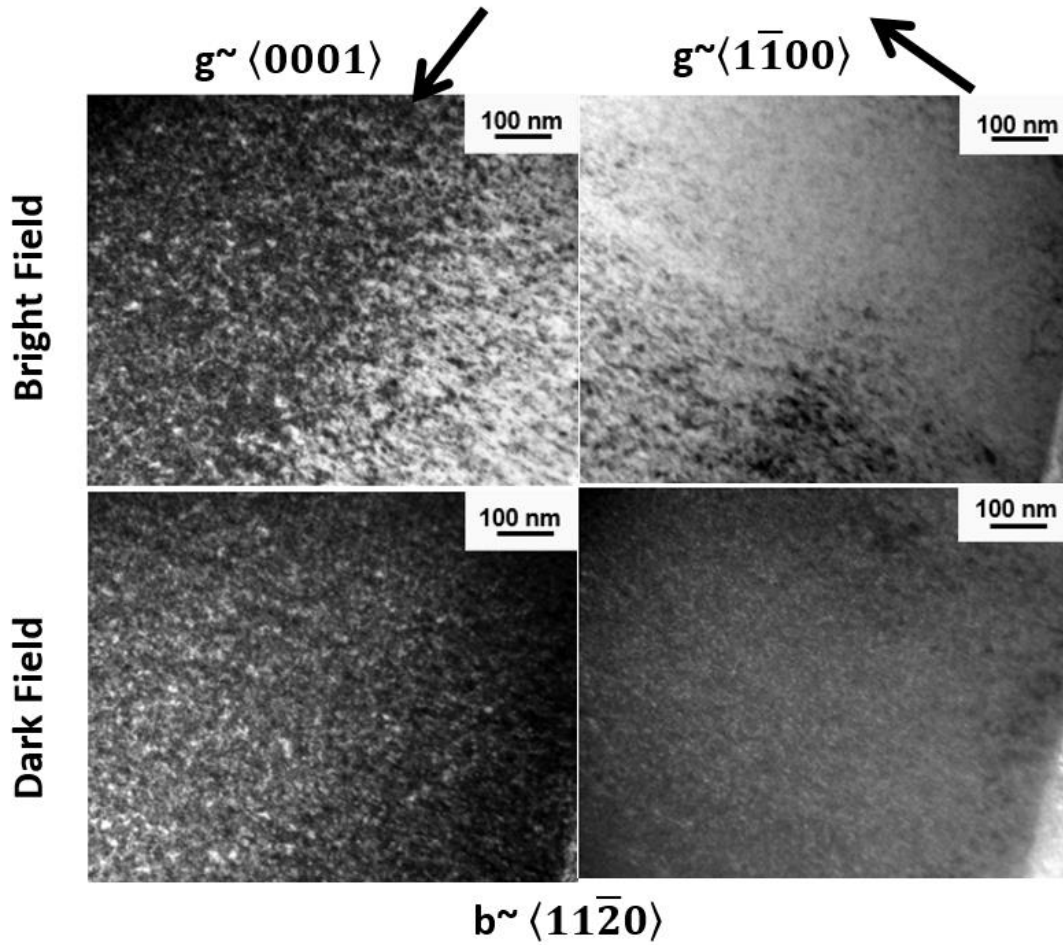


Figure 6.21 High magnification bright field and dark field cross-sectional TEM micrographs of 5.8 MeV Ni ions irradiated Ti_3AlC_2 to a midrange dose of 30 dpa at a temperature of 400 °C. The basal and prism zone axis directions are indicated by $\langle 0001 \rangle$ and $\langle 1\bar{1}00 \rangle$ diffraction vectors respectively.

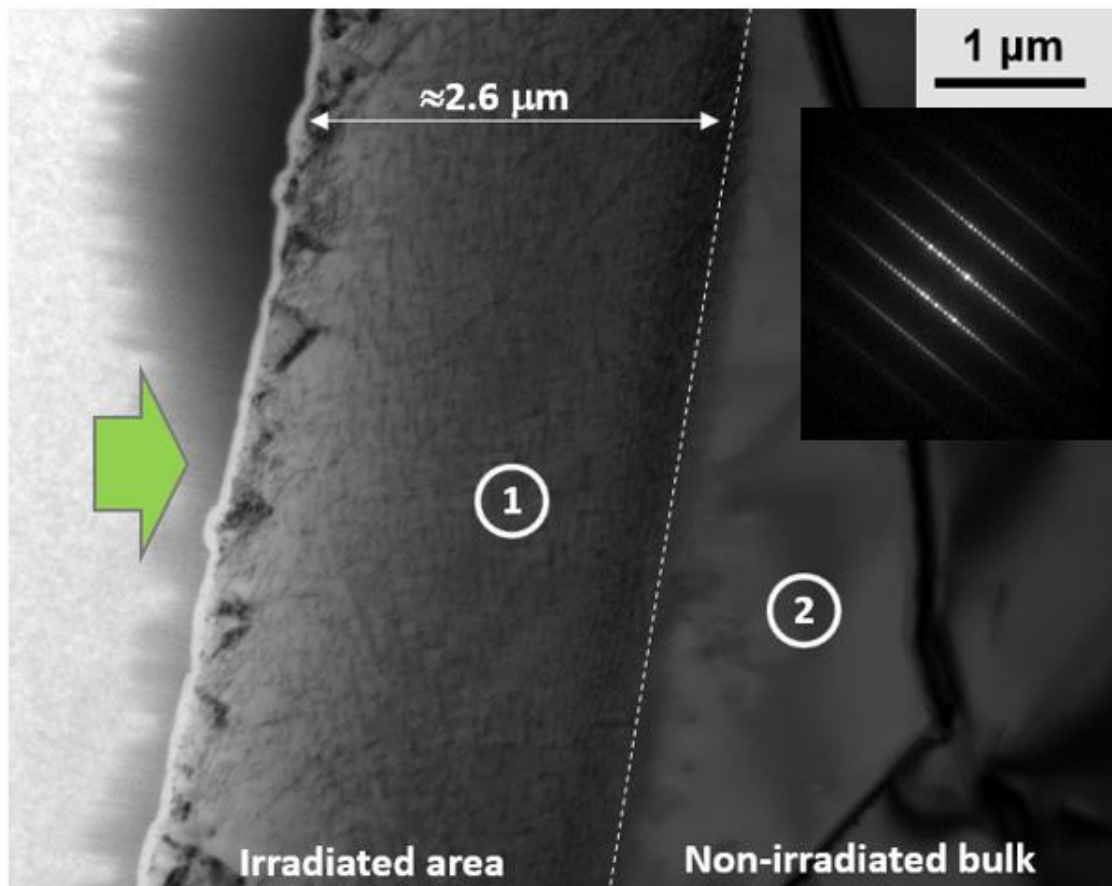


Figure 6.22 Cross-sectional TEM micrograph of the full Ti_3AlC_2 foil irradiated to 30 dpa at 700 °C using 5.8 MeV Ni ions, with ion direction denoted by the green arrow. The dashed white line denotes the transition depth between the ion irradiated area and the non-irradiated bulk. Region 1 denotes the selected area for ion radiation damage characterization and Region 2 denotes the selected area for pristine crystal characterization. SAED pattern for the pristine crystal can be seen in the upper right-hand corner

Ti₃AlC₂ phase and the beam direction was determined to be the $\langle 11\bar{2}0 \rangle$ prismatic direction.

Following this confirmation of the specific phase, standard two-beam conditions were used to obtain bright field and dark field images along the $\langle 0001 \rangle$ (basal) and $\langle 1\bar{1}00 \rangle$ (prism) zone axis for Ti₃AlC₂ irradiated to a midrange dose of 30 dpa at 700 °C, shown at low magnification in Fig. 6.23 and high magnification in Figs. 6.24. It is important to note that the irradiated region for sampling (1) was chosen at a depth of ~1.3 μm, corresponding to the nominal midrange dose of 30 dpa. Again, under- and over-focus showed a distinct lack of voids.

Contrary to the 400 °C irradiated material, the irradiated microstructure did not contain a large density of small, point defects, but instead consisted of a lower density of large defect clusters for both the basal and prism diffraction vectors. These grouped defect clusters appeared to form a hatch or diamond pattern for the basal zone axis and a striped pattern for the prism zone axis at low magnifications, as seen in Fig. 6.23. At higher magnifications seen in Fig. 6.24, the defects appear to be comprised of an ordered array of basal defects that coalesce in a stacking sequence at ± 35 degree angles from the basal direction in addition to what appears to be very large defects located on the basal plane. The fact that these defects can also be seen for the prism diffraction vector suggests a prismatic component as well. Full characterization of these defect clusters is needed before any definitive conclusions as to their nature can be drawn, but the general features of a significantly coarsened defect cluster microstructure without an evidence of voids suggests a higher mobility of interstitial defects when compared to the 400 °C irradiation temperature and immobile vacancies at 700 °C

The final sample observed under TEM was the Ti₃SiC₂ 30 dpa-700 °C sample. This sample was chosen to confirm that no voids were present in the silicon based MAX phase at high irradiation temperatures. A TEM micrograph of the entire cross-section foil and SAED results for the underlying unirradiated region (2) can be seen in Fig. 6.25. As can be seen, the ion irradiated region

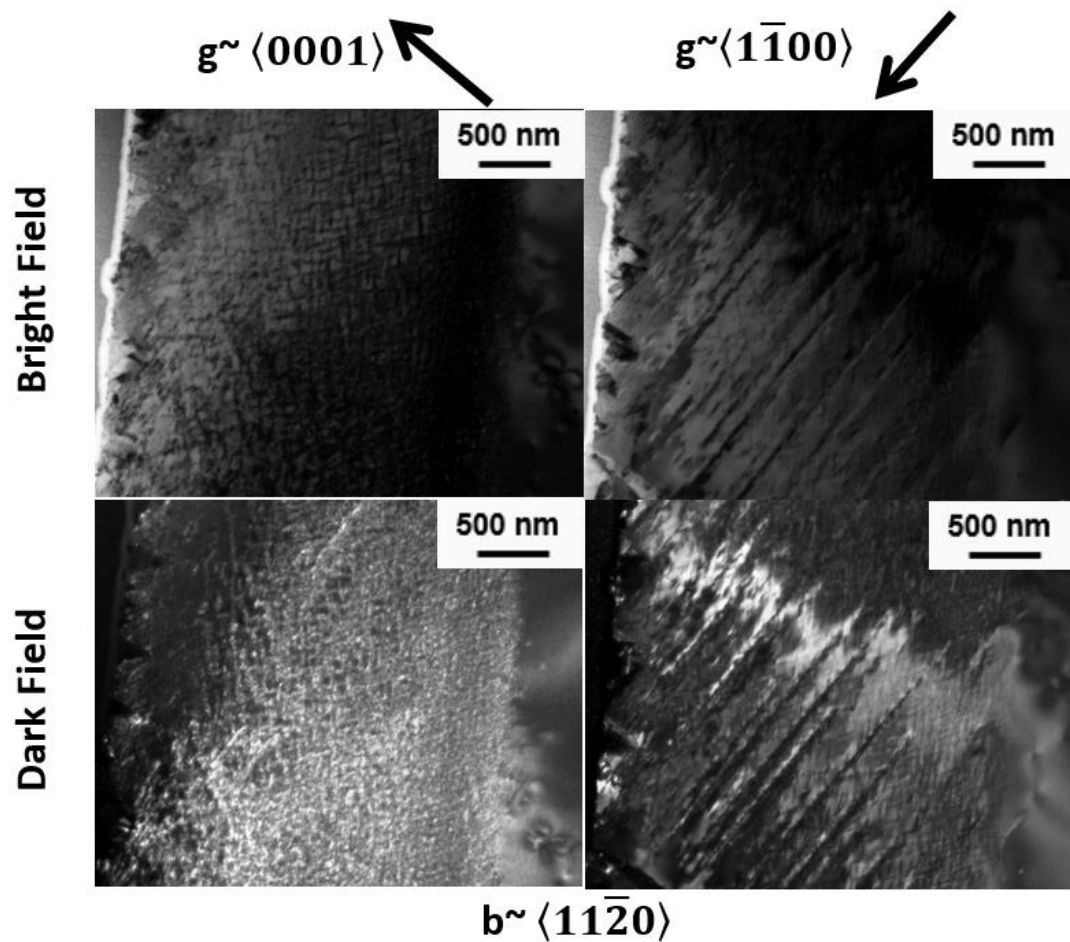


Figure 6.23 Low magnification bright field and dark field cross-sectional TEM micrographs of 5.8 MeV Ni ions irradiated Ti_3AlC_2 to a midrange dose of 30 dpa at a temperature of 700 °C. The basal and prism zone axis directions are indicated by $\langle 0001 \rangle$ and $\langle 1\bar{1}00 \rangle$ diffraction vectors respectively.

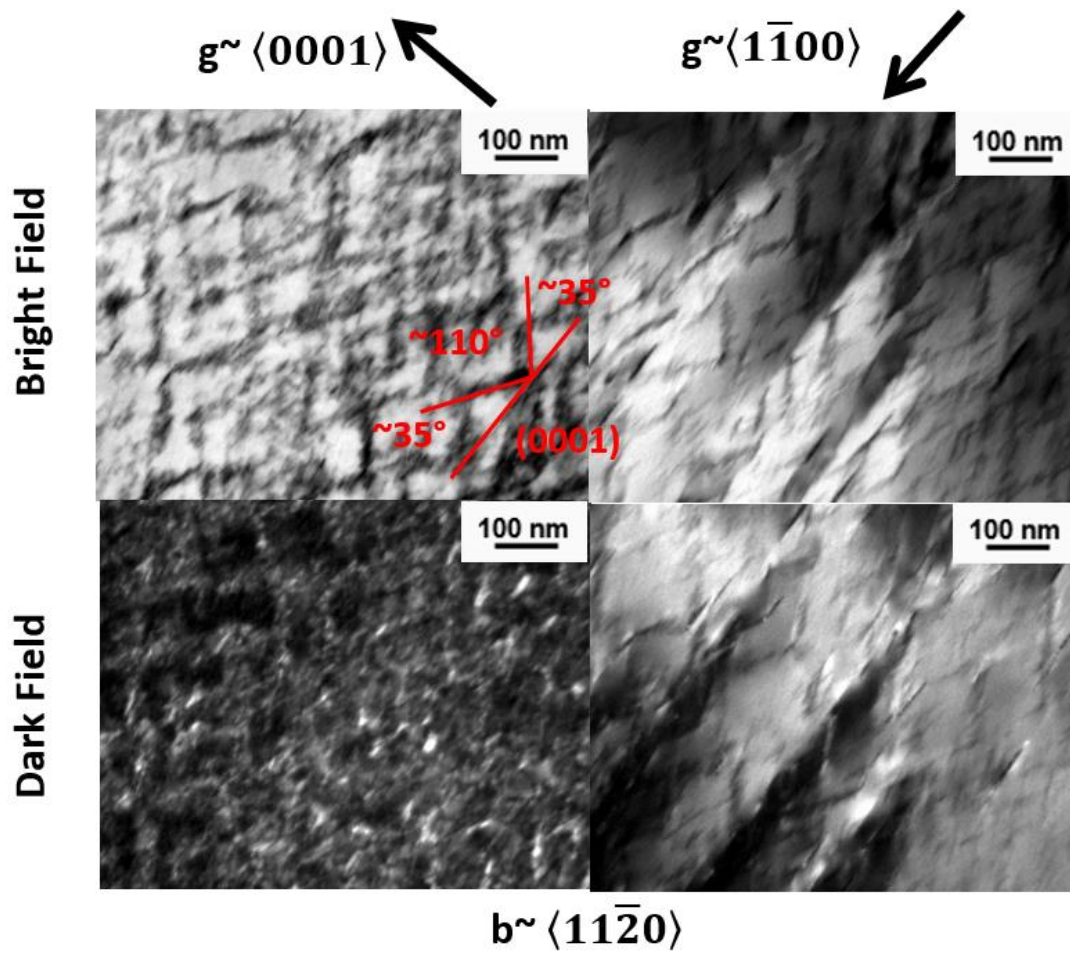


Figure 6.24 High magnification bright field and dark field cross-sectional TEM micrographs of 5.8 MeV Ni ions irradiated Ti_3AlC_2 to a midrange dose of 30 dpa at a temperature of 700 °C. The basal and prism zone axis directions are indicated by $\langle 0001 \rangle$ and $\langle 1\bar{1}00 \rangle$ diffraction vectors respectively. The red marking show the estimated stacking sequence of small defects with respect to the basal plane.

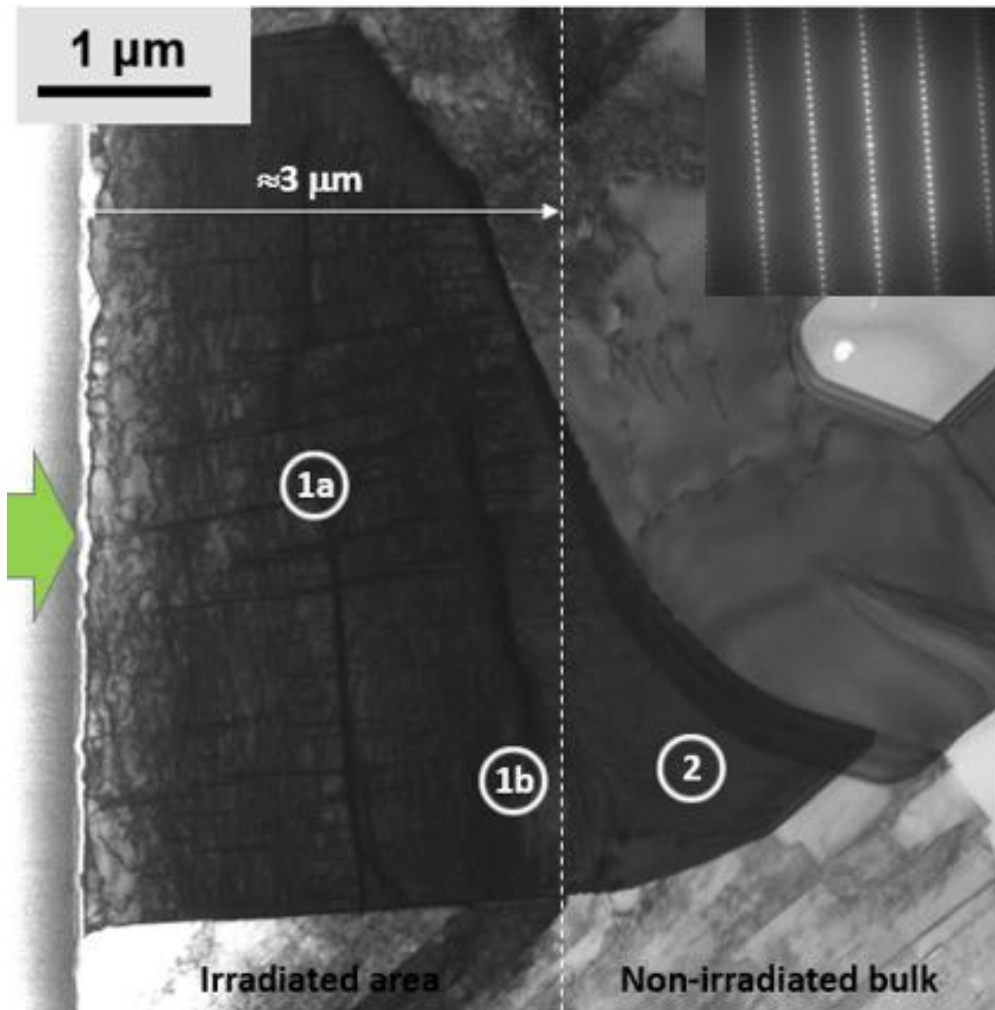


Figure 6.25 Cross-sectional TEM micrograph of the full Ti_3SiC_2 foil irradiated to 30 dpa at 700°C using 5.8 MeV Ni ions, with ion direction denoted by the green arrow. The dashed white line denotes the transition depth between the ion irradiated area and the non-irradiated bulk. Region 1a and 1b denotes the selected areas for ion radiation damage characterization and Region 2 denotes the selected area for pristine crystal characterization. SAED pattern for the pristine crystal can be seen in the upper right-hand corner

extended to a depth of approximately 3 μm , which is again consistent with SRIM ion penetration depth calculations when taking into consideration the sample surface contamination discovered during SEM analysis. Again, before any micrographs of the irradiated region were taken, SAED was used on the unirradiated region, well beyond the range of the ions (2) (displayed in the upper right hand corner), in order to determine both the phase and orientation of the grain. Comparing experimental and ICSD diffraction pattern spacing, the grain was confirmed to be the nominal Ti_3SiC_2 phase and the beam direction was determined to be the $\langle 2\bar{1}\bar{1}0 \rangle$ prismatic direction.

Following this confirmation of the specific phase, standard two-beam conditions were used to obtain bright field and dark field images along the $\langle 0001 \rangle$ (basal) and $\langle 01\bar{1}0 \rangle$ (prism) diffraction vectors for Ti_3SiC_2 irradiated to a midrange dose of 30 dpa at 700 °C, shown at low magnification in Fig. 6.26 and high magnification in Figs. 6.27. It is important to note that the irradiated region for sampling the basal plane defects (1a) was chosen at a depth of $\sim 1.5 \mu\text{m}$, corresponding to the nominal midrange dose of 30 dpa, while the depth for observing the prism defects was chosen near the end of the ion damage region (1b) due to very high defect concentrations in the midrange region. Again, under- and over-focus showed a distinct lack of voids, certifying that vacancy mobility is limited in both the aluminum and silicon based MAX phase at 700 °C.

Similar to the 700 °C irradiated Ti_3AlC_2 , the Ti_3SiC_2 irradiated microstructure did not contain a large density of small, point defect clusters, but instead consisted of a lower density of larger defect clusters for both the basal and prism diffraction vectors. However, these grouped defect clusters did not form the same ordered patterns seen in the Ti_3AlC_2 , but instead exhibited what appears to be large stacking faults along the basal plane and dislocation loops along the prism axis. Again, full characterization of these defect clusters is needed before any definitive conclusions as to their nature can be drawn, but the general irradiation damage seen in Ti_3SiC_2 appears to be less severe than that observed

in the Ti_3AlC_2 , and is consistent with previous presented XRD and nanoindentation hardness results.

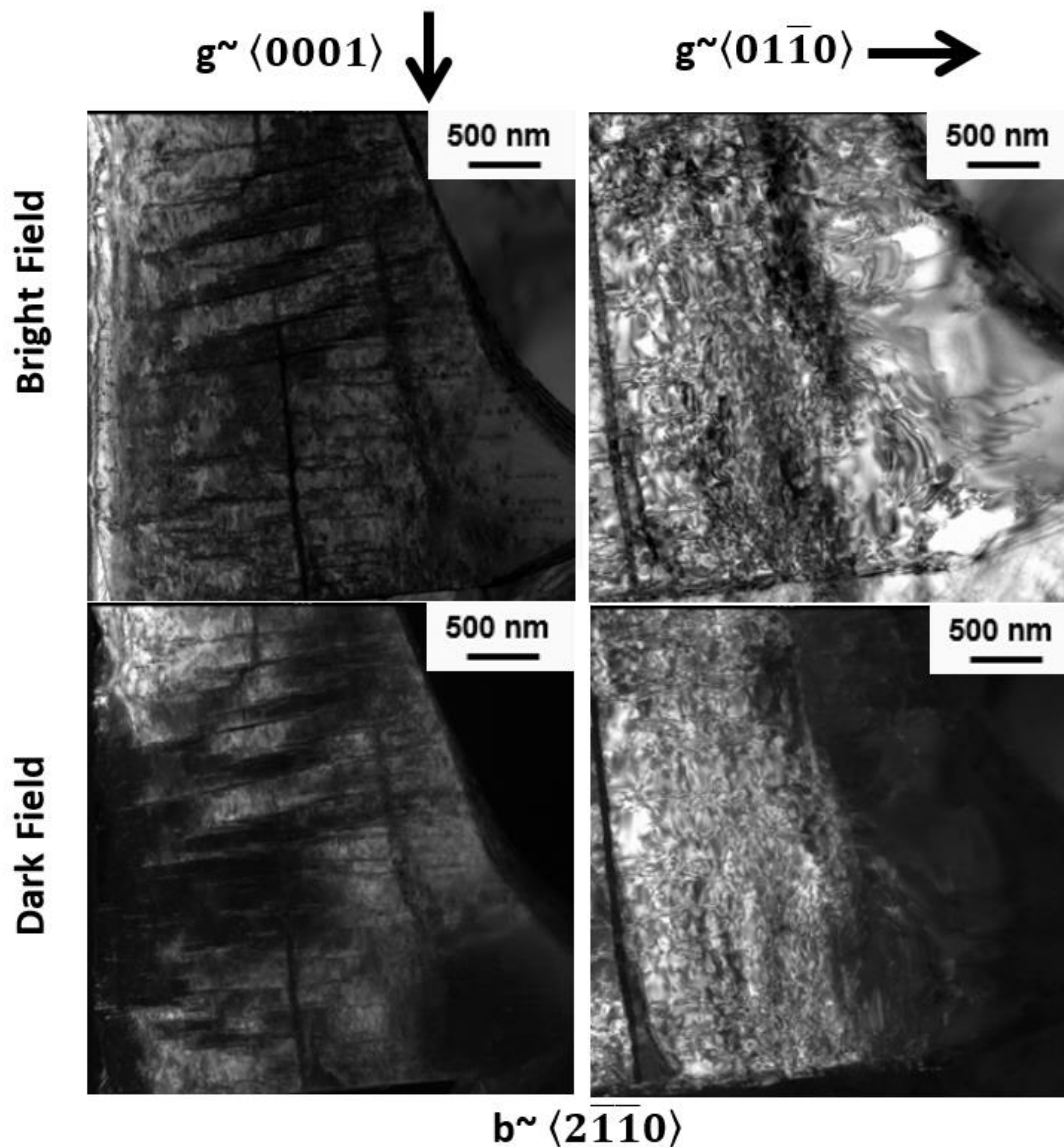


Figure 6.26 Low magnification bright field and dark field cross-sectional TEM micrographs of 5.8 MeV Ni ions irradiated Ti_3SiC_2 to a midrange dose of 30 dpa at a temperature of 700°C . The basal and prism zone axis directions are indicated by $\langle 0001 \rangle$ and $\langle 01\bar{1}0 \rangle$ diffraction vectors respectively. As noted in the text, the $\langle 01\bar{1}0 \rangle$ diffraction vector images were obtained near the end of the ion range rather than in the midrange region.

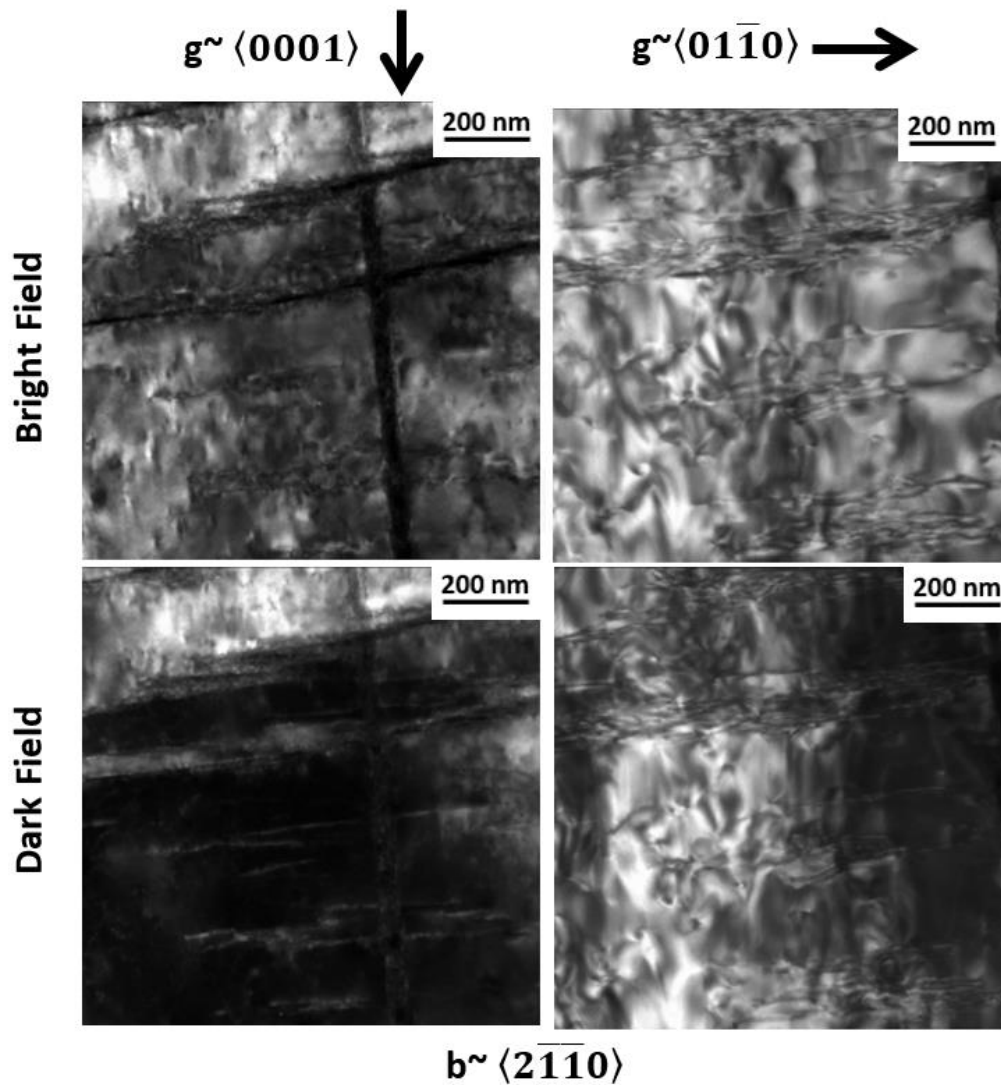


Figure 6.27 High magnification bright field and dark field cross-sectional TEM micrographs of 5.8 MeV Ni ions irradiated Ti_3SiC_2 to a midrange dose of 30 dpa at a temperature of 700 °C. The basal and prism zone axis directions are indicated by $\langle 0001 \rangle$ and $\langle 01\bar{1}0 \rangle$ diffraction vectors respectively. As noted in the text, the $\langle 01\bar{1}0 \rangle$ diffraction vector images were obtained near the end of the ion range rather than in the midrange region.

7 Discussion and Conclusions

7.1 Discussion

From the GXRD patterns it is apparent that all three materials maintain crystallinity following irradiation at all four conditions, and this was verified in selected TEM examinations of three specimens. However, it can clearly be seen from the XRD patterns collected (Fig. 6.4-6.7) that considerable disorder has been introduced to the materials, especially at the low temperature irradiation conditions, and is manifested in the peak position shifts, reduction in intensities, and broadening, as well as what could possibly be the appearance of new peaks. Due to current lack of knowledge surrounding the full interpretation of diffraction patterns with regard to MAX phases, this experiment sought only to observe the relative change in diffraction patterns and approximate lattice parameter changes as a way of quantifying any swelling.

It is important to note the reasoning behind omitting the use of Rietveld refinement during analysis. Rietveld refinement is a popular technique that uses a least squares approach to refine the height, width, and position of reflections to determine many aspects of a materials structure, most notably of which is phase percentages. Though it has its numerous merits, Rietveld refinement of XRD patterns should not be considered a fool-proof approach as it has many potential artifacts associated with it. Firstly, when applying Rietveld refinement, the instrumental broadening effect, or inaccuracy of diffraction peaks widths due to the equipment and optics used, needs to be taken into account. This is very difficult to accurately incorporate for glancing incidence X-ray diffraction machines and can result in large error in peak widths, and thus substantial errors in any refinement. Secondly, Rietveld refinement is based on reasonable starting structural models, which can be found in databases such as ICSD, and works superbly for bulk, pristine materials. However, when applying to materials with unknown irradiation response mechanisms, such as MAX phase, one cannot

assume that pristine models will accurately portray the actual crystal structure. Evidence of this variability in interpretation of XRD data can be seen in the literature where some researchers have used Rietveld refinement fitting to claim that MAX phases tend to revert to TiC under irradiation [35] while other researchers use the appearance of new diffraction peaks as evidence of a new, disordered phase under irradiation (so called β -phase), of which little is currently known [27, 29]. In either case, no concrete evidence as to the actual structure of MAX phase following irradiation has been given and more work is required to understand the microstructural morphology of irradiated MAX phases before Rietveld refinement becomes a reliable analysis method for these materials. Therefore, while considered, full Rietveld refinement was ultimately seen as an unreliable quantitative analysis method for the GXRD data on irradiated MAX phase materials.

Instead of Rietveld refinement, CMPR and Highscore Plus were used to determine accurate peak positions and refine the lattice parameters given by ICSD for pristine materials in order to provide an estimation of lattice parameters following irradiation. Using this method, the GXRD patterns collected from the ion irradiated MAX phase samples revealed a distortion of lattice parameters (LPs) under ion irradiation for all three compositions (LP Table 5 and Fig. 6.8). For Ti_3AlC_2 , four samples at a combination of both irradiation doses and temperatures were explored, revealing a lack of lattice parameter dilation on irradiation dose, suggesting radiation damage saturation at damage levels below 10 dpa. Contrary to the weak dose dependence, lattice dilation had significant dependence on irradiation temperatures. For all three materials, the low temperature irradiations produced the largest deviations in both the c-LP and a-LP, with all three materials experiencing an increase or swelling of their c-LP. Ti_2AlC exhibited the largest increase in c-LP, subsequently followed by Ti_3AlC_2 and lastly by Ti_3SiC_2 . For a-LP at the low temperatures, both the aluminum MAX phases showed a decrease in a-LP while the silicon MAX phase showed a slight increase in a-LP. Again, the Ti_2AlC showed the largest deviation from pristine,

with both the Ti_3AlC_2 and Ti_3SiC_2 had very similar magnitudes of deviation, if with opposite signs. For most samples, irradiation at high temperatures resulted in only slight variation of LPs from their pristine values, with the exception being high temperature irradiated Ti_3AlC_2 , in which there was still noticeable, though not nearly as severe, c-LP swelling. Overall, the c-LP showed more distinct deviation from pristine samples than the a-LP for all three materials at the low temperature irradiations. The significant swelling at lower irradiation temperatures, and the subsequent decrease of swelling as irradiation temperature is increased, are consistent with what is typically observed in irradiated materials in the “point defect swelling” regime where interstitials are mobile but vacancies are immobile, as mentioned in Chapter 2. Furthermore, the lack of dose dependence in lattice parameter swelling suggests that defect saturation is reached at some displacement level beneath the minimum 10 dpa dose analyzed in this research, again congruent with the “point defect swelling” regime, which typically saturates at low doses ($\sim 0.1\text{-}1$ dpa). Comparisons with previous ion irradiation experiments for Ti_3SiC_2 lends credence to these claims, as the 400°C irradiation c-LP data falls within the hypothesized region (i.e. intermediate to the 300°C and 500°C low dose data) assuming damage saturation at low doses (~ 0.2 dpa). Figure 7.1 depicts the relative c-LP swelling using a combination of previous and current data for Ti_3SiC_2 ion irradiations (a-LP parameter comparisons are not presented due to the relatively small dilations from pristine values).

Recognizing the likelihood of point defect swelling saturation above minimal doses allowed for the additional comparison of data points, and allowed an attempt to establish c-LP swelling trends as a function of temperature. Additionally, these results agree well with preliminary neutron irradiation studies at 360 and 695°C to 0.1 dpa in which Ti_3AlC_2 and Ti_2AlC exhibited significantly more swelling than Ti_3SiC_2 [35]. Comprehensive plots including data points and linear fits for c-LP and a-LP swelling from previous ion irradiation experiments for Ti_3SiC_2 [29, 32] and the aforementioned neutron irradiation experiment for

Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 is shown in Figs. 7.2 (a) and (b) respectively. Due to limited experimental data, the Ti_3AlC_2 and Ti_2AlC data fits are confined to the 360 -700 °C range.

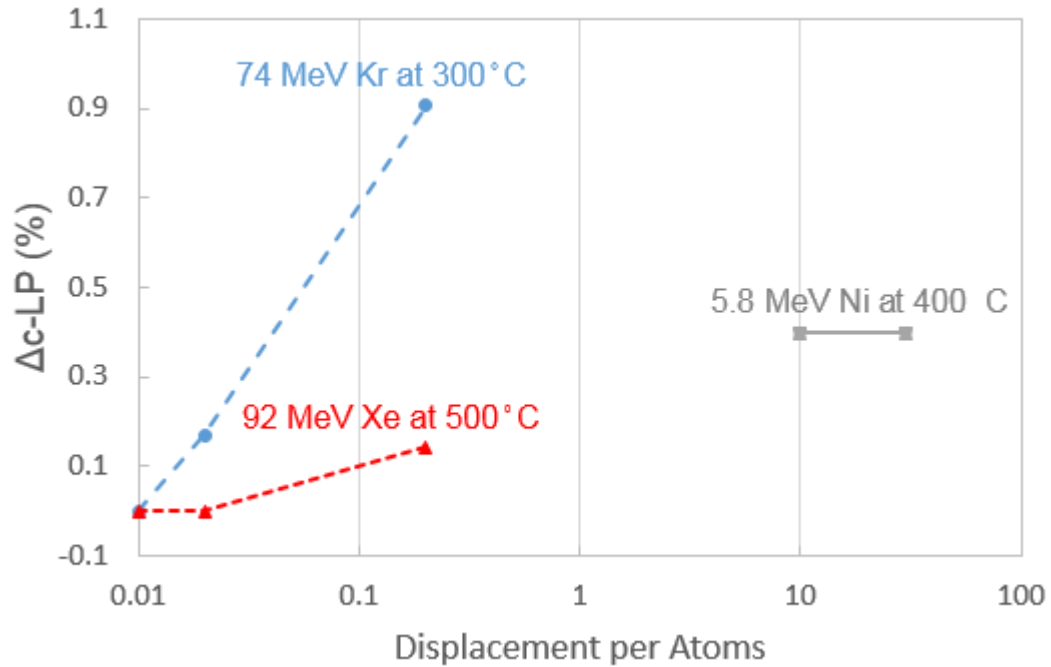


Figure 7.1 Comparison of c lattice parameter swelling as a function of irradiation dose for ion irradiated Ti_3SiC_2 [31].

When viewing this comprehensive comparison of all relevant lattice parameter swelling information, it becomes apparent that Ti_3SiC_2 exhibits the smallest amount of both c- and a-LP distortion, specifically as irradiation temperature decreases, though more experimental data is required for relative swelling behaviors below ~400 °C. The significantly larger anisotropic distortion of LPs in the aluminum based MAX phases at low temperatures is believed to be responsible for the surface/grain boundary cracking of the 400 °C irradiated samples observed by SEM. As mentioned in Chapter 2, anisotropic swelling is a major concern in hexagonal close packed ceramics as significant differences in a- and c-LP swelling can cause large stresses at grain boundaries, and

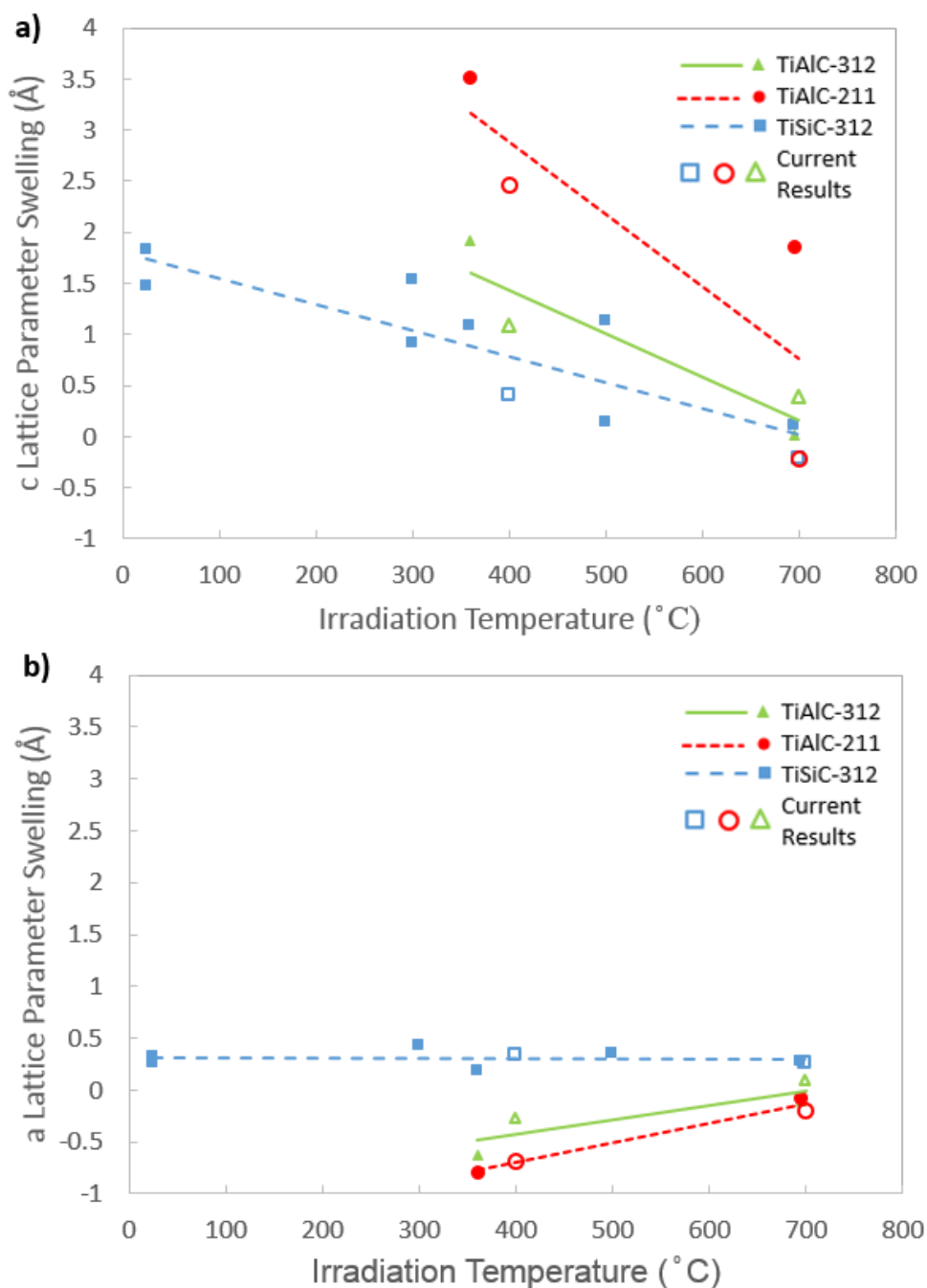


Figure 7.2 Comprehensive plot of (a) c lattice parameter swelling and (b) a lattice parameter swelling as a function of irradiation temperature for ion irradiated Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 . Empty symbols represent the current results, filled symbols represent previous results from literature, and lines represent fits to combined data [29, 32, 35].

depending on grain size and material parameters [57], can result in cracking. This can be seen for many traditional ceramics such as BeO, Al₂O₃, SiC, and AlN [15-17, 57-59].

In order to obtain a quantitative estimation of the critical differential strain required for grain boundary cracking, the analytical technique developed by Clarke et al. in their 1964 studies on grain boundary cracking in BeO was used [60]. Their analysis considered the misfit strain introduced at grain boundaries from anisotropic lattice expansion that led to grain boundary cracking. Spontaneous cracking is predicted to occur for misfit strains above a critical value given by Eq. (5), where the critical differential strain (ε) is related to the grain boundary surface energy in the absence of anisotropic strain (γ), the elastic modulus (E), and the average grain diameter ($2l$).

$$\varepsilon \sim \left(\frac{24\gamma}{El} \right)^{\frac{1}{2}} \quad (5)$$

The grain diameters were measured for each of the materials by Darin Tallman at Drexel University [35] and were independently confirmed using Electron Back Scattering Diffraction in the present study. The nominal average grain diameter for Ti₃AlC₂, Ti₂AlC, and Ti₃SiC₂ were determined to be 16(6), 10(4), and 8(3) μm respectively. The elastic moduli are given in Table 1 and the grain boundary surface energy was assumed to be 1.5 N/m, a typical value for Al₂O₃. A comparison of the calculated critical differential strain and the experimental differential strains for the three materials irradiated at the two temperature conditions can be seen in Table 6. As can be seen, only the low temperature irradiated aluminum base MAX phase samples experienced differential swelling sufficient to induce grain boundary cracking (an order of magnitude larger than the predicted critical value), again supporting the conclusion that anisotropic swelling is the cause of grain boundary cracking.

Finally, total volumetric swelling for all three materials was calculated and compared to volumetric swelling in traditional HCP ceramics as a function of temperature. As can be seen in Fig. 7.4, the results for total volumetric swelling

in the MAX phase agrees very well with traditional ceramics in the point defect swelling regime, with the MAX phases exhibiting slightly less overall swelling. Additionally, it can be seen that the Ti_3SiC_2 actually exhibits similar total volumetric swelling to Ti_2AlC , and more volumetric swelling than Ti_3AlC_2 , yet remained un-cracked at the low temperature irradiation conditions, again lending credence to the belief that the grain boundary cracking stems from anisotropic swelling rather than total volumetric swelling.

Table 6 Comparison of experimental differential strain to estimated critical differential strain required for grain boundary cracking.

Sample	ϵ at 400 °C	ϵ at 700 °C	ϵ critical
Ti_3AlC_2	1.36E-02	2.96E-03	3.89E-03
Ti_2AlC	3.15E-02	2.77E-04	5.10E-03
Ti_3SiC_2	6.97E-04	4.88E-03	5.14E-03

The increase in hardness in the irradiated MAX phases could not be attributed to oxide formation or dramatic chemical change at the sample surface, and as such, must be directly related to the formation of irradiation defects, as previously reported in other ceramics [17, 50, 61]. Furthermore, this increase in hardness is consistent with the conclusion that the materials are not being amorphized, as that would have led to a drop, rather than increase in hardness [62]. The lack of hardness change between doses at both the low temperature and high temperature irradiation conditions suggest that radiation induced hardness reaches a saturation point somewhere below the Ni ion fluence level associated with the 10 dpa midrange dose at both 400 °C and 700 °C. Additionally, the progressive recovery of induced hardness with increasing irradiation temperature suggests radiation defect recombination/annealing for all

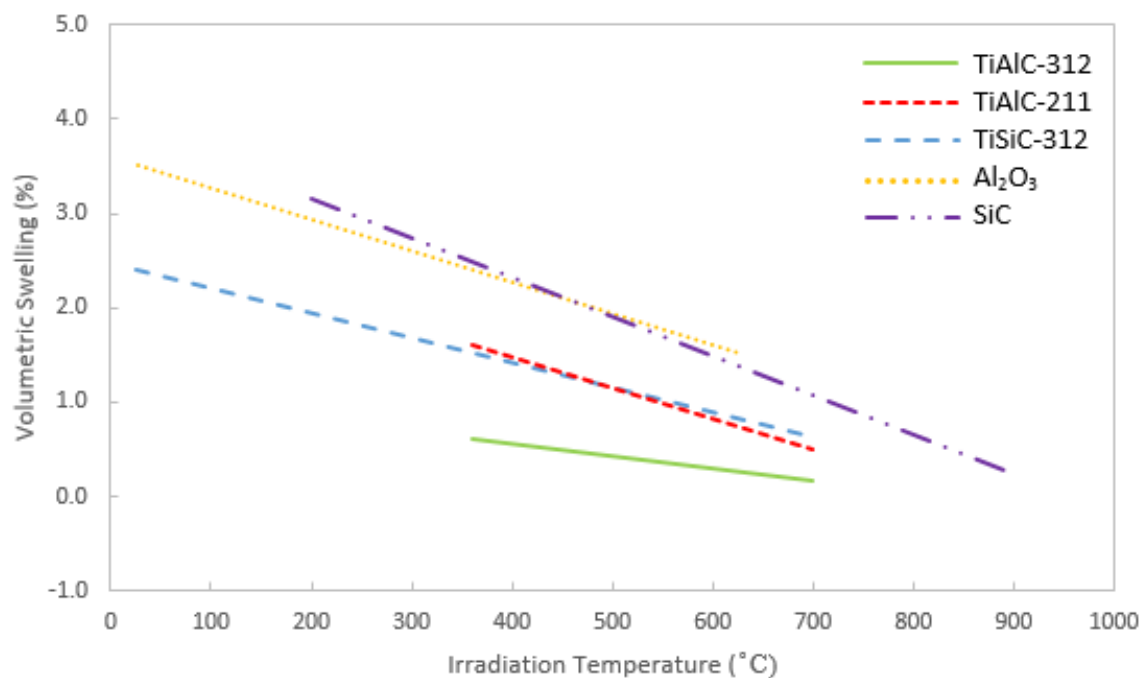


Figure 7.3 Comprehensive plot of fitted total volumetric swelling as a function of irradiation temperature for irradiated Ti_3AlC_2 , Ti_2AlC , Ti_3SiC_2 , Al_2O_3 , and SiC [15, 29, 32, 35, 58].

three materials. The present results are consistent with the general evolution of radiation induced hardness as introduced in Chapter 2, wherein hardness is more prominent at lower irradiation temperatures and saturates after small doses [9, 10]. Additionally, it is congruent with previous nanoindentation results on MAX phase ceramics, where radiation hardness saturated in Ti_3SiC_2 after approximately 3.2 dpa of 92 MeV Xe ions (fluence of 10^{19} ions m^{-2}) at room temperature and a reduction in radiation induced hardness in $\text{Ti}_3(\text{Si}_{0.95}\text{Al}_{0.05})\text{C}_2$ irradiated at room temperature began to appear at annealing temperatures as low as 300 °C and was virtually fully annealed by 800 °C [8, 41], as seen in Fig. 7.4.

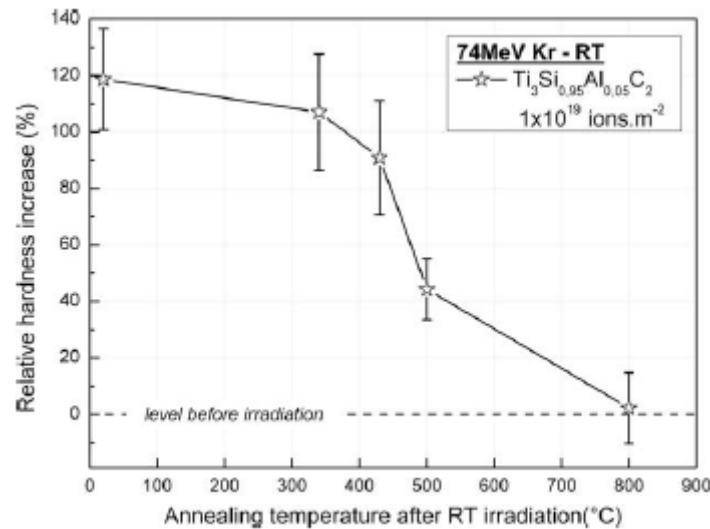


Figure 7.4 Effect of post-irradiation annealing on surface hardness of $\text{Ti}_3(\text{Si}_{0.95}\text{Al}_{0.05})\text{C}_2$ following room temperature, Kr irradiation to approximately 1 dpa (to 10^{19} ions m^{-2}) [8].

In terms of elastic modulus, the majority of samples underwent a slight increase, with the exceptions being the low temperature irradiation aluminum based MAX phases, which instead underwent a slight decrease in elastic modulus. This effect has been seen in other ceramics where, after low doses, the pinning of dislocations lead to material strengthening and an increase in

elastic modulus [17]. Following the SEM observations, it can be concluded that the outlying samples that experienced a decrease in elastic modulus were in fact the ones suffering from grain boundary/surface cracking, which was believed to be the direct cause for the decrease in elastic modulus.

One last topic related to indentation is with respect to the damage tolerance properties of the MAX phases. Vickers or Berkovich indentation in brittle solids traditionally result in sharp cracks emanating from the corners of the indent, which is indicative of low toughness. In pristine MAX phases, instead of crack formation at corners, one typically observes delaminations or slip bands, kinking of individual grains, grain push-outs and pull-outs around the area of indentations [63]. SEM images of Vickers indentation in pristine Ti_3SiC_2 for (a) 3 N and (b) 10 N can be seen in Fig. 7.5.

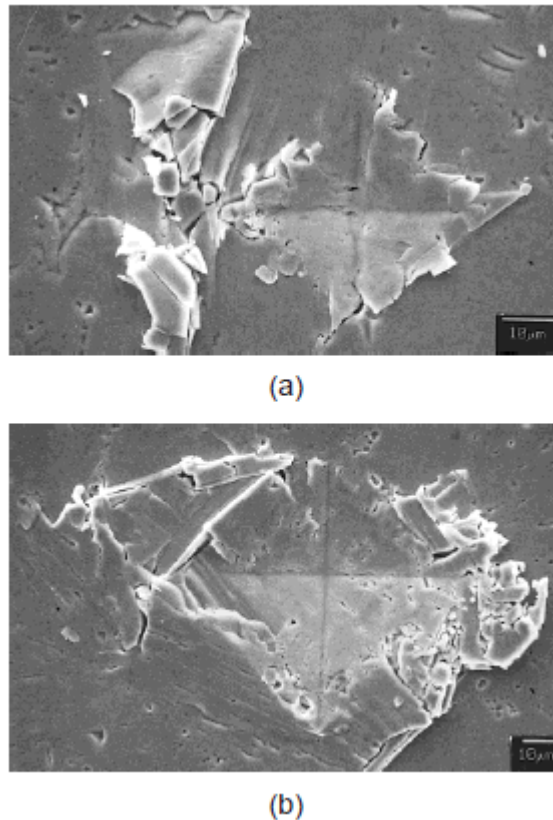


Figure 7.5 Vickers indentation images for (a) 2 and (b) 10 N in pristine Ti_3SiC_2 [63].

SEM examination of indentations showed that no cracks were induced during indentation in the silicon base MAX phase at any of the four irradiation conditions or in the high temperature irradiated aluminum based MAX phases (Figs. 6.16-6.18). It is far from conclusive, but the presence of characteristic shear bands/sliding features in the materials that did not exhibit corner cracking suggests that the MAX phases are still able to confine localized mechanical damage and are reasonably damage tolerant at those conditions, albeit to what extent is still unknown. This can be attributed to the preservation of the typical layered structure of the MAX phases, and agrees with the GXRd results wherein the most heavily disordered structures appeared to be those of the aluminum MAX phases at the low irradiation temperatures. Due to the fact that indentation induced cracks in the low temperature irradiated aluminum MAX phases, it can be suggested that irradiation at these conditions for these materials affected the microstructure in such a way as to decrease the damage tolerance.

The TEM micrographs provided in the previous Chapter exhibit several key features that further support the results discussed above. The appearance of a standard crystalline SAD pattern in the irradiated 30 dpa-400 °C irradiated Ti_3AlC_2 , which is arguably one of the most damaged materials, along with the crystalline diffraction patterns observed in both the 30 dpa-700 °C irradiated Ti_3AlC_2 and Ti_3SiC_2 confirms that crystallinity is indeed maintained in all three materials at all irradiation conditions. The high density of small defect clusters in the 30 dpa-400 °C irradiated Ti_3AlC_2 sample implies interstitials are sufficiently mobile to create small defect clusters while the lack of voids up to a dose of 30 dpa implies immobile vacancies at this temperature. This suggests that at 400 °C all three MAX phase are between Stage I and Stage III recovery, or the so called “point-defect swelling regime, as mentioned in Chapter 2.

The micrographs of 30 dpa-700 °C irradiated Ti_3AlC_2 appear to show large, grouped clusters of small basal plane defects that coalesce at ± 35 degree step angles. This is analogous to “rafting” of small defect clusters that has been previously observed in other metallic materials, such as BBC iron, tungsten, and

molybdenum [64], and full identification of these defect clusters will require more extensive imaging analysis. In any case, it is clear that the defect are better defined and with a lower density, leading to the conclusion that interstitials are more mobile than those at the 400 °C irradiation condition. The lack of voids implies that vacancies are still immobile at the 700 °C irradiation condition.

The micrographs of 30 dpa-700 °C irradiated Ti_3SiC_2 coincide with the results shown for Ti_3AlC_2 irradiated at the same condition in that they show larger, better defined defect clusters with a lower density. Again, these larger defects coupled with the lack of voids implies that interstitials have significantly higher mobility than vacancies at the 700 °C irradiation conditions in Ti_3SiC_2 . The lack of “rafting” in the Ti_3SiC_2 could be indicative of fundamental differences in radiation response between the aluminum and silicon based MAX phase, however, full identification of these defect clusters through extensive imaging analysis is required before any conclusion can be draw.

Overall, the micrographs of 30 dpa-700 °C irradiated Ti_3AlC_2 and Ti_3SiC_2 , depicting larger, more fully formed defects with a lack of voids suggests that all materials are below recovery Stage III at 700 °C. This region is defined by high interstitial mobility, which allows them to coalesce to form large defect structures, and the lack of void formation implies that Stage III recovery, or vacancy mobility, has not been reached. This microstructural evidence suggests that the point defect swelling regime extends between at least 400 and 700 °C and explains why there is significantly more swelling at lower irradiation temperatures in all three materials. Additionally, these results agree with several studies that suggest amorphization (which occurs for irradiation temperatures below recovery Stage I) during irradiation of MAX phase ceramics is possible only for irradiation temperatures well below room temperature and that voids do not form below 900 °C [8, 25, 27, 29, 31, 32, 37, 41].

Before concluding the discussion, it is important to note one possible contradicting study by Whittle et. al [37], who characterized Ti_3AlC_2 and Ti_3SiC_2 that had been irradiated by 1 MeV Xe ions at low temperature (50 and 300K) with

TEM analysis. Using SAED, they showed that Ti_3SiC_2 exhibited less recovery from radiation damage than did Ti_3AlC_2 , suggesting the difference in the Si-C and Al-C orbital overlap as a possible explanation, with the Si-C orbital overlap leading to the formation of SiC nano-defects. While this thesis research makes no conclusions as to the validity of this argument, as more conclusive studies are needed to either confirm or deny this trend in radiation resistances at low temperatures, the conclusions presented regarding radiation resistance between Ti_3AlC_2 and Ti_3SiC_2 at 50 and 300 K are believed to have no direct relevance to the current temperature regime of interest. It is believed that the mobility of interstitial defects in the range 400 °C to 700 °C in both materials is sufficient enough that effect of orbital overlap in the manners described have no direct relation on radiation response. As such, the results presented here in have neither confirm, deny, or any other means, directly relate to those proposed by Whittle.

7.2 Conclusions

The present high dose, high temperature ion irradiation study of MAX phase ceramics confirms that three of the most well established MAX phases, Ti_3AlC_2 , Ti_2AlC and Ti_3SiC_2 , remain fully crystalline up to very high heavy ion doses of ~30 dpa (~60 dpa in the peak damage region). However, GXRD analysis revealed modification of all three crystal structures following irradiation, with significant shift in peak positions, broadening, and change in intensities of peaks. Analyzing the Ti_3AlC_2 samples at all irradiation conditions revealed that there was very little deviation between dose conditions, suggesting a saturation of radiation damage below the nominal 10 dpa midrange dose obtained in the lowest fluence samples in this study. In contrast, the diffraction patterns of the irradiated materials for two irradiation temperatures exhibited significant differences. In all cases, the lower temperature diffraction patterns exhibited large deviations from the pristine case, with the high temperatures irradiated patterns remaining similar to pristine, indicating a clear correlation between irradiation temperature and

radiation damage response. Analyzing the low temperature irradiated samples resulted in a significant increase of the c-LP for all three materials and a slight deviation of the a-LP from pristine, with Ti_2AlC exhibiting the largest deviations and Ti_3SiC_2 exhibiting the smallest deviations. For the high temperature irradiations, the majority of the lattice parameters did not exhibit pronounced deviation from pristine, with the exception of the Ti_3AlC_2 c-LP which still exhibited swelling. GXRD pattern and lattice parameter analysis suggest that the silicon base MAX phase is more radiation tolerant than their aluminum based counterparts at these elevated temperature, high dose irradiation conditions, contrary to findings at room temperature.

Nanoindentation investigation into ion irradiated MAX phases revealed similar trends as the GXRD results. They showed that, through the introduction of defects, the MAX phase exhibit the traditional radiation induced hardening, and further support the conclusion that the materials are not being amorphized, as there was no drop in hardness. Observing hardness at a representative indentation depth of 400 nm showed that Ti_3AlC_2 exhibits the most relative hardening while Ti_3SiC_2 exhibits the least, with Ti_2AlC falling in between. The lack of dose dependence on induced hardness again suggests damage saturation at some point below the 10 dpa midrange dose fluence level, and the strong irradiation temperature dependence confirms radiation defect annealing. Nanoindentation also showed that the majority of irradiated samples experienced a slight increase in elastic modulus, as would be expected of irradiated materials, with the exception being the low temperature irradiated aluminum based MAX phases.

SEM surface analysis showed that these low temperature irradiations of the aluminum base MAX phase resulted in significant surface cracking along grain boundaries. This is correlated to the substantial, anisotropic lattice parameter swelling observed by GXRD for these conditions. Additionally, the lack of indentation induced corner cracking in the silicon based and high temperature irradiated aluminum based MAX phase suggests the retention of the pristine

MAX phase damage tolerance at these conditions. The induction of grain boundary and corner cracking in the 400 °C irradiated aluminum based MAX phase again suggests that the silicon based MAX phase are more radiation damage tolerant at these conditions

Selected TEM analysis was consistent with the conclusions that the MAX phase materials remained crystalline at all irradiation conditions and that the typical, “point-defect” swelling behavior is responsible for the anisotropic swelling exhibited at the 400 °C irradiation conditions. Furthermore, micrographs at the 700 °C irradiation conditions confirmed the absence of voids and development of large defect structures in both the aluminum and silicon based MAX phases. This again is consistent with the conclusion that for irradiation between 400 °C and 700 °C, all three MAX phases are within or above interstitial and interstitial cluster mobility recovery states (between recovery Stage I and Stage III).

All analysis suggest that the aluminum based MAX phases are not well suited for application in extreme nuclear environments at irradiation temperatures near 400 °C. Both Ti_3AlC_2 and Ti_2AlC exhibit severe anisotropic swelling at an irradiation temperature of 400 °C, to the point that the stress becomes large enough to induce grain boundary cracking. Additionally, both exhibit significantly more crystalline disruption and radiation hardening than their silicon based counterpart post irradiation at both 400 and 700 °C. Though they are not well suited for application near 400 °C, they are still potential candidates for very high temperature application (>700 °C) as long as there is a reasonable operating temperature regime before the formation of voids (e.g. void formation above 800 °C). On the contrary, Ti_3SiC_2 exhibits only slight radiation induced swelling at both 400 and 700 °C, with no evidence of cracking. It also exhibits the least amount of crystalline lattice disorder and radiation hardening, and maintains signs of damage tolerance against nanoindentation similar to that of pristine MAX phases, following irradiation at 400 and 700 °C. These results suggest that Ti_3SiC_2 is a promising candidate in the 400-700 °C operating window for application in advanced nuclear fission and fusion reactor environments.

8 Future Work

As can be seen by the results given in the previous chapters, nuclear collisions dislodge substantial numbers of atoms in MAX phase ceramics under irradiation, resulting in significant property changes. This thesis has begun to show general trends in the radiation response of several popular MAX phase ceramics with respect to dose and temperature dependence, specifically at the relatively unexplored high dose and high temperature regimes. However, as with most research, there still remain important, immediate questions to be answered. This section will discuss recommendations for near-term follow-on ion irradiation studies, as well as touch on some long-term goals for research involving the application of MAX phase ceramics in nuclear reactor environments.

Follow-on work as it pertains directly to the ion irradiation studies of MAX phase ceramic presented in this thesis research should focus on three major goals; full TEM quantification of defects observed in the samples irradiated at 700 °C, low dose irradiations (0.1-1 dpa) at both 400 °C and 700 °C to definitively determine the saturation dose, and high temperature irradiations (>800 °C) at 10 and 30 dpa to determine the onset temperatures for void swelling.

The most direct step following the results presented in this research would be the continuation of TEM analysis of the 700 °C ion irradiated MAX phases in order to fully characterize the “rafting” defects and other large defect formations observed. This analysis would also include high resolution TEM analysis in order to observe the laminar c lattice stacking sequence, and subsequent disorder under irradiation. Full characterization of large defect structures in the MAX phase have not been completed to date, and could provide information crucial to understanding the difference in behavior between compositions at these relevant operating conditions.

The second goal would be the completion of a new set of ion irradiations in the suggested saturation dose range (~0.1-1 dpa) for 400 °C and 700 °C in order to provide complete information for these temperatures. Though the data from

past experiments agrees reasonably well for damage saturation in Ti_3SiC_2 , it would be beneficial to construct a full dose-dependent damage spectrum (involving analysis of both lattice dilation and hardness) for all three materials using congruent irradiation conditions. This would allow for a definitive, all-inclusive verification of radiation damage saturation in all three MAX phase materials.

The final goal would be the identification of the interstitial and vacancy migration temperature in all three MAX phase materials through additional 10 and 30 dpa irradiations at both very low ($<0^\circ\text{C}$) and very high temperatures ($>800^\circ\text{C}$). Analysis of previous experiments suggests that interstitials remain mobile down to room temperature and that vacancies are not expected to gain mobility until upwards of 900°C . While this provides a good frame work, more experiments are needed to better quantify the actual temperature dependence of these recovery regimes. Ion irradiation experiments would be a fast and effective way of determining these properties as bulk testing is not needed. For example, MAX phases could be irradiated at step increments both at very low ($<0^\circ\text{C}$) and very high ($>800^\circ\text{C}$) temperatures in order to determine, as accurately as possible, the temperature dependence of these recovery stages. This analysis of defect mobility could also be augmented by isochronal annealing experiments, positron annihilation spectroscopy, and various other tools. Understanding the recovery stage temperature dependence in different MAX phases would represent a major advance for determining the radiation response in a relatively unknown family of materials.

Looking to the future, long term research of MAX phase ceramics should generally revolve around understanding the microstructural evolution and phase changes of MAX phases under irradiation conditions as well as developing a more comprehensive knowledge set for post irradiation physical and mechanical property changes.

As discussed in the previous chapters, phase changes under irradiation are commonplace in many materials, and due to the complex nanolaminate structure

of the MAX phase, it is highly probable that different MAX phases would exhibit significant phase distortion under irradiation. Evidence of this has been documented via X-ray diffraction. However, very little is known as to what is actually happening in the crystal structure. Hypotheses include the reversion of MAX phases to MX and higher order MAX phases, or the possible emergence of a disordered phase, but as of yet, nothing is confirmed. The reliance of physical properties on the MAX phases' structure makes it imperative that a better understanding of the structure changes under irradiation be gained. It is recommended that bulk neutron irradiations be conducted and analyzed so that the true phase morphology can be documented without any of the associated artifacts of ion irradiation (such as depth dependence and implantation) that make identification difficult. Once more information is gained on phase transformations, better refinement and analytical methods can be used reliably.

Finally, as has been mentioned previously, the addition and evolution of defects and modification of crystal structure through irradiation are directly manifested in the physical and mechanical property changes observed in irradiated materials. These physical and mechanical property changes are ultimately the primary concern when considering engineering materials for use in extreme nuclear environments. Degradation of materials in the presence of extreme neutron field environments can lead to reduced performance, or in severe cases, sudden failure. For this reason, it is imperative that a full, comprehensive study of physical and mechanical property changes be conducted on the MAX phase before any serious thought can be put towards application. Current ion irradiation results have begun to show volumetric swelling and hardening at relevant operating conditions, but as of now, only small scale testing has been completed on irradiated MAX phases. Only one neutron irradiation experiment has been complete, and for that, only XRD estimation of lattice parameter swelling was considered. In order to fully understand the mechanical changes in MAX phases post irradiation, bulk neutron irradiated samples will be needed in order to perform large-scale, comprehensive tests.

These bulk tests could include volumetric displacement tests as well as XRD to determine swelling both on a macro and micro level, tensile tests, fracture toughness tests, electrical/thermal conductivity tests, thermal shock/cycling tests, etc.

Though the mechanical properties of the MAX phases render them good candidates for advanced nuclear reactor applications and the fundamental understanding of the structure and properties of the MAX phases has come a long way in the two decades since their inception, there still remain outstanding scientific questions and technological hurdles to overcome when considering MAX phase for application in reactor environments. These obstacles can only be overcome with continued research and experimental data on which the MAX phases can be fully characterized and fundamentally understood. The increased and continued interest in the large family of composite ceramics known as the MAX Phase is essential in moving a very promising type of material closer to practical application in nuclear energy systems.

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APPENDIX

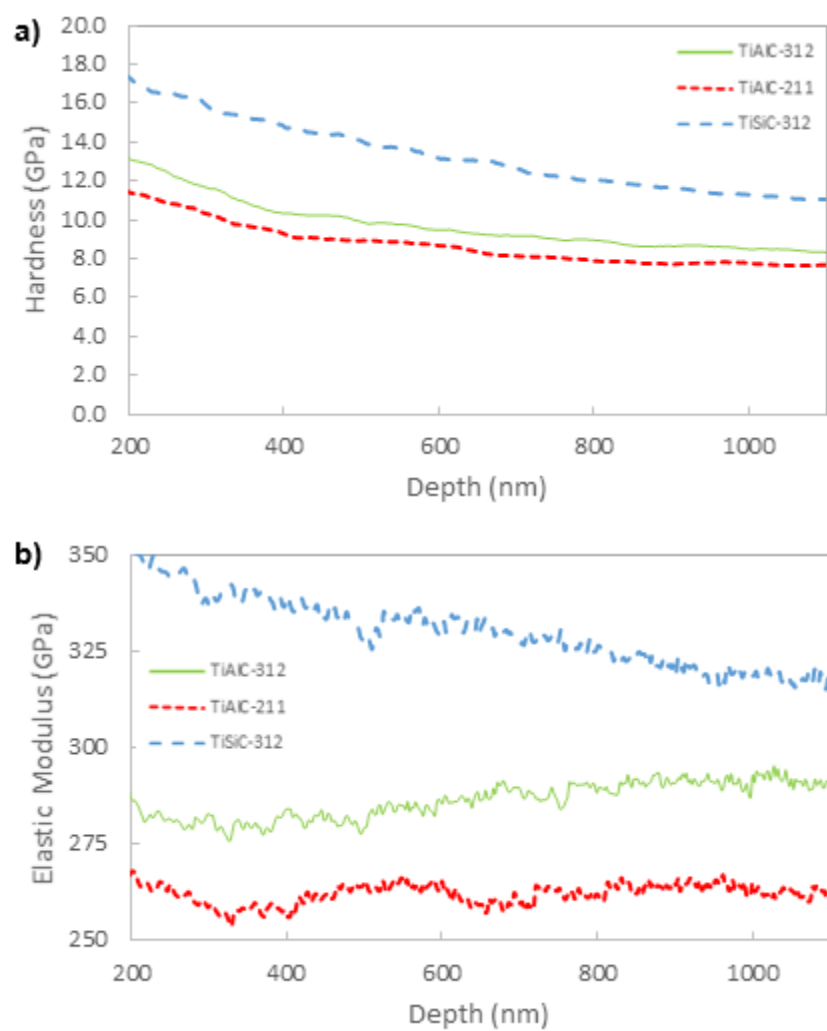


Figure 0.1 Unirradiated nano-indentation (a) hardness and (b) elastic modulus for Ti_3AlC_2 , Ti_2AlC , and Ti_3SiC_2 as a function of depth.

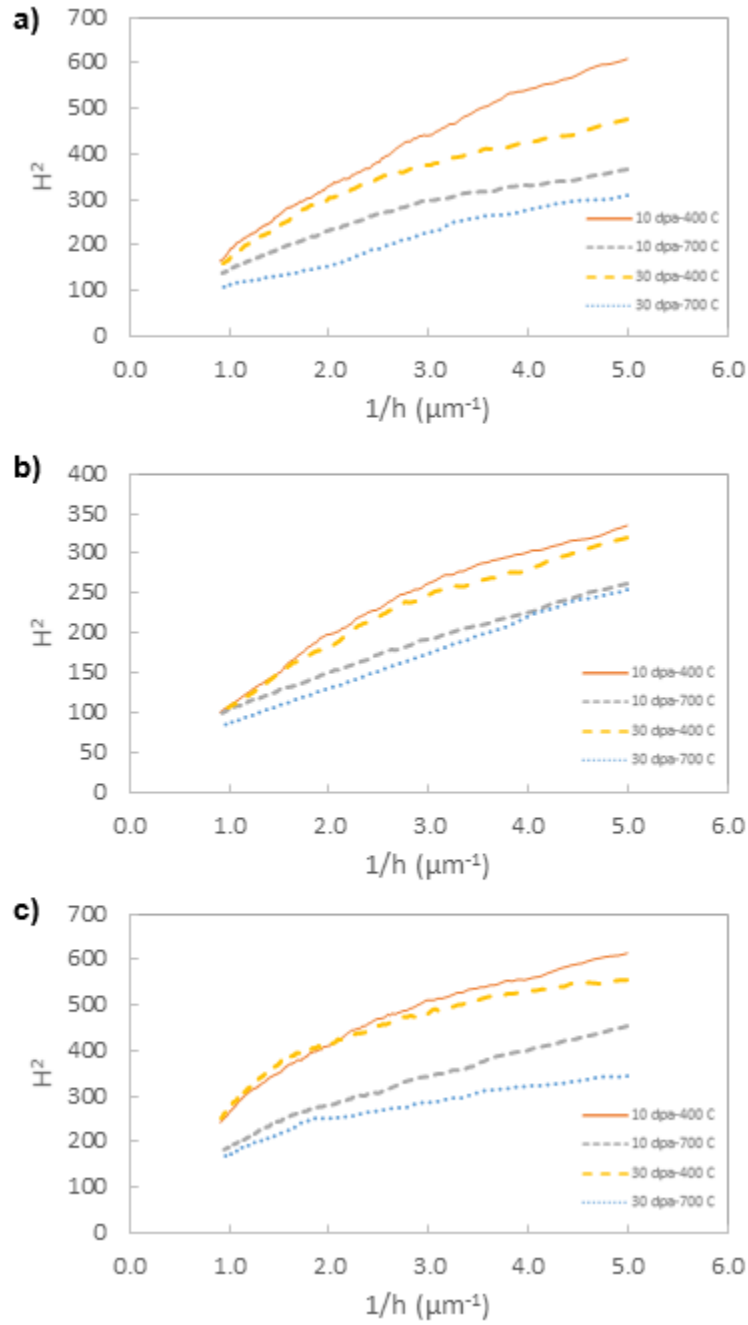


Figure 0.2 Nix Gao plot for (a) Ti_3AlC_2 , (b) Ti_2AlC , and (c) Ti_3SiC_2 irradiated using 5.8 MeV Ni^{4+} ions at the four irradiation conditions.

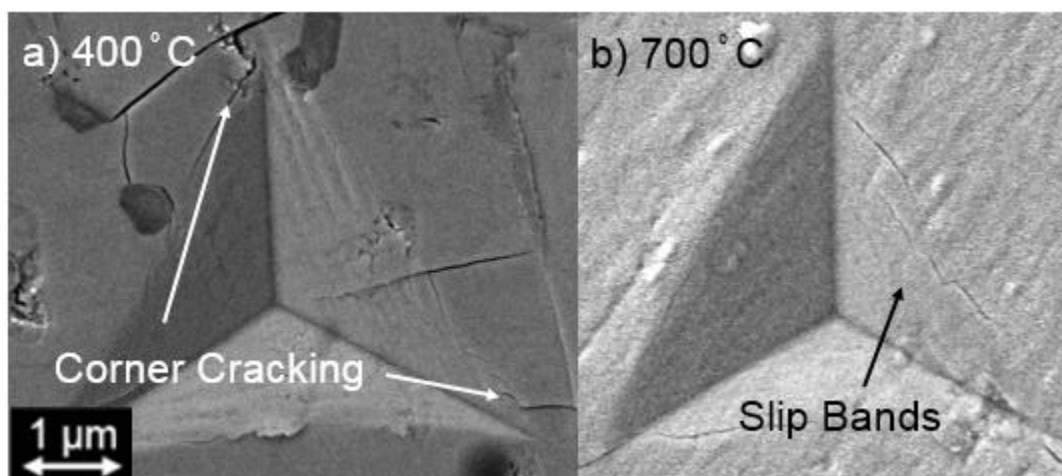


Figure 0.3 SEM morphology of indents on (a) 30 dpa-400 °C, and (b) 30 dpa-700 °C Ni ion irradiated Ti_3AlC_2 .

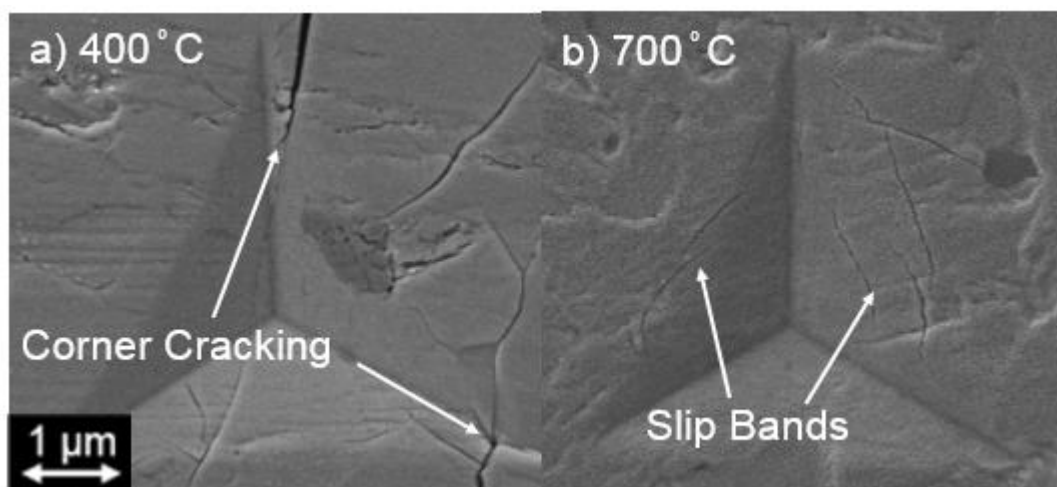


Figure 0.4 SEM morphology of indents on (a) 30 dpa-400 °C, and (b) 30 dpa-700 °C Ni ion irradiated Ti_2AlC .

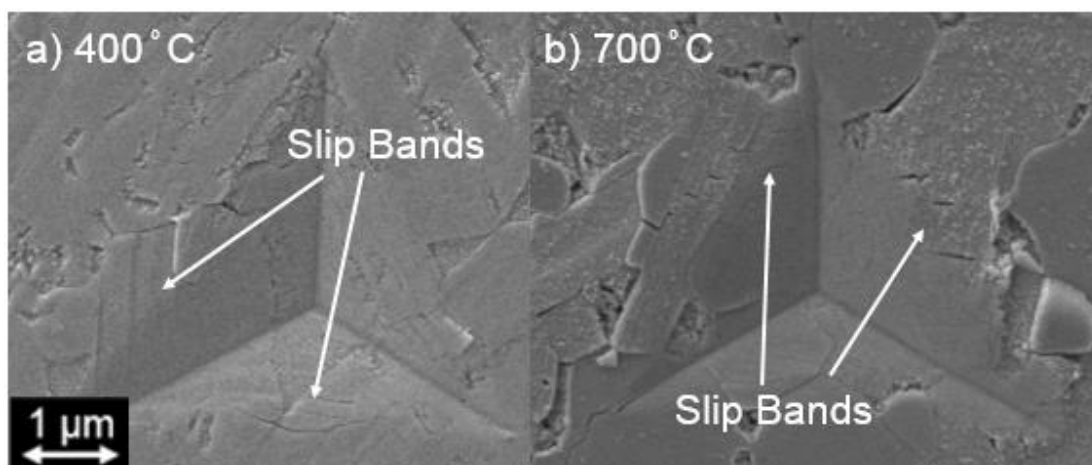


Figure 0.5 SEM morphology of indents on (a) 30 dpa-400 °C, and (b) 30 dpa-700 °C Ni ion irradiated Ti_3AlC_2 .

VITA

Daniel W. Clark was born on July 21st, 1991. He graduated with his B.S. in Nuclear Engineering from Texas A&M University in May 2013, and upon completion, was accepted into the University of Tennessee Nuclear Engineering Departments graduate program as a graduate research assistant. Working underneath the advisory of Dr. Steven Zinkle, he graduate with a M.S. in Nuclear Engineering in December 2015 with a specialization in Nuclear Materials. This thesis is the culmination of his two years of research at the University of Tennessee and Oak Ridge National Laboratory. His wear abouts are currently unknown.