

Study on Evolution of Irradiation Induced Microstructure and Hardening of Zircaloy-2 Under Applied Stress

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Study on Evolution of Irradiation Induced Microstructure and Hardening of Zircaloy-2 Under Applied Stress

(ジルカロイ 2 合金の応力下における照射組織と
硬さ変化に関する研究)

by

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ABSTRACT

Zircaloy-2, typically serving as the fuel cladding closest to the fuel in boiling water reactors, must withstand the simultaneous effects of neutron radiation, mechanical stress and corrosion during reactor operation. Neutron radiation, a significant factor during service, induces various phenomena in zirconium alloy components, including early-stage radiation-induced hardening, irradiation growth, corrosion, and hydrogen embrittlement. Stresses imposed on the cladding during radiation exposure arise from a variety of sources, including hoop stress caused by the thermal expansion of UO_2 pellets and stresses due to radiation-induced volume expansion or distortion. These factors gradually contribute to the degradation of material performance over time. Additionally, the microstructural evolution associated with these phenomena remains insufficiently understood. Understanding these mechanisms is crucial for ensuring the cost-effective and safe operation of reactors.

This study systematically investigates the microstructural evolution and radiation-induced hardening of Zircaloy-2 subjected to 3.2 MeV Ni^{3+} ion irradiation under applied stress. Techniques such as TEM examination, nano-indentation measurements, and energy-dispersive spectroscopy analysis were employed.

The outcomes demonstrate that $\langle a \rangle$ loops were observed to nucleate with a diameter of about 4 nm at doses below 0.05 dpa. As the dose increased, the size and number density of $\langle a \rangle$ loops increased, reaching saturation density at around 0.1 dpa. Radiation-induced hardening is confirmed, primarily attributed to $\langle a \rangle$ loops.

Observations include the dissolution of Fe atoms from $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates at both 300 °C and 400 °C, while $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates remain stable at same irradiation conditions. The increase in temperature appears to facilitate the

complete dissolution of $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates. With the same irradiation dose, the Fe content in $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates at 400 °C is lower than that in samples irradiated at 300 °C. The influence of stress on precipitation dissolution is not distinctly observed under the experimental conditions.

The formation of $\langle c \rangle$ loops at 300 °C requires dose exceeding 30 dpa, while at 400 °C, a threshold dose of 20 dpa is necessary. Applied tensile stress at 400 °C up to 100 MPa exhibits no significant effect on $\langle c \rangle$ loops formation.

This study offers comprehensive insights into the microstructural changes and hardening mechanisms in Zircaloy-2 induced by ion irradiation under applied stress. It discusses the influence of temperature, applied stress, and irradiation dose on precipitate dissolution and loop formation. While the influence of applied stress on dislocation loop behavior and precipitate dissolution may not be significant under the considered experimental conditions, we have systematically initiated a discussion concerning the effect of applying different levels of stress at varying radiation doses on the microstructure evolution and the behavior of Zircaloy-2. In future research, it is essential to investigate higher stress values and explore other behaviors of zirconium alloys affected by irradiation under applied stress conditions.

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CHAPTER 1. Introduction

1.1 General Introduction

Since the beginning of the 21st century, the global landscape of international relations has changed with the resurgence of the world economy. With the rapid growth of population and industrialization, the energy crisis and environmental pollution have become two of the most pressing challenges. Additionally, recent events such as the outbreak of the COVID-19 pandemic and the Russia-Ukraine war have intensified the urgency of addressing the energy crisis.

Given the finite and non-renewable nature of fossil fuels, there has been a growing emphasis on renewable energy sources like solar, wind, and hydroelectric power in recent years. These sources are favored for their lower environmental impact and reduced dependence on finite resources. What's more, nuclear energy also remains a vital component of many countries' energy mix for its stable supply, efficiency, low operational costs, and the absence of greenhouse gas emissions during operation. The development and utilization of nuclear energy can play a pivotal role in solving these challenges, providing essential energy support, ensuring national security, and protecting the environment.

Over the past half-century, nuclear reactor designs have become more diverse, with longer lifespans and enhanced safety measures. Countries around the world are actively developing nuclear power. Currently, there are 412 operational nuclear power reactors worldwide, boasting a combined total capacity of 370,170 megawatts electric (MWe) [1]. Japan operates 11 nuclear power reactors, contributing approximately 6.1% to the nation's total power production in 2022 [2]. Prior to the Fukushima accident in March 2011, nuclear power contributed to more than 11% of total energy [3]. In order to ensure a stable energy supply and achieving carbon neutrality by 2050, Japan plans to

restart nuclear reactors, with the aim of reaching 20-22% of the total energy mix by FY 2030, as outlined in the Sixth Strategic Energy Plan [2]. As of December 31, 2021, China (excluding nuclear power and other relevant data in Taiwan) had 51 operational nuclear power units and an additional 20 units under construction. Commercial nuclear power units generated a cumulative annual power output of 407.520 billion kWh in 2021, constituting approximately 5.02% of the country's total power generation. Early in 2022, the 14th Five-Year Plan for the Modern Energy System, explicitly stating China's commitment to "actively develop nuclear power in a safe and orderly manner", which plans to achieve an installed nuclear power capacity of approximately 70 GW by 2025 [4]. As of 2022, per capita electricity generation from nuclear sources varies among different countries. France relies significantly on nuclear power, contributing to 63% of its per capita electricity. Finland follows with a 34% share, while Russia has a 20% contribution. The United States has an 18% share, the United Kingdom 15%, and Germany 6.3% [5, 6].

Water cooled reactors have played a significant role in the commercial nuclear industry since its inception, currently representing over 95% of all operational civilian power reactors worldwide. Among water-cooled reactors, Light Water Reactors (LWRs) stand out as the most prevalent, categorized into two distinct types: Pressurized Water Reactors (PWRs) and Boiling Water Reactors (BWRs). PWRs employ a two-step process, producing steam for turbines in separate steam generators, while BWRs utilize steam generated directly within the reactor core to power the steam turbine. In the early stages of nuclear reactor development, zirconium alloys were adopted for critical components like nuclear fuel cladding and pressure tubes due to their excellent properties, including low thermal neutron absorption cross-section, favorable post-alloying processing characteristics, exceptional corrosion resistance at 300 °C, and good mechanical properties [7-10].

Although zirconium alloys have reached a level of maturity and have been in service in LWRs for an extended period, there remains a critical need to further research and develop new zirconium alloys to improve the economic and safety aspects of nuclear power plants. For example, Zircaloy-2, a commonly employed material for nuclear fuel cladding in BWRs, undergoes significant challenges in its prolonged exposure to the demanding service environment. Subjected to extended immersion in coolant and direct contact with nuclear fuel, the material's performance degrades over time. Many questions persist regarding the damage mechanisms experienced by zirconium alloys during service, including early-stage radiation-induced hardening, irradiation growth, and phenomena related to hydrogen embrittlement [11-14]. Moreover, the microstructural evolution and property changes associated with these phenomena remain inadequately understood. Additionally, in real operational conditions, various factors such as nuclear fuel pellet swelling and component deformation subject zirconium alloys to external stresses during service. Unraveling these complexities is crucial for enhancing the durability and reliability of zirconium alloys in nuclear applications.

This research aims to simulate neutron radiation damage levels through ion irradiation while controlling the application of external tensile stress and maintaining temperature conditions to consider conditions as closely as possible to those encountered in practical working environments. By conducting performance testing and microstructural characterization of materials with different damage levels and considering the influence of complex factors, this study systematically investigates the microstructural evolution and property degradation of zirconium alloys under applied stress. This approach can provide some data basis for evaluating zirconium alloys in nuclear reactors and supports the development of new zirconium alloys.

1.2 Chapter Overview

This thesis mainly focuses on the study of the microstructural evolution and macroscopic properties of Zircaloy-2 after irradiation under external tensile stress, including the radiation-induced hardening in the initial stage of irradiation, the growth mechanism with high burnup, the microstructure evolution, and the characterization and dissolution phenomena of precipitates during the irradiation.

Although zirconium alloys have proven to be mature materials for over 50 years as cladding tubes in nuclear power plants, there is a need to investigate fully irradiation damage in practical working environments. Specifically, there is limited research on the radiation effects with externally applied stress. Considering that microstructural characterization should be consistent with macroscopic performance and that irradiation-induced dislocation loops of hexagonal close packed (hcp) structures are the cause of various performance degradation. The study will conduct microstructural characterization and analysis at different damage stages according to the level of irradiation dose. Therefore, the structure of this thesis is arranged as follows, and the interrelationships between different chapters are shown in the structural diagram presented in Figure 1.1.

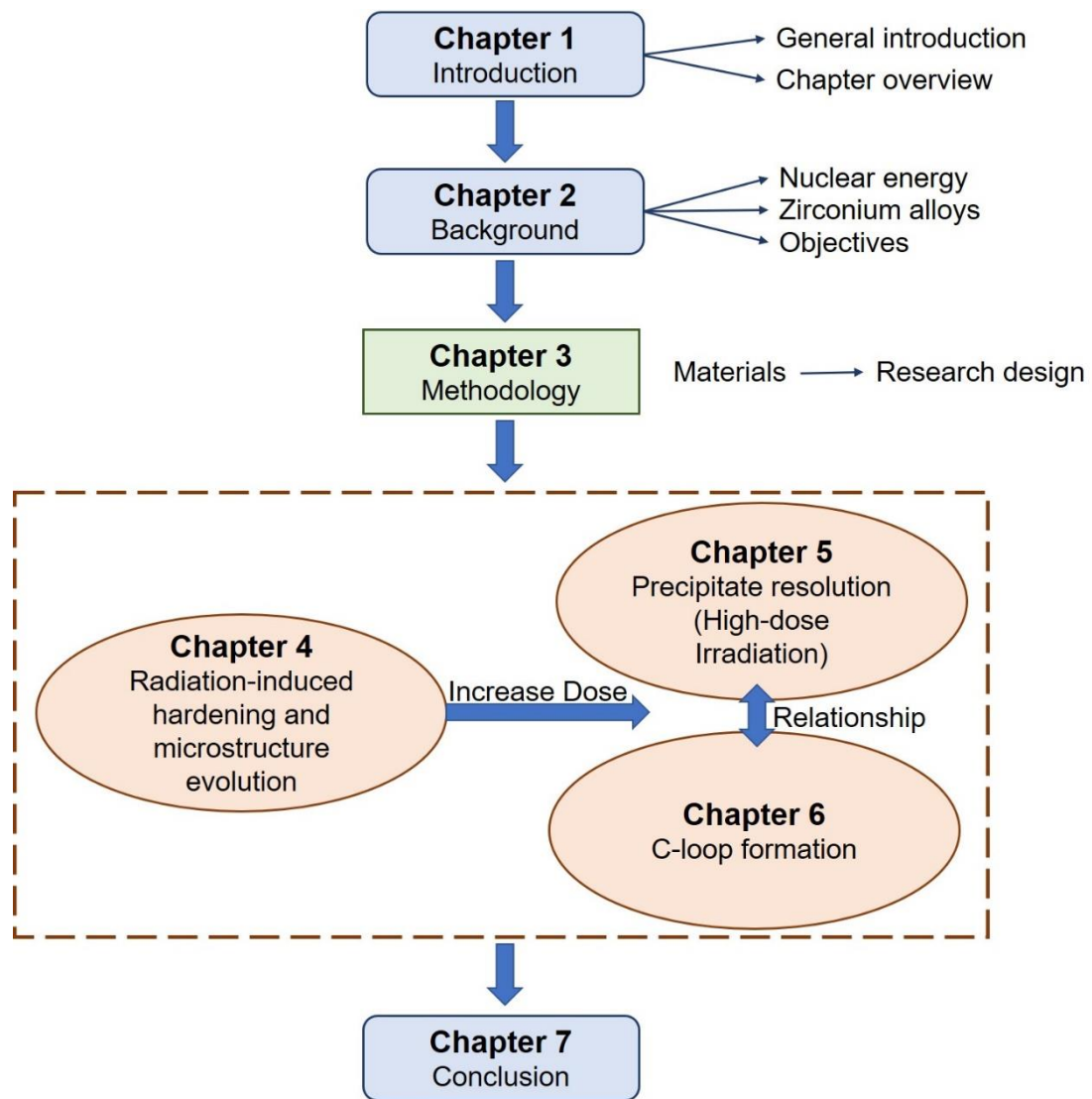


Figure 1.1 Thesis Outlines and Relationship Between Chapters

Chapter 1 provides a general introduction to this work. Zirconium alloys are commonly used in the nuclear field due to their excellent performance. However, performance degradation may occur during service, which poses a certain threat to the safety of nuclear power plants. Furthermore, most studies have focused on the research of irradiation damage without applied stress conditions. The main motivation of this thesis is to analyze the influence of stress conditions on the microstructure and macroscopic properties of Zircaloy-2 at various irradiation stages.

Chapter 2 provides background information on the energy crisis, with a focus on the proportion of nuclear energy in the energy mix of each country. It also discusses the properties and uses of zirconium alloys in nuclear reactors and introduces the main irradiation damage phenomena and latest developments related to zirconium alloys. The necessity of radiation damage under stress conditions in this research is also explained.

Chapter 3 provides a detailed description of the material and experimental procedures used in this study. This includes the chemical composition of Zircaloy-2, sample sizes, and specimen preparation processes. The chapter also describes the irradiation experiments facility, outlining critical factors such as temperature control. Additionally, the chapter expounds on the stage used to apply tensile stress to the specimens throughout the irradiation process. Additionally, this chapter introduces the methods used for hardness testing, which include Vickers hardness test and nano-indentation test. Moreover, various techniques used for the microstructural characterization of the irradiated specimens are discussed, such as transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) analysis.

Chapter 4 presents the results and discussions of the study on the mechanism of radiation-induced hardening in the initial stage of irradiation. It includes an analysis of the dose-dependence of microstructure, size distribution of dislocation loops with different doses, dose-dependence of radiation-induced hardening, and the effect of applied stress on microstructure evolution and hardening.

Chapter 5 presents results and discussions on the resolution of precipitates during high-dose irradiation under applied stress. It includes a comparison of

precipitate resolution under different temperatures and an examination of the influence of applied stress on precipitate dissolution.

Chapter 6 discusses the results and analyses of c-component dislocation loops formation during high-dose irradiation under applied stress. It explores the threshold dose for c-component dislocation loops formation at different temperatures and assesses the effect of applied stress on the microstructure of c-component dislocation loops.

Chapter 7 provides the conclusion of this thesis, summarizing the key findings and contributions, and discussing their implications and potential future research directions.

CHAPTER 2. Background

2.1 Nuclear Energy

With the rapid growth of population and industrialization, the energy crisis and environmental pollution have become two of the most pressing challenges. Energy is essential for providing basic services and powering the economy, and its availability and affordability are key factors in determining a country's development.

Deepened by the outbreak of Covid-19 and the Russian-Ukraine War (RUW), the energy sector has been affected due to the lockdown restrictions. At the same time, the RUW has created uncertainty in the energy market, as it is difficult to predict the potential for disruption to energy flows. Global gas and electricity prices remain sky high, with energy cartels and fossil-fuel-rich states are back in the driving seat [15].

The energy crisis is an opportunity as well as a challenge. In recent times, there has been a growing emphasis on harnessing renewable energy sources like solar, wind, and hydroelectric power. This shift is driven by their diminished environmental impact and reduced reliance on finite resources. With this trend, nuclear energy also plays an important role as a crucial energy source for numerous nations. The advancement and effective utilization of nuclear energy can serve as a pivotal solution to address contemporary challenges, offering essential energy support, fortifying national security, and safeguarding the environment.

The International Energy Agency's (IEA) Tracking Clean Energy Progress

(TCEP) evaluates critical components of the energy system for clean energy transitions. The Net Zero Emissions by 2050 Scenario (NZE) outlines a global pathway to achieve net zero CO₂ emissions by 2050, ensuring universal energy access by 2030 and enhancing air quality. In the context of nuclear energy, the report highlights a significant development. Nuclear capacity additions increased by 40%, with 8 GW newly installed [16]. This growth is noteworthy as it follows a period of stability in capacity additions from 2019 to 2021.

Nuclear power plants harness energy through a process known as nuclear fission, involving the splitting of uranium atoms. This releases a substantial amount of heat energy, which is then utilized to heat water and generate steam. The produced steam drives turbines, ultimately generating electricity. Notably, nuclear power facilities exhibit high energy efficiency, producing a significant amount of power from a relatively small fuel quantity compared to other energy sources. One key advantage of nuclear power is its fuel efficiency. Once fuel is loaded into the reactor, a nuclear power plant can operate continuously for about a year without the need for additional fuel. This longevity contributes to a stable and consistent energy supply. Nuclear power generation stands out in terms of environmental protection on a global scale. The process is characterized by the absence of atmospheric pollutants that typically lead to acid rain, air pollution or global warming during power generation, making it a cleaner option in comparison to some other energy production methods. Additionally, nuclear plants are able to generate large amounts of energy without taking up too much space, making them a viable option for areas with limited land availability.

According to the latest statistics from the International Atomic Energy Agency (IAEA) [17], the global landscape of nuclear power programs is marked by a dynamic and evolving scenario. Presently, there are 412 nuclear power reactors in operation worldwide, collectively generating an impressive total capacity of 370,170 MWe, as illustrated in Figure 2.1, which shows the number of reactors divided by country. Concurrently, the construction of 58 nuclear power reactors is in progress, holding the promise of an additional total capacity of 60,207 MWe. Additionally, 209 reactors have been decommissioned, contributing to a cumulative capacity of 105,095 MWe. The collective operating experience of these reactors spans 19,677 years.

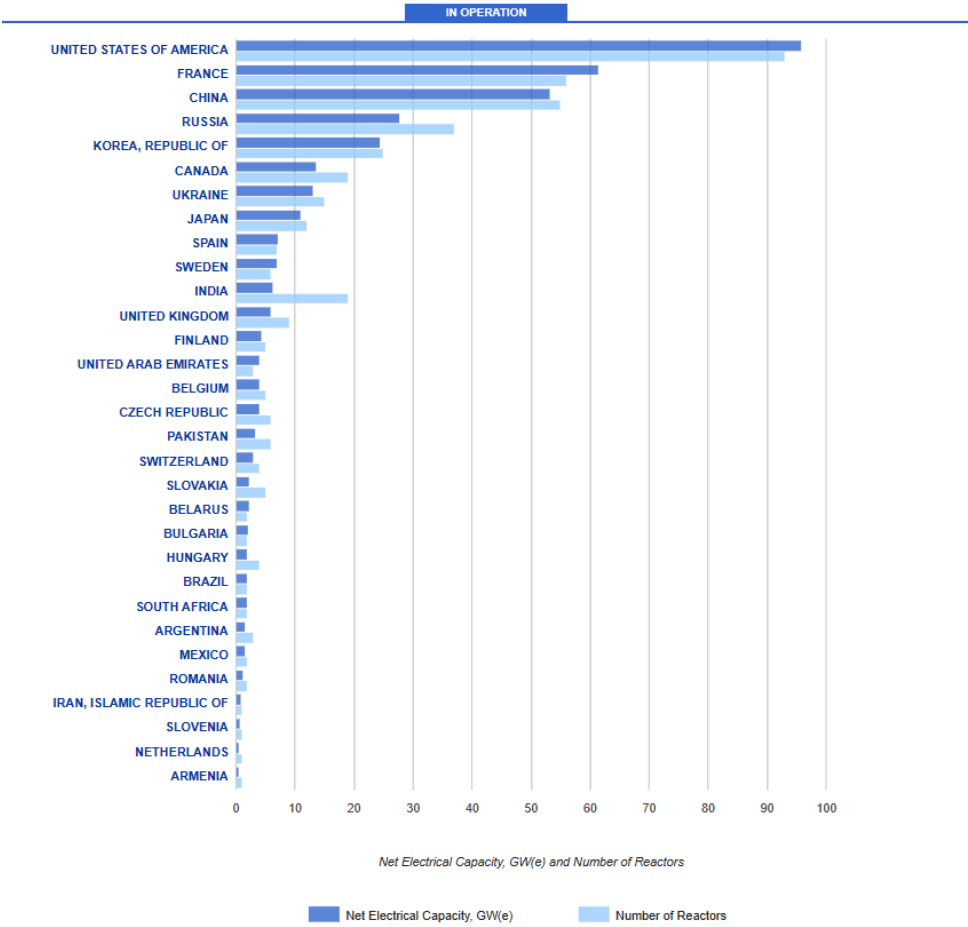


Figure 2.1 Number of Reactors and Net Electrical Capacity [17]

The predominant type of nuclear reactor in operation is the LWRs. LWRs utilize light water for both moderating neutrons and recovering heat, enabling efficient and continuous nuclear fission. These reactors are further classified into two primary types based on the steam generating mechanism: the boiling water reactor (BWR) and the pressurized water reactor (PWR). Figure 2.2 is the number of operational reactors categorized by type and net electrical power. Additionally, Figure 2.3 offers a schematic representation of BWRs and PWRs, illustrating on their respective designs [18]. In BWRs, water directly boils to produce steam, while in PWRs, water remains pressurized, preventing direct boiling. LWRs play a pivotal role in nuclear power generation, significantly contributing to the global energy production landscape.

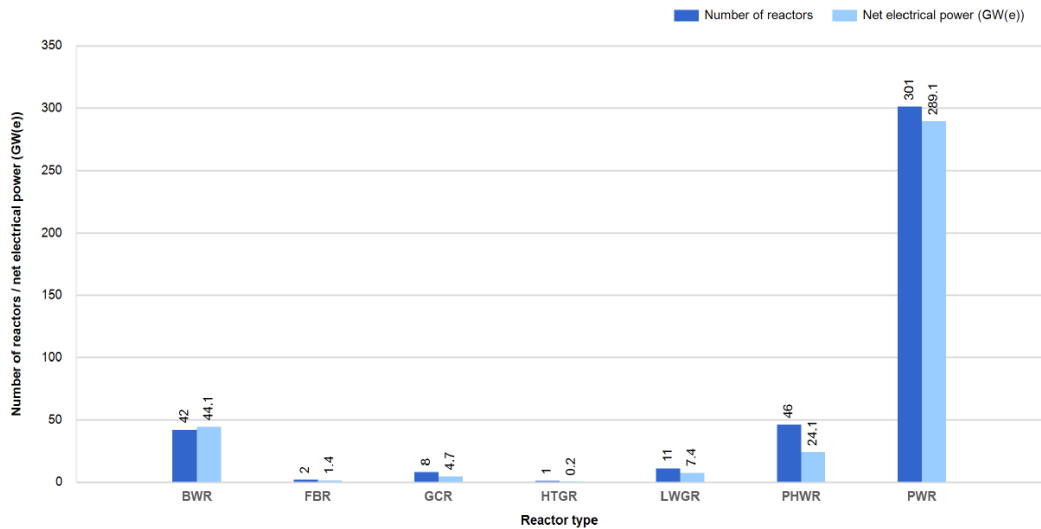


Figure 2.2 Number of Operational Reactors by Type and Net Electrical Power [17]

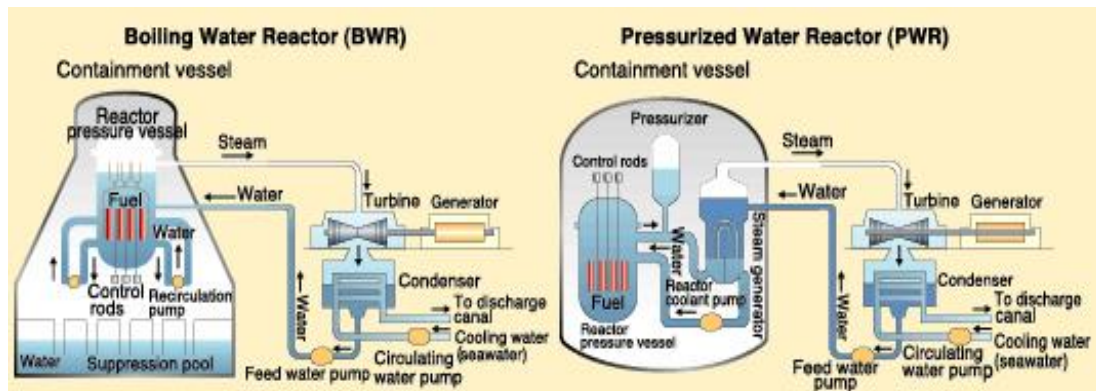


Figure 2.3 Schematic of BWRs and PWRs [18]

Despite its potential advantages, the use of nuclear energy also raises important questions of safety and security. Nuclear plants are expensive to construct and maintain, and the process of nuclear fission creates hazardous materials and radiation, which must be safely disposed of and monitored. Additionally, the potential for a nuclear accident creates a risk of energy insecurity.

Three significant nuclear accidents have occurred in the past involving the United States, the Soviet Union, and Japan. The 1979 Three Mile Island incident led to a partial meltdown, releasing radioactive gases and iodine into the environment, rated at Level 5 on the International Nuclear Event Scale [19]. The 1986 Chernobyl disaster caused massive releases, rated at the highest Level 7, impacting the Northern Hemisphere [20]. The 2011 Fukushima Daiichi accident, triggered by an earthquake and tsunami, prompted emergency measures in Japan, also rated at Level 7 [21]. Despite these incidents, continuous efforts are underway to minimize the possibilities of accidents and enhance safety in nuclear plants. The focus remains on continuous improvement and stringent regulatory measures, alongside a commitment to

gaining a more comprehensive understanding of every aspect of nuclear power plants. This includes a thorough evaluation and broader upgrades to ensure heightened safety standards throughout the entire nuclear facility.

Nuclear energy systems must meet design criteria encompassing tensile properties, thermal creep, cyclic fatigue, creep-fatigue, radiation resistance, and chemical compatibility. Three key materials challenges must be addressed for the continued safe, reliable, and cost-effective use of water-cooled nuclear reactors for electricity production. These challenges include enhancing the understanding of fundamental mechanisms causing corrosion and stress corrosion cracking in austenitic steels and nickel base alloys, developing a predictive grasp of the multi-physics phenomena leading to radiation hardening and degradation in ductility and fracture toughness of complex structural alloys, and innovating nuclear fuels to improve reliability in LWR systems and exploring new LWR fuel systems with enhanced accident tolerance without compromising normal operating performance achieved by current fuels [22]. Addressing other materials challenges in nuclear energy involves enhancing fuel system reliability and bolstering reactor tolerance during accidents. Ongoing construction of power plants prioritizes improved efficiency, passive safety, and economic viability [22-25].

In conclusion, nuclear energy stands as a promising source capable of delivering substantial, clean, reliable, and cost-effective power. Nuclear fission has to play a major role in this necessary transformation of the 21st century energy-supply system. Its increasing abundance underscores its growing importance in the global energy landscape. Nuclear energy holds the potential to shape a future electric grid entirely reliant on green energy, presenting

diverse applications across various sectors [26-28]. However, it is imperative to approach its utilization with careful consideration, acknowledging and addressing potential safety and security risks associated with its implementation. Balancing the tremendous benefits with responsible usage is key to maximizing the positive impact of nuclear energy on our energy systems.

2.2 Zirconium Alloys and Radiation Effects

2.2.1 Zirconium Alloys

Zirconium (Zr) is a silver-grey metallic element with atomic number 40. It has a high melting point of 2125 K (1852 °C), excellent corrosion resistance, good mechanical properties including high strength and toughness. These features make zirconium well-suited for a broad range of applications in industries such as aerospace, navigation, nuclear reactors, and biological medicine [8, 29].

At room temperature, Zirconium exhibits a hcp crystal structure, known as α -Zr with a c/a ratio of 1.593 (slightly lower than the ideal 1.633). The lattice parameters are $a=3.232$ Å and $c=5.147$ Å. When heated to 863 °C, it undergoes a phase transition to a body-centered cubic (bcc) crystal structure, known as β -Zr [29, 30].

To meet properties of engineering requirements, Zirconium is often used especially in combination with other metals such as tin (Sn), niobium (Nb), oxygen (O). Heat treatments are applied to achieve homogeneous solid solutions, phase transformations, and precipitation control to optimize the structure of the alloys.

Zirconium alloys also have excellent nuclear properties, including outstanding mechanical properties dimensional stability, irradiation resistance, low neutron absorption, and corrosion resistance. These attributes make them highly suitable for applications in nuclear industries [8].

2.2.2 Development History of Zirconium Alloys [7-9, 31]

In December 1947, scientists from Oak Ridge National Laboratory successfully removed 2% hafnium impurity from the produced zirconium metal, reducing the absorption of the neutrons and making it highly suitable for reactor tubes. Due to its excellent resistance to corrosion by hot water, zirconium alloys were used on an industrial scale for the Navy's submarine nuclear reactors fuel cladding in the United States in the 1960s. As zirconium production increased, it started to be used on a commercial scale in the U.S., and more plants were opened to meet the growing demand.

To address the corrosion resistance issue at around 300 °C, reducing the nitrogen content in the ingots and adding small amounts of tin (less than 2.5%) were found to be effective methods. This led to the development of Zircaloy-1, but it did not consistently demonstrate good corrosion resistance over time.

By accidentally adding a piece of stainless steel to a batch of zirconium, Zircaloy-2 was created, which showed significantly enhanced corrosion resistance. Then it was selected for use in the Nautilus submarine in 1952. Because of hydrogen absorption by the cladding, nickel in Zircaloy-2 was replaced by iron, which was called Zircaloy-4 and adopted in all U.S. submarines.

These zirconium alloys have different applications in different types of nuclear reactors. For instance, Zircaloy-4 is commonly used in PWRs, whereas Zircaloy-2 is typically used in BWRs. Heavy water-moderated CANDU reactors utilize Zr–Nb alloys to achieve higher strength and absorb less hydrogen. Furthermore, researchers have designed new alloys based on variations of the zirconium with 1% niobium alloy, such as M5, or by utilizing quaternary alloys such as Zirlo and E635. These alloys have been tested and used in many countries for decades and were believed to be reliable under normal and accidental operation conditions. At present, the main alloys used for fuel cladding tubes and structural materials in BWRs, PWRs, and CANDU reactors are basically three types: Zr-Sn series, Zr-Nb series, and Zr-Sn-Nb series. Table 2-1 lists the typical compositions of these zirconium alloys.

Table 2-1 Chemical Composition of the Commercial Zirconium Alloys in wt.% [31]

Alloy	Sn	Nb	Fe	Cr	Ni	O	Zr
Zircaloy-2	1.2-1.7		0.07-0.2	0.05-0.15	0.03-0.08	0.12	Bal.
Zircaloy-4	1.2-1.7		0.18-0.24	0.07-0.13		0.1-0.14	Bal.
Zr-2.5Nb		2.4-2.8				0.12-0.15	Bal.
M5		1				0.11-0.16	Bal.
ZIRLO	1	1	0.1			0.09-0.12	Bal.
E110		1				0.05-0.07	Bal.
E635	1.2	1	0.35			0.05-0.07	Bal.

2.2.3 Radiation Effect of Zirconium Alloys

Zirconium alloys commonly used as fuel rod cladding, which transfer the nuclear heat generated from stacked Urania pellets to the water coolant and also act as a primary barrier to prevents radioactive fission products from leaving the fuel pellets and escaping into the reactor coolant and contaminating it [22]. In such a service environment, cladding must withstand simultaneous exposure to neutron irradiation, mechanical stress, and corrosion due to water or steam. The primary radiation effects on zirconium alloys can be summarized as follows.

(a) Radiation-induced defect clusters in zirconium alloys

During neutron irradiation, high-energy neutrons collide with the nuclei of Zr atoms in the crystal lattice, leading to the displacement of the Zr atoms from their lattice sites. These self-interstitial atoms (SIA) can move around and react with other atoms to form clusters, such as dislocation loops, voids, and stacking faults.

Griffiths et al. showed that there are mainly two types of dislocation loops induced by irradiation in zirconium alloys. One type is the $\langle a \rangle$ dislocation loops, which occur in large numbers in the initial stage of irradiation. Another type is $\langle c \rangle$ type dislocation loops, formed only above a threshold dose [32, 33]. Barashev et al. [34] proposed a reaction-diffusion model based on the production bias model, and obtained the dependence of vacancy and interstitial loop number densities on the irradiation dose using available experimental data as shown in Figure 2.4.

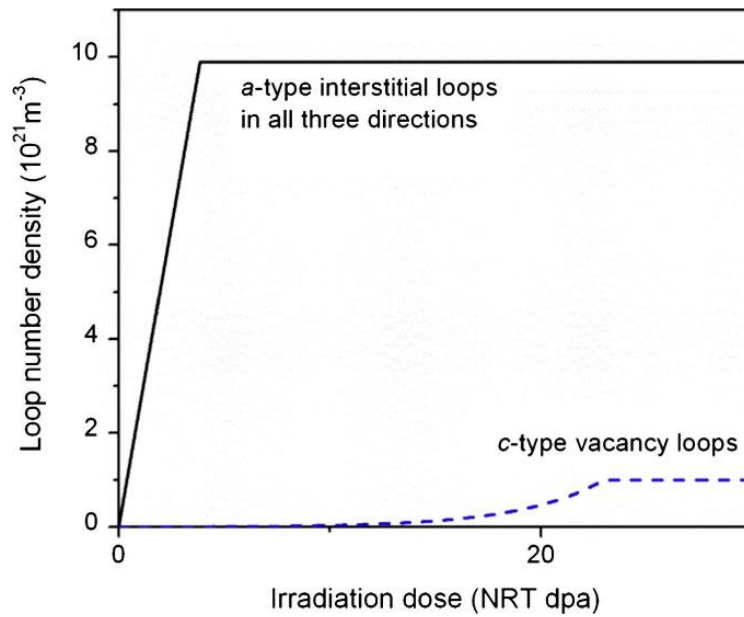


Figure 2.4 Dependence of Vacancy and Interstitial Loop Number Densities on the Irradiation Dose [34]

Jostsons et al. [35] discovered that vacancy and interstitial $\langle a \rangle$ loops could co-exist during irradiation by normal inside/outside contrast shown in Figure 2.5, which had the same Burgers vectors of $1/3\langle 11\bar{2}0 \rangle$. The size, density and nature of dislocation loops are all temperature dependent. At about 573 K (300 °C), the average loop diameter was typically around 5-20 nm, and the density was about $2 \times 10^{22} \text{ m}^{-3}$. There was a tendency for the size of dislocation loops to increase, while the density decreases with increased temperature. Moreover, the proportion of vacancy loops decreased when the temperature was higher than 700 K (427 °C) [33, 35, 36].

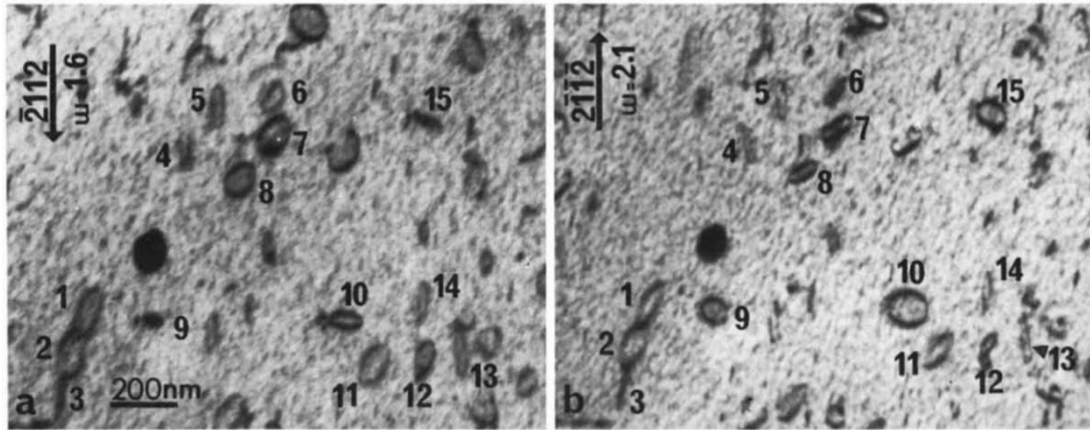


Figure 2.5 Characterization of <a> Loops in Zone-Refined Zirconium Irradiated at 668 K (395 °C) to Fluences to 6.4×10^{23} neutrons/m² (>1 MeV) with $z \approx [2\bar{1}13]$. Loops in Outside Contrast in (a) are Vacancy and in (b) are Interstitial [35]

Holt and Gilbert [37] observed the presence of <c> loops in annealed Zircaloy-4 when it was irradiated at temperatures between 550–580 K and to fluences between 3.5 and 8.6×10^{25} n/m², $E > 1$ MeV. Griffiths [33] also reported the observation of <c> loops in Zircaloy-4 at a higher temperature above 625 K (350 °C). <c> loops are vacancy in nature with Burgers vectors of $1/6\langle 20\bar{2}3 \rangle$ only observed in one heavily oxidized sample. Loops with Burgers vectors of $1/2\langle 0001 \rangle$ have been observed in some other specimens irradiated at higher temperature. Many studies have shown that the generation of <c> loops is influenced by temperature, material purity. And <c> loops are more likely to form near second-phase particles (SPP) [33, 36, 38].

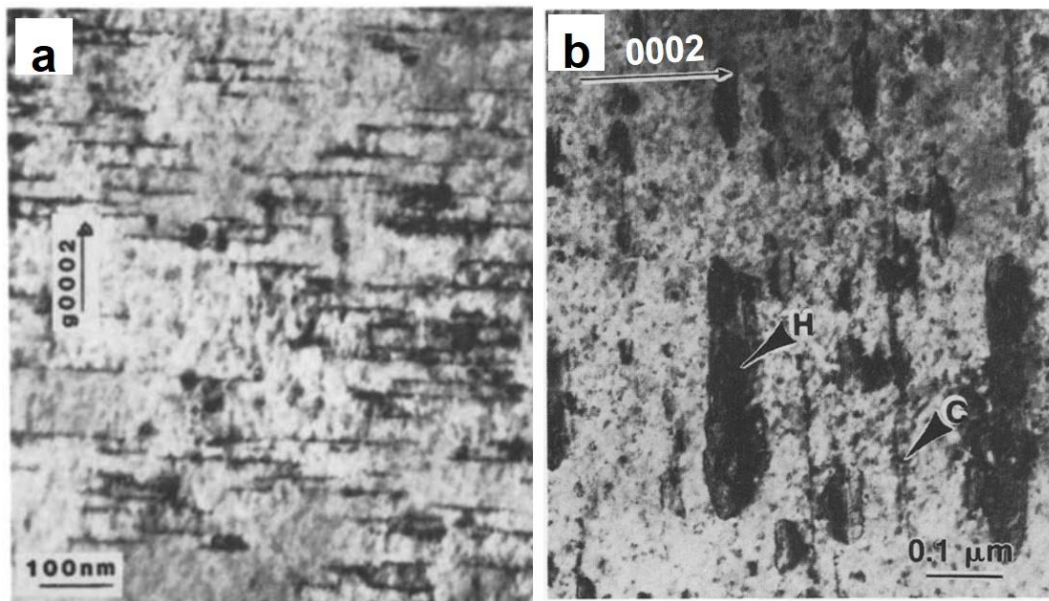


Figure 2.6 <c> Loops in Zircaloy-4: (a) Irradiated at 560 K to a Fluence of $8.5 \times 10^{25} \text{ n/m}^2$ [37]; (b) Irradiated at 690 K to a Fluence of $5.5 \times 10^{25} \text{ n/m}^2$. Hydride(H) also Shown [33]

In irradiated zirconium, the gather of vacancies is predominantly in the form of dislocation loops, and the formation of cavities is a rare occurrence [39]. The formation of cavities depends on the purity of the material and the presence of insoluble gases like helium. Griffiths et al. [39] demonstrated that the addition of niobium and tin to the alloy effectively suppresses the formation of c-component dislocation loops and cavities. Additionally, the existence of basal plane <c> loops appears to be linked with the formation of cavities. Material with a high concentration of <c> loops has fewer cavities, suggesting that cavities may have a higher interstitial bias compared with loops. And the vacancy supersaturation required for nucleation may be lower for the loops compared with the cavities [40]. During electron irradiation of impure zirconium in the presence of a pre-implanted insoluble gas such as helium, voids are easily formed [33, 39].

(b) Precipitates evolution and element redistribution in zirconium alloys

Intermetallic second-phase particles are present in all zirconium alloys and play important roles both during fabrication, where they limit grain growth, and in service, where they influence mechanical properties and corrosion resistance. These alloys both contain particles with compositions of $\text{Zr}(\text{Cr}, \text{Fe})_2$, with a hcp crystal structure. In Zircaloy-4, $\text{Zr}(\text{Fe}, \text{Cr})_2$ particles are often faceted and typically have a length ranging between 100 and 250 nm [41]. Meanwhile, Zircaloy-2 also contains particles of a body-centered tetragonal (bct) structure, $\text{Zr}_2(\text{Ni}, \text{Fe})$ [38, 42]. Figure 2.7 shows the second-phase particles in Zircaloy-2 and Zircaloy-4. Figure 2.7(a) and Figure 2.7(b) illustrate the presence of these second-phase particles in Zircaloy-2 [43], while Figure 2.7(c) depicts $\text{Zr}(\text{Fe}, \text{Cr})_2$ in Zircaloy-4 [41].

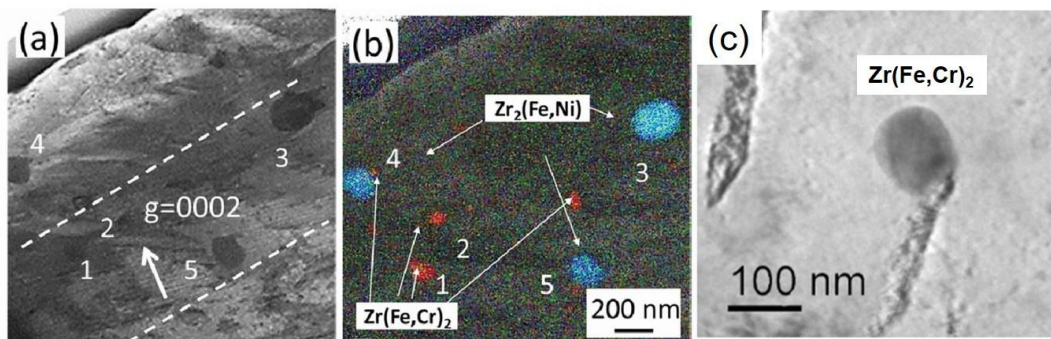


Figure 2.7 Second-Phase Particles in the Zircaloy-2 (a, b) [43] and Zircaloy-4 (c) [41]

Gilbert et al. [42] first published that $\text{Zr}(\text{Cr}, \text{Fe})_2$ precipitates in zircaloys become amorphous under neutron irradiation up to 570 K (297 °C), resulting in volume changes and a reduction in relative iron concentration in the precipitate. In contrast, $\text{Zr}_2(\text{Ni}, \text{Fe})$ particles exhibit different behavior, with available data do

not fully establish whether the iron concentration is a factor.

Griffiths et al. [44] further investigated intermetallic SPPs in both Zircaloy-2 and Zircaloy-4 during neutron radiation. They found that at low temperatures below 350 K (77 °C), both particle types become amorphous. At intermediate temperatures of 520-600 K (245-327 °C), $\text{Zr}_2(\text{Ni}, \text{Fe})$ particles remain crystalline, while $\text{Zr}(\text{Cr}, \text{Fe})_2$ particles become amorphous, particularly when chromium content is high or solute is depleted below the stoichiometric value. At higher temperatures about 640-710 K (367-437 °C), both types of SPPs undergo radiation-induced dissolution, forming precipitates in the matrix and at grain boundaries. Additionally, Sn-rich precipitates form at these temperatures, likely due to radiation-enhanced diffusion.

Many studies have also observed particle dissolution and element segregation after different irradiation conditions in zirconium alloys [45-47]. The studies have proposed models suggesting that amorphization results from deviations in stoichiometry, attributed to a ballistic interchange of iron and zirconium atoms across the precipitate-matrix interface, which corroborates the observations [47, 48].

Harte et al. [49-51] investigated the irradiation-induced precipitation in proton- and neutron-irradiated Zircaloy-2 at the nano-scale using atom probe tomography (APT), ultra-high spatial resolution scanning transmission electron microscopy (STEM), and X-ray energy-dispersive spectroscopy (EDS). Their findings revealed Fe-depletion in both types of SPPs after irradiation, with $\text{Zr}(\text{Fe}, \text{Cr})_2$ showing heterogeneous depletion and $\text{Zr}_2(\text{Fe}, \text{Ni})$ displaying homogeneous depletion. Moreover, the study detected a delay in the dissolution of $\text{Zr}_2(\text{Fe}, \text{Ni})$ SPPs compared to $\text{Zr}(\text{Fe}, \text{Cr})_2$. These dissolution

processes resulted in matrix supersaturation with solute for both irradiation types, highlighting that proton irradiation effectively emulates neutron radiation effects.

Watanabe et al. [43] discussed the relationship between the dissolution of precipitates and the formation of <c> loops in different zirconium alloys following ion irradiation. Their findings suggest that the dissolution of Fe-enriched precipitates is associated with an increased formation of <c> loops. Additionally, Francis et al. [52] explored the impact of Nb precipitates/clusters on the evolution of dislocation loop size and densities, contributing to enhanced resistance against irradiation-induced growth.

(c) Irradiation hardening of zirconium alloys

Radiation-induced hardening (RIH) is a widespread phenomenon observed in various metallic materials under low to intermediate temperature irradiation. It serves as a crucial indicator of a material's radiation resistance, often accompanied by increased yield and tensile strength and reduced ductility. Byun and Farrell [53] conducted a comprehensive characterization of irradiation hardening behaviors in bcc, face-centered cubic (fcc), and hcp alloys and pure metals subjected to neutron or proton and neutron irradiation at low temperatures (<200 °C). They identified that the transition from low-dose to high-dose irradiation hardening occurs either when the tensile specimen experiences prompt plastic instability at yield or when defect cluster density reaches saturation. Understanding RIH is vital for evaluating material degradation upon irradiation, particularly embrittlement, and for screening new materials for future nuclear energy systems [53, 54].

Lambrecht et al. [55] investigated the relationship between irradiation-induced

microstructural features and the hardening of reactor pressure vessel steels. Their findings revealed that dislocation loops, while strong obstacles to dislocation motion, have a minor impact on the overall hardening due to their low concentration. Precipitates also play an important role in the hardening despite being relatively soft due to their small size and coherent nature. Vacancy clusters contribute to loop and precipitate formation but have limited direct influence on hardening.

However, Dong et al. [56], Carolina Vazquez et al. [57], and Yang et al. [58] and others [59, 60] have conducted calculations to investigate irradiation-induced hardening under low doses, focusing on situations where the density of dislocation loops is nearly saturated. They utilized empirical formulas to simulate and confirmed the mechanism where the generation of <a> type dislocation loops during the early stages of irradiation leads to hardening. Consideration of the existing limitations, notably the lack for stress conditions in real-world environments and the absence of detailed information on the dose-dependent evolution of microstructure, a comprehensive understanding of the impact of irradiation induced hardening during operation necessitates further research.

(d) Irradiation growth and other irradiation damages in zirconium alloys

Irradiation growth, characterized by dimensional changes at constant volume during irradiation without applied stress, has been extensively studied [61-63]. In the 1960s, Buckley observed that zirconium single crystals exhibited expansion along the a-axis direction and contraction along the c-axis direction under neutron irradiation [64, 65], as illustrated in Figure 2.8, which presents the results of irradiation growth. The single crystal elongated at a rate that

gradually decreased over time, from about $2 \times 10^{-6} \text{ h}^{-1}$ to zero after 1500 hours and 0.07% strain.

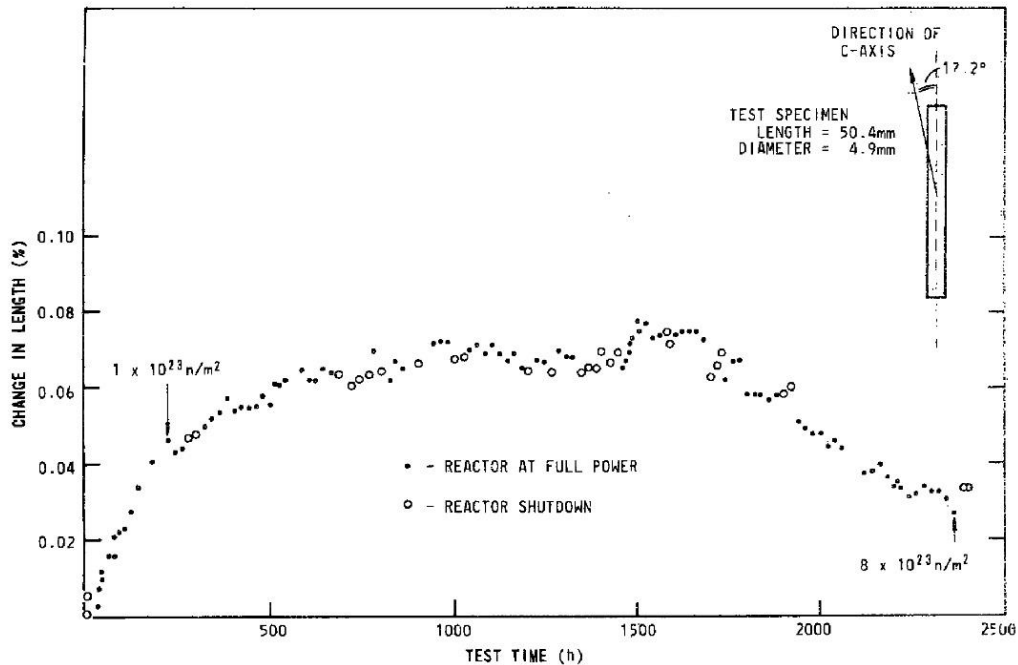


Figure 2.8 Irradiation Growth of Zirconium Single Crystal at 473 K (200 °C) in a Neutron Flux of $1.15 \times 10^{17} \text{ n/m}^2\text{-s}$ (>1 MeV) [64]

Various researchers [66, 67] have attempted to reveal the intrinsic mechanisms of this growth phenomenon, endeavoring to establish irradiation growth models. Carpenter et al. [68] proposed that most experiments showed there is an increase in growth rate at higher fluences (approximately $3 \times 10^{21} \text{ n/m}^2$ at 553 K), similar to the "breakaway" phenomenon observed in Zircaloy-2, which has been linked to the nucleation and growth of c-component vacancy loops on basal planes. The growth mechanism at elevated fluences exhibits similarity to Buckley's proposed mechanism [65, 69]. Crystals subjected to severe deformation exhibit exceptionally high growth rates, persisting in a steady-state

manner to high fluences. This growth aligns with the annihilation of an excess of interstitials at a-type dislocations, coupled with the loss of corresponding vacancies to a high density of oriented twin boundaries and c-component dislocations. Griffiths et al. [70] also delve into the accelerated irradiation growth observed in sponge zirconium, Zr-2.5 wt.% Nb, Zircaloy, and Excel (Zr-3.5Sn-1.0Nb-1.0Mo-0.10 by wt.%) alloys in comparison to high-purity crystal-bar zirconium. This phenomenon manifests at irradiation temperatures ranging from 550-710 K (277-437 °C) and fluences between 0.1 to 10×10^{25} n/m² (E>1 MeV). It underscores the presence of an incubation period or fluence before the onset of accelerated or breakaway growth, emphasizing the variability based on the specific material, its metallurgical condition before irradiation, and the irradiation temperature. The study further proposes a similar viewpoint, revealing a correlation between accelerated irradiation growth and the appearance of c-component vacancy loops on basal planes. Moreover, it underscores that the formation of these loops is intricately linked to both specimen purity and irradiation temperature, as previously discussed. Materials with a high interstitial-solute content, containing c-component loops, exhibit high growth rates even at low fluences. In sponge zirconium and zircalloys, the formation of c-component loops and the associated acceleration of growth during irradiation occur due to the presence of intrinsic interstitial solutes (mainly oxygen, carbon, and nitrogen) supplemented by interstitial iron, chromium, and nickel resulting from the radiation-induced dissolution of precipitates.

Numerous irradiation growth models have been established based on different theories and equations [71-73]. The current systematic molecular dynamics

simulations, focusing on the structure, energetics, induced strain fields, and the impact on dimensional changes of interstitial and vacancy dislocation loops in pure hcp zirconium, offer a coherent understanding of the radiation-induced growth observed in single crystal zirconium. This work serves as a foundation for subsequent investigations into the influence of alloying elements and impurities.

In addition to the before-mentioned irradiation damages in zirconium alloys, practical operations encounter additional challenges. Due to prolonged exposure of cladding tubes to coolant, issues such as hydrogen pick-up, waterside corrosion, stress corrosion, and fracture phenomena also become notable. However, a detailed exploration of these challenges is beyond the scope of this study.

In order to sustain the role of nuclear power in carbon-free electricity generation, the development of more efficient advanced reactors is crucial, while ensuring safety and security. These advanced designs operate in harsher environments, demanding accelerated materials development to withstand radiation-induced degradation. Traditional reactor irradiation campaigns are time-consuming and expensive, hindering research progress. Over decades, researchers and organizations have sought ways to expedite radiation damage studies for nuclear materials. Ion irradiation emerges as a viable solution, compressing irradiation time from years to days and offering cost-effective predictions of microstructure and mechanical property changes. Ion beams enable the exploration of damaging degradation processes, like irradiation-induced swelling, at significantly higher damage rates. Despite progress, challenges remain in deploying ion beam data for reactor materials qualification due to a

lack of detailed mechanistic understanding.

To achieve economic efficiency and enhance safety, numerous scholars have turned to ion irradiation as the optimal method for studying neutron radiation. By comparing results from both neutron and ion irradiation and providing theoretical explanations, researchers can effectively simulate and observe similar radiation phenomena using ion irradiation [74-77]. This approach offers distinct advantages, making ion irradiation a preferred means of investigating neutron irradiation processes.

2.3 Objectives of This Thesis

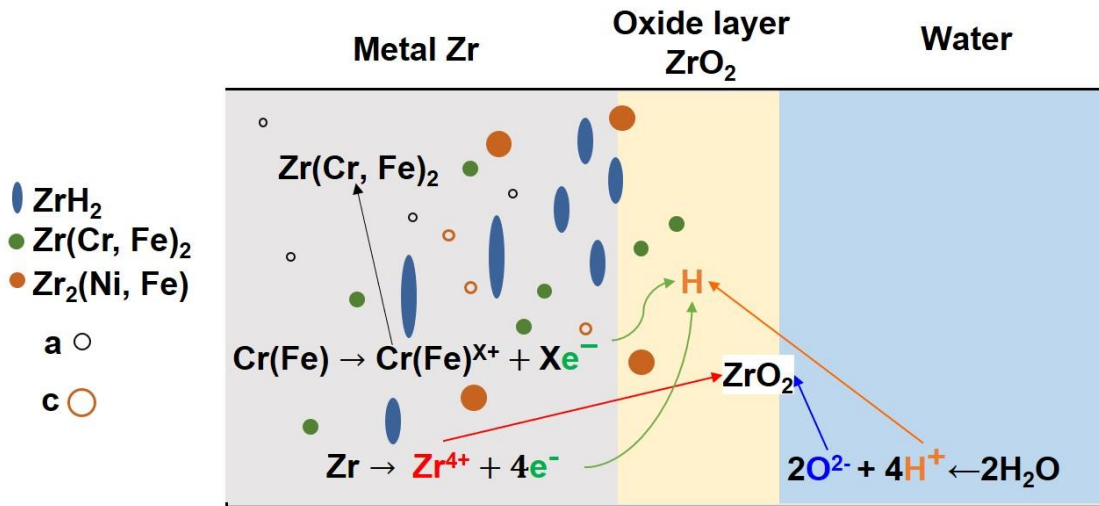


Figure 2.9 Schematic of Irradiation Effects in Zirconium

Three issues of fundamental importance are addressed in this thesis:

- (1) Study the dose dependence of microstructure evolution and irradiation-induced hardening in Zircaloy-2 at low doses (below 1 dpa) and the influence of applied stress on irradiation-induced hardening.

- (2) Investigate precipitate dissolution in Zircaloy-2 at different temperatures and analyze the effect of applied stress on precipitate dissolution.
- (3) Examine the formation of <c> type dislocation loops in Zircaloy-2 at higher doses at 300 °C and 400 °C and assess the effect of applied stress.

CHAPTER 3. Material and Experimental Procedures

This chapter provides a comprehensive description of the material composition used in this thesis, the irradiation experimental process and the instrumentation used for microstructural analysis.

The initial section introduces the chemical composition of the material, including pre-treatments such as thinning and polishing of different types of samples. Subsequently, it will detail the irradiation experimental process, specifically addressing stress conditions during the irradiation experiments on the samples, also along with the temperature control during high-dose ion irradiation. Following the completion of preliminary preparations, the next section introduces the accelerator located at the Research Institute for Applied Mechanics (RIAM) at Kyushu University, where ion irradiation experiments on the samples were conducted.

Finally, the chapter proceeds to discuss hardness testing applied to various processed specimens, as well as characterization techniques such as microstructure characterization, and elemental distribution analyses.

3.1 Material

The material used in this study was Zircaloy-2, and its chemical composition is presented in Table 3-1. Among the alloying elements, Sn is solid-soluble in the zirconium matrix phase, whereas Fe, Ni, and Cr form Intermetallic second-phase particles with compositions of $\text{Zr}_2(\text{Ni, Fe})$ and $\text{Zr}(\text{Cr, Fe})_2$, precipitating within the matrix, as illustrated in Figure 3.1.

Table 3-1 Chemical Compositions of Zircaloy-2 in wt.%

Alloy	Sn	Fe	Cr	Ni	H(wtppm)	Zr
Zircaloy 2	1.38	0.15	0.09	0.05	46	Bal.

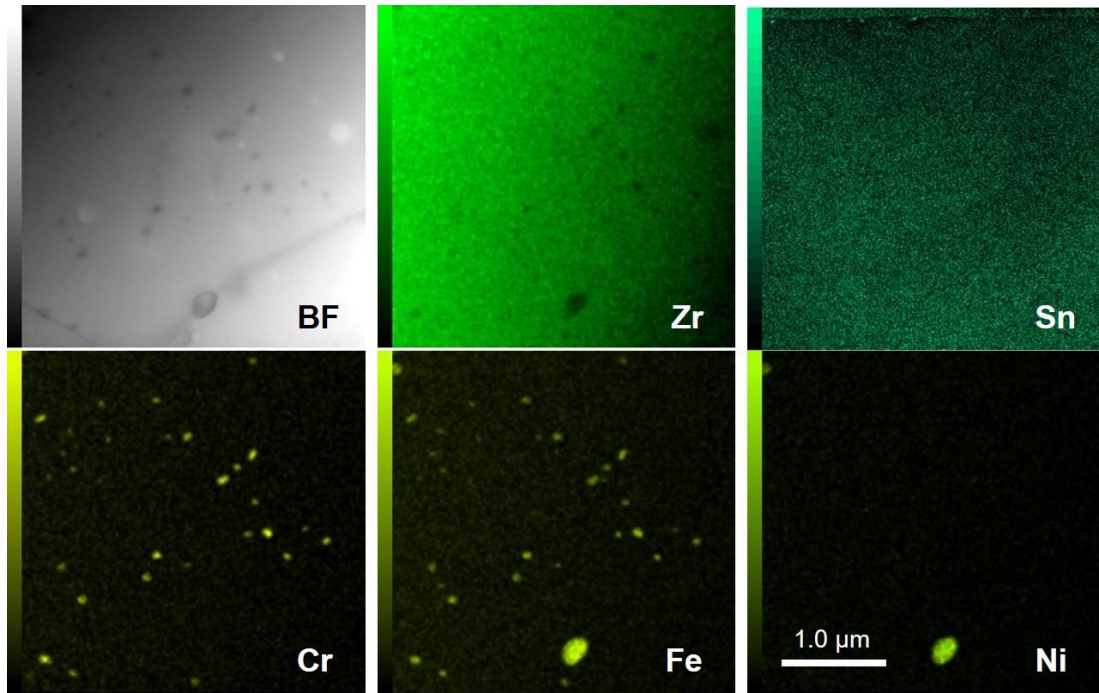


Figure 3.1 EDS Element Mapping Results of Zircaloy-2 After Annealing, with Intermetallic Second-Phase Particles of $Zr_2(Ni, Fe)$ and $Zr(Cr, Fe)_2$ within the Matrix.

3.2 Sample Preparation

The material was initially cold-rolled at room temperature to achieve a thin sheet with a thickness of approximately 0.13 mm. The schematic representation of the cold-rolling process is illustrated in Figure 3.2, where the hcp crystal structure's c-axis is nearly perpendicular to the rolling plane after the rolling.

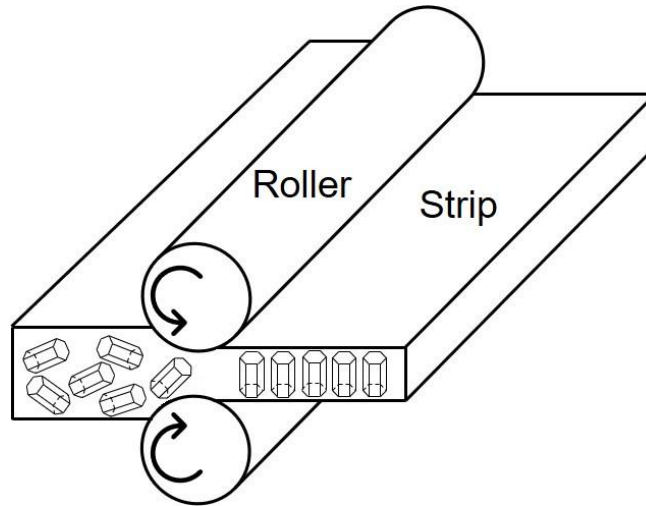


Figure 3.2 Schematic Representation of Cold-Rolling Process

The $\Phi 3$ mm disk specimens and tensile samples were obtained by punching the thin sheet. As illustrated in Figure 3.3, the tensile samples have a nominal length of 4.9 mm and a gauge width of 1.2 mm, with a thickness about 0.10 mm. For the thicker tensile samples with a thickness of 0.25 mm, they were punched from a sheet with an approximate thickness of 0.26 mm, then slightly thinned and polished.

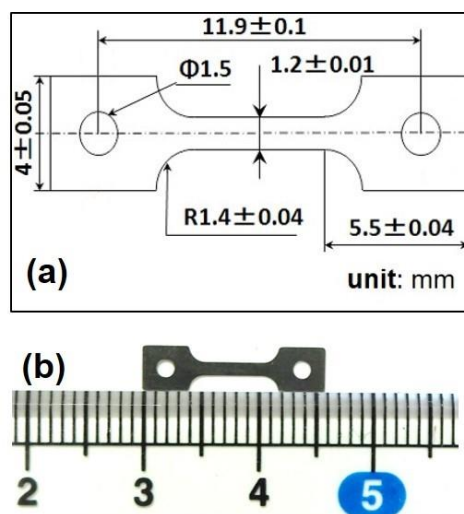


Figure 3.3 Dimensions of Tensile Sample, with a Nominal Length of 4.9 mm and a Gauge Width of 1.2 mm

The disk specimens were subjected to mechanical grinding using abrasive papers with #2000 grit, resulting in a thickness reduction to 0.1 mm. Subsequently, the specimens underwent annealing at 630 °C for 2 hours and were air-cooled to room temperature. Finally, electrochemical polishing was conducted in a solution composed of 10% HClO₄ and 90% C₂H₅OH at - 55 °C and 19 V.

To achieve a final thickness of 0.1 mm or 0.25 mm, the tensile samples were subjected to mechanical grinding using abrasive papers ranging from #800 to #2000 grit, as well as diamond sandpaper with #8000 grit. The 0.3 µm Al₂O₃ suspension was used to achieve a finely polished mirror surface. The surface appearance after polishing is depicted in Figure 3.4. Finally, the samples also underwent annealing at 630 °C for 2 hours and were air-cooled to room temperature.

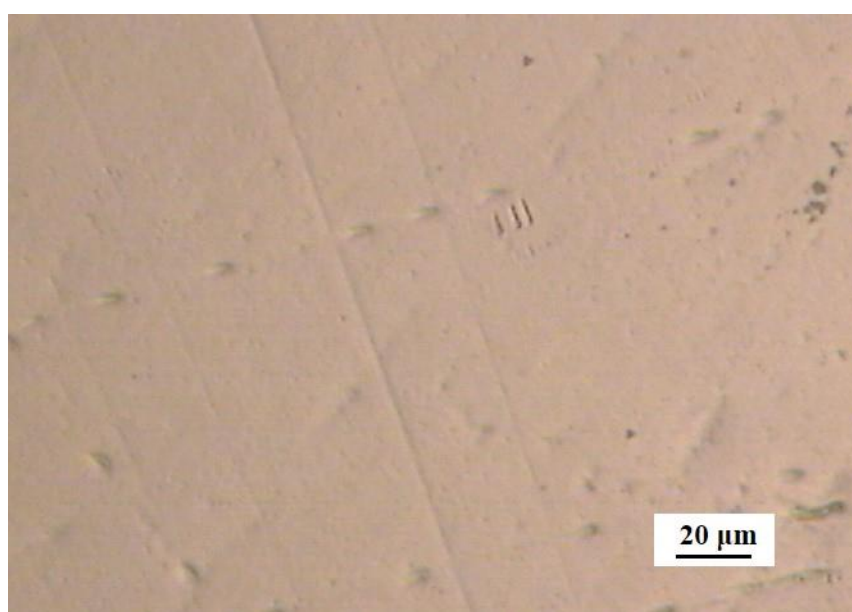


Figure 3.4 Surface Appearance of Tensile Samples After Polishing for Nano-Indentation Test

3.3 Ion Irradiation Experiment

3.3.1 Tandem Accelerator Facility at Kyushu University

Considering the advantages of economic efficiency and safety, this study utilized ion irradiation as a simulation of the neutron irradiation process to obtain similar irradiation phenomena [74, 75].

Figure 3.5 illustrates the tandem ion accelerator utilized for this research and its schematic diagram, which is located at the Research Institute for Applied Mechanics (RIAM) at Kyushu University. The ion accelerator consists of a duo-plasma ion source with an accelerating unit with a maximum voltage of 30 kV, along with a 10 kV D_2^+ irradiation capability, facilitating triple ion beam irradiation.

The basic principle of the 3.2 MeV Ni^{3+} ion irradiation used in this experiment is as follows: Cesium ions, accelerated to 7 keV, collide with a nickel target, leading to the transformation of nickel into Ni^- in the heavy ion source. Ni^- is accelerated by a 20 keV positron and guided to an acceleration tube by a low-energy magnet. The acceleration tube is grounded at the entrance and exit at 0 V, with a voltage of 800 keV is applied inside. Ni^- is stripped of its electrons by N_2 gas in the accelerating tube and becomes Ni^{3+} . Through a second acceleration within this tube, Ni^{3+} gains 3.2 MeV of energy, four times the initial 800 keV. Exiting the acceleration tube, Ni^{3+} is directed by a high-energy magnet to the irradiation target chamber, where only Ni^{3+} is bent, converged by a lens, and irradiated onto the sample.

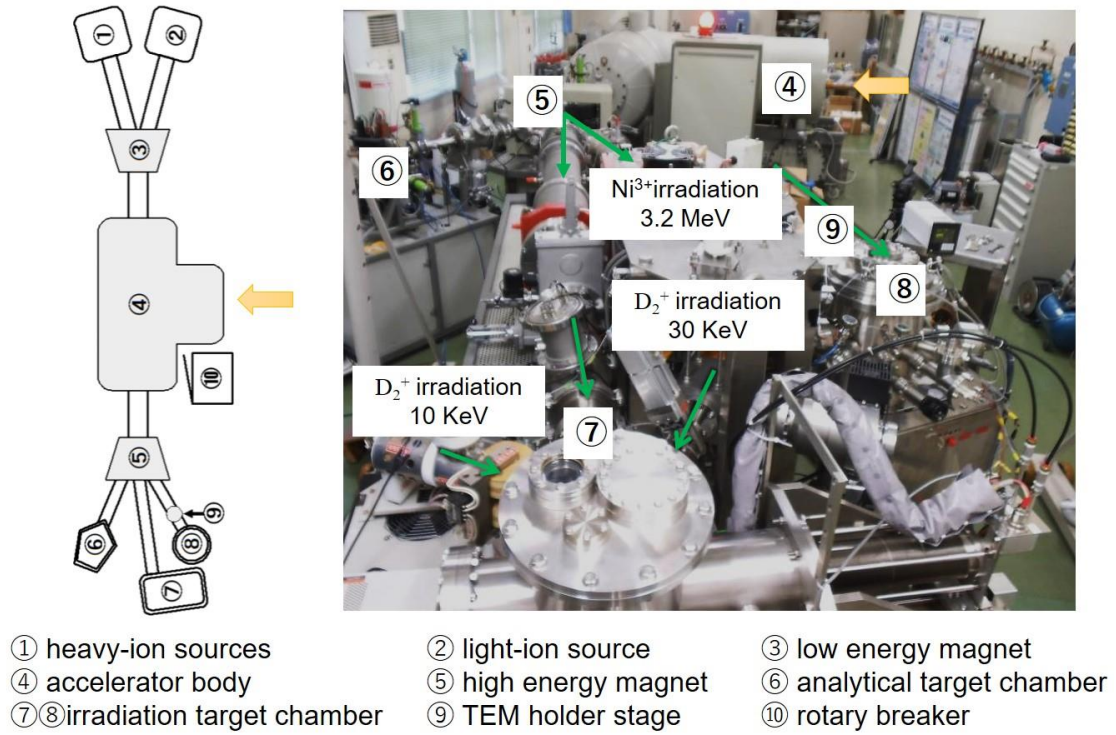


Figure 3.5 Tandem Accelerator Facilities for 3.2 MeV Ni³⁺ Ion Irradiation at Kyushu University

To conduct ion irradiation, it is essential to calculate the necessary irradiation time based on the required irradiation damage dose. The injection time is calculated using the formula as follows:

$$\text{Injection time (s)} = \frac{\text{Effective area (m}^2\text{)} \times \text{Beam charge (C)} \times \text{Dose (ions/m}^2\text{)}}{\text{Beam current (A)}}$$

where the injection time is measured in seconds (s), the beam current is in amperes (A) determined during the experiment, and the effective area is a $\Phi 2$ mm spot. The beam charge is the product of the ion valence state and the charge of one electron, measured in coulombs (C). The ion dose is expressed

as ions per unit area (ions/m²). The dose given a beam current of 1 nA, the calculation flux as follows:

$$\text{Flux} = \frac{1 \times 10^{-9} \text{ (A)}}{\pi \times (1 \times 10^{-3})^2 \text{ (m}^2\text{)} \times 3 \times 1.6 \times 10^{-19} \text{ (A}\cdot\text{s)}} = 6.63 \times 10^{14} \text{ m}^{-2}\text{s}^{-1}$$

Ion irradiation damage is quantified in displacements per atom (dpa), representing the number of times each atom is displaced from its lattice position. In this experiment, the damage and distribution resulting from 3.2 MeV Ni³⁺ ion irradiation were calculated using the Stopping and Range of Ions in Matter (SRIM) software [78]. The calculation result is depicted in the Figure 3.6, where the threshold energy for displacement is assumed to be 40 eV [43]. The peak damage was located at a depth of 1.4 μm, and the damage rate was 1×10^{-4} dpa/s at the damage peak in this case.

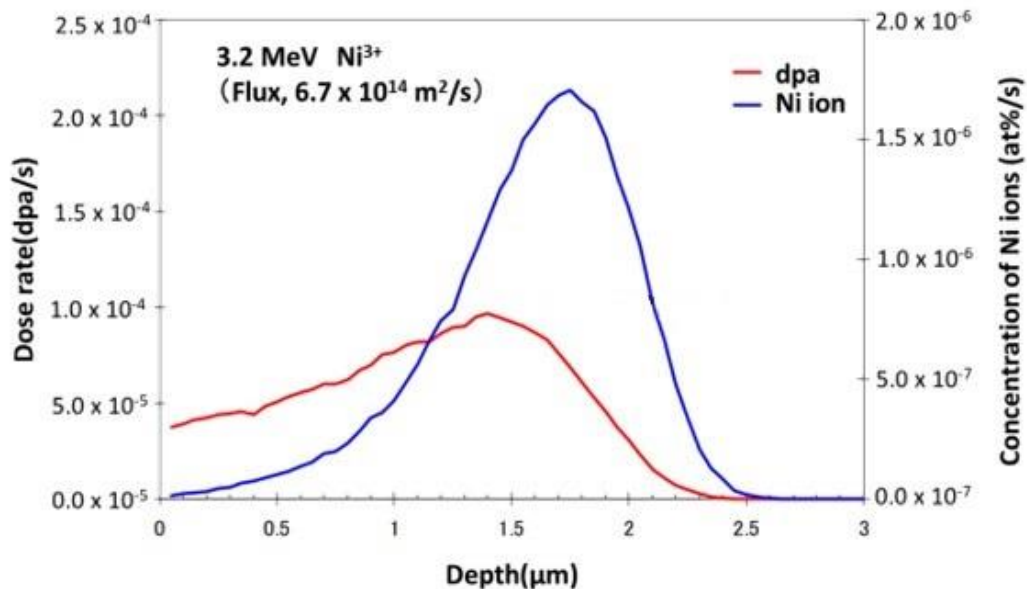


Figure 3.6 SRIM Calculation of the Damage Distribution and the Concentration of Ni³⁺ atoms by 3.2 MeV Ni³⁺ Ions Irradiation [43]

3.3.2 Applied Stress Control During the Irradiation

The primary challenge in this experiment lay in conducting ion irradiation under external stress conditions. Given the sensitivity of the sample behavior to temperature variations, it is critical to maintain precise control of the external tensile stresses during irradiation at different temperature settings.

Figure 3.7 illustrates the specialized stage used in the experiment for ion irradiation under applied stress [79]. It shows the actual sample stage image, accompanied by the dimensions of the sample stage and an enlarged detail providing regarding the control conditions for the tension samples. This device was inserted and tested in a beamline of the tandem-type accelerator, as mentioned in Section 3.3.1 in the text.

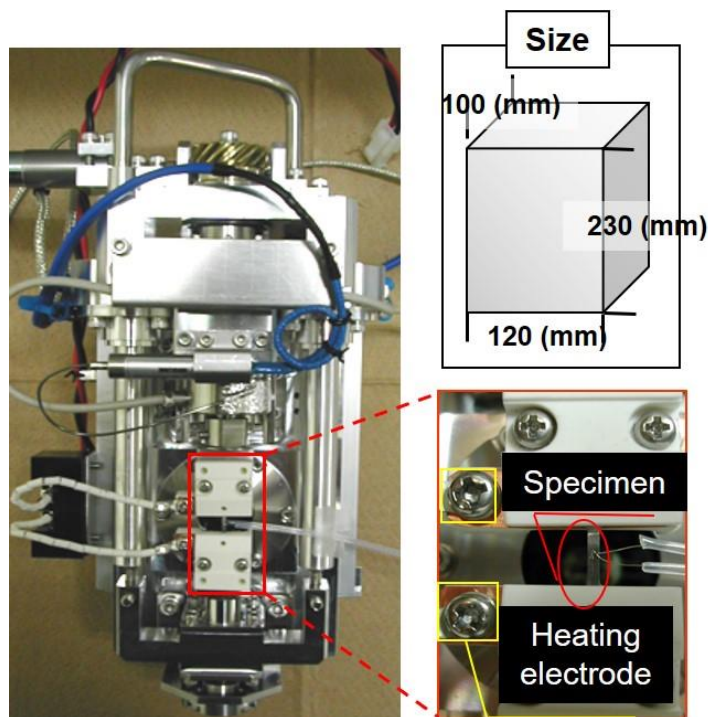


Figure 3.7 Tensile Sample Stage Used for Ion Irradiation [79]

Throughout the experiment, varying time intervals could be chosen for recording applied loads and displacement. Precise temperature control during irradiation was achieved using an infrared temperature sensor. The adjustment of temperature and correction of sample emissivity were facilitated by a thermocouple spot-welded to the specimen. Initial temperature calibration was conducted on standard samples at different input values. Subsequently, setting the calibrated values enabled the control of the sample temperature. For thicker tensile samples, the thermocouple was soldered to the backside to monitor the temperature throughout the entire irradiation process, and a real-time temperature monitor is shown in Figure 3.8. Irradiation was conducted on the front side with temperature recording using a thermocouple soldered to the backside throughout the entire process. Upon checking the appearance, the temperature test thermocouple had no effect on the surface of the sample, with no observed color change or deformation after irradiation.

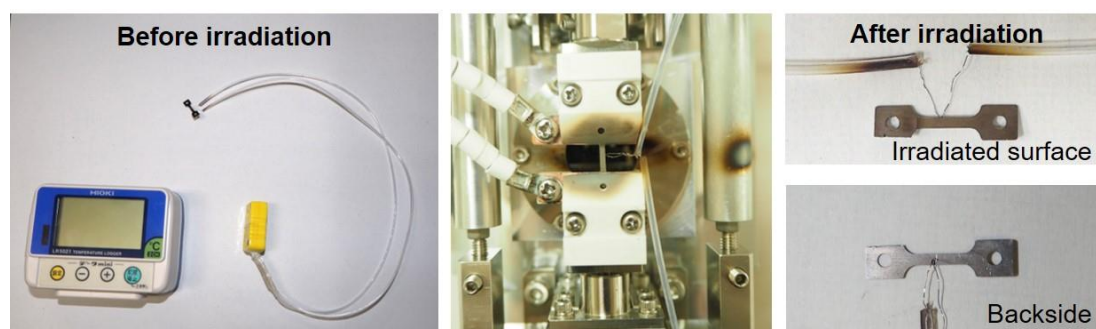


Figure 3.8 Temperature Monitoring During Irradiation of Thicker Tensile Samples with Backside Thermocouple Soldered and Real-Time Display

The sample stage was utilized to test the stress-strain curves of Zircaloy-2 at different temperatures, revealing the strength close to standard data [80-82]. Figure 3.9 illustrates the stress-strain curves of Zircaloy-2 at room temperature,

300 °C, and 400 °C. In this study, for irradiation under stress, it was essential to maintain the applied stress at different temperatures for an extended duration to achieve the desired damage level. Considering that stresses on core components originate from various sources in real operational environments and significantly vary based on different nuclear power plants and service conditions, there is no publicly available standardized stress data for current plants. Materials that experience the most extreme conditions (stress, corrosion, and radiation) are crucial for maintaining plant safety and reliability.

In our study, we irradiated the samples under the maximum applied tensile stress possible based on the stress-strain curves tested with annealing samples. Consequently, the applied stresses were chosen as outlined in the accompanying Table 3-2. It is noteworthy that exceeding the maximum stress values indicated in the table may lead to sample breakage during irradiation.

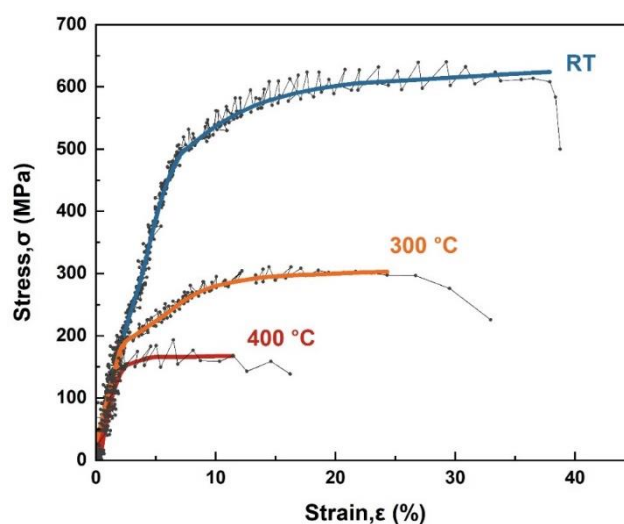


Figure 3.9 Stress-Strain Curve of Zircaloy-2 at Different Temperatures Tested with the Miniature-Sized Tensile Machine Used in the Present Study

Table 3-2 Summary of Tensile Stress Conditions Applied to Samples at Different Temperatures.

Temp Stress	RT	300 °C	400 °C
50 MPa			○
100 MPa		○	○
150 MPa	○		
200 MPa		○	
250 MPa	○	○	
350 MPa	○		
450 MPa	○		
500 MPa	○		

The precise control of temperature and stress was crucial during high-dose ion irradiation at 300 °C and 400 °C, as illustrated in Figure 3.10. Concurrently, the accelerator was turned on, and the beam was adjusted to stabilize in preparation for irradiation. Then, the set value was fine-tuned after heating up to align the stabilization temperature with the target temperature. To ensure the stability of the temperature control system, a duration of about 10 hours was dedicated. Following this, stress was applied to the samples, and irradiation began once the applied stress reached the target value. The injection time was determined based on the required damage dose to achieve the desired damage effect. After irradiation was completed, stress was gradually released, followed by a controlled cooling process. Throughout these operations, constant monitoring of temperature and stress was maintained to ensure the accuracy of the experimental conditions.

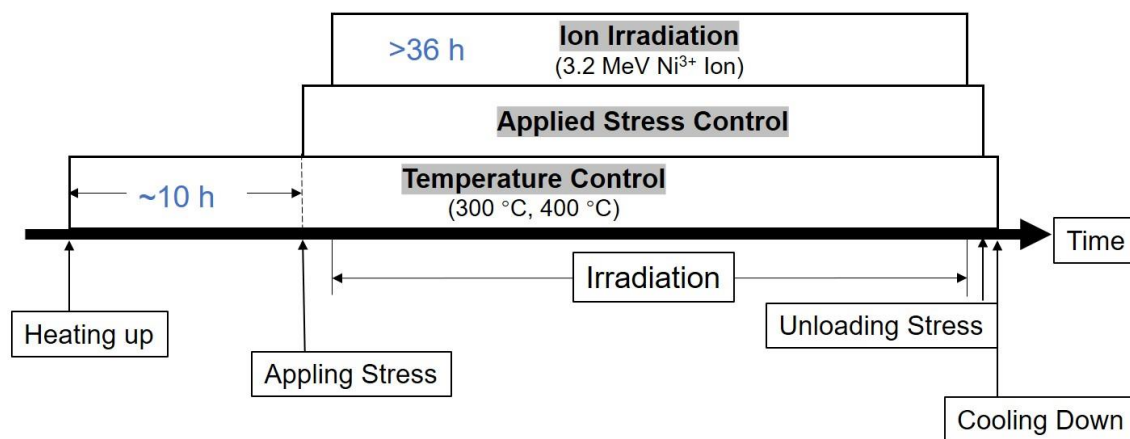


Figure 3.10 The Process of High-Dose Irradiation Under Applied Stress

3.4 Hardness Test

3.4.1 Vickers Hardness Test

For the unirradiated samples subjected to different applied stresses to investigate the individual effect of applied stress on material hardness, Vickers hardness test was conducted using a Shimadzu HVM-1-SNJ Vickers Hardness Tester. The hardness tests were performed with a load set to 490.3 mN and applied for 15 seconds.

3.4.2 Nano-indentation Test

For the radiation-induced hardening, the nano-indentation test was conducted at RT using an Elionix ENT-1100 instrument with a Berkovich type indenter. To assess hardness within the ion-irradiated layer, the indenter load (L) was set to 1000 mgf, and the indentation depth (d) was kept less than 300 nm. This ensured that the hardness evaluation within the 3.2 MeV Ni^{3+} ion irradiated

layer because the depth of the affected zone is empirically 3–5 times the indentation depth [58]. The computer system continuously monitored L and d , represented by the following equation [83]:

$$L/d = A + Bd \quad (1)$$

where A and B are material-dependent constants, independent of the load and indenter displacement. The value of B is given by the following equation [83]:

$$B \text{ (GPa)} \approx 0.287 H_v \approx 89 \sigma_b \quad (2)$$

where H_v represents Vickers hardness, and σ_b is the ultimate tensile stress. Figure 3.11 depicts the Load/depth-depth curves of unirradiated Zircaloy-2. As stated by Inamura et al. [83], hardness results are notably affected by the surface status of the samples when the depth is less than 100 nm. To ensure reliable nano-indentation hardness measurements, the hardness of ion-irradiated materials was determined by comparing B values at a depth of 100–200 nm in this study. This depth range was chosen as the irradiation damage peak occurs at approximately 1.4 μm , ensuring it is deeper than 3–5 times the indentation depth [84, 85].

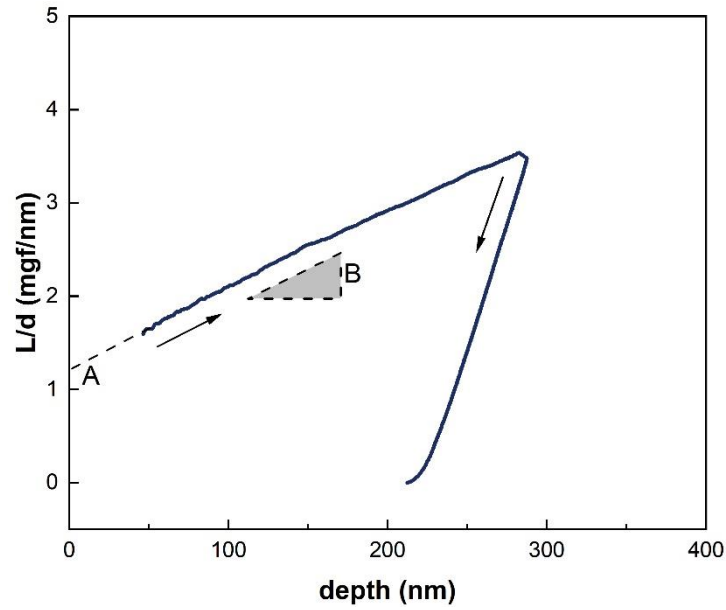


Figure 3.11 Load/depth-depth Curve of Zircaloy-2

3.5 Microstructure Analysis

3.5.1 Twin-Jet Electrolytic Thinning

The microstructure analysis was primarily conducted using TEM. The preparation of high-quality TEM samples is crucial for obtaining detailed microstructural images and diffraction patterns. In this study, we used twin-jet electrolytic thinning, a technique suitable for electrically conducting samples such as metals and alloys.

This method, as depicted schematically in Figure 3.12(a) [86], involves applying a specific voltage to achieve anodic dissolution, resulting in a polished surface without etching or pitting. The voltage is applied between the pipette tip and the specimen. The twin-jet apparatus used in this experiment is the Struers TenuPol-5 electro polisher, as shown in Figure 3.12(b). This twin-jet apparatus pumps electrolyte onto both sides of the dimpled disk, ensuring uniform

polishing. Laser or light sensors are employed to detect transparency, signaling an immediate cutoff of the electrolyte flow to prevent the loss of the thin area.

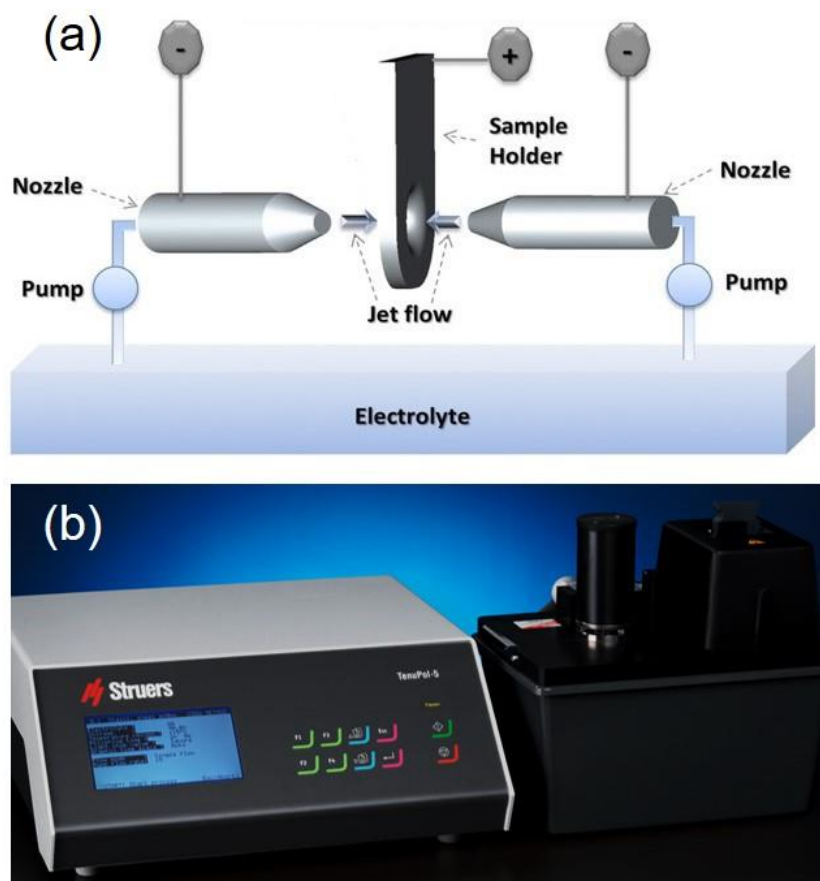


Figure 3.12 (a) Schematic of Twin-Jet Electropolishing Apparatus [86], (b) Struers TenuPol-5 Electro Polisher

In the case of Zircaloy-2 used in the experiment, several attempts were made to get a thin and bright viewing area, and the polishing conditions shown in Table 3-3 were finally determined. The pump flow rate could be slightly adjusted during examination of the flow under various temperature conditions.

Table 3-3 Method Parameters of Twin-Jet Electrolytic Thinning

Material: Zircaloy-2 Ø3 mm	
Electrolyte	5% HClO ₄ + 95% C ₂ H ₅ OH
Temperature	-55 °C
Voltage	19 V
Current	30-50 mA
Flow mode	Single flow
Polishing time	3 minutes
Light stop value	12
Pump flow rate	17

This technique is an optimal method to make Zircaloy-2 TEM specimens with minimal preparation artifacts. It also proved to be an ideal method for subsequent studies of irradiation induced dislocations.

3.5.2 Focused Ion Beam (FIB)

After Ni³⁺ ion irradiation, the tensile sample underwent preparation for TEM observation through thinning via FIB, specifically using the HITACHI FB-2100 model, as illustrated in Figure 3.13. The process involved coating the sample with a tungsten deposition film, after which the focused Ga ion beam rastered across the sample surface, progressively sputtering material layer by layer. The initial pre-cut sample, measuring approximately 13 µm long and 3 µm wide, was meticulously pre-thinned to around 80 nm by controlling milling parameters such as ion beam current and dwell time. Finally, the sample was mounted onto a Molybdenum (Mo) or Copper (Cu) mesh for subsequent observation.



Figure 3.13 Overview of HITACHI FB-2100 FIB Instrument

However, it's noteworthy that FIB-prepared TEM samples often contain considerable damage from the gallium ion beam. To address this issue, it becomes necessary to trim the damaged region created by the gallium ion beam using a beam of lower intensity. In this context, a dual-ion mill device manufactured by GATAN (Figure 3.14(a)) was employed for polishing, involving Ar milling at 3 kV for 30 min followed by 1.5 kV for 15 min with an inclination of 15°. Subsequently, another processing step was conducted using a Precision Ion Polishing System (PIPs) (Figure 3.14(b)), renowned for precise centering, control, and reproducibility of the milling process. The PIPs process was carried out at 0.3 keV for 3 min with an inclination of 10°, repeated twice, to refine the TEM specimens. This method, particularly advantageous for EDS chemical

analysis, ensures the mitigation of gallium ion beam-induced damage and enhances the quality of the TEM samples.

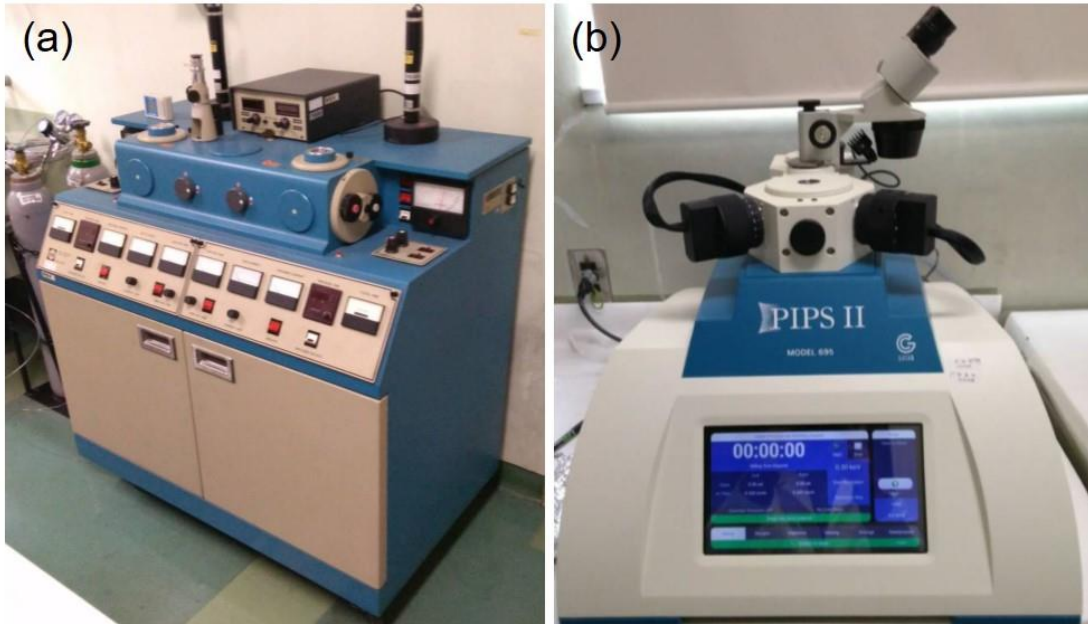


Figure 3.14 Overview of (a) Gatan Dual Ion Milling for Ar Milling and (b) PIPs II for Precision Ion Polishing

3.5.3 Transmission Electron Microscope (TEM)

For samples subjected to 3.2 MeV Ni^{3+} ion irradiation, microstructural observation was carried out using the JEOL JEM-2000FX TEM at an electron acceleration voltage of 200 kV, as depicted in Figure 3.15.

The characterization of dislocation loops generated under various doses and irradiation conditions was conducted. The two-beam condition was utilized to identify the types of dislocation loops, and statistical analyses of the quantities and sizes of these loops under different irradiation doses were conducted using Nano-measurer software [87].

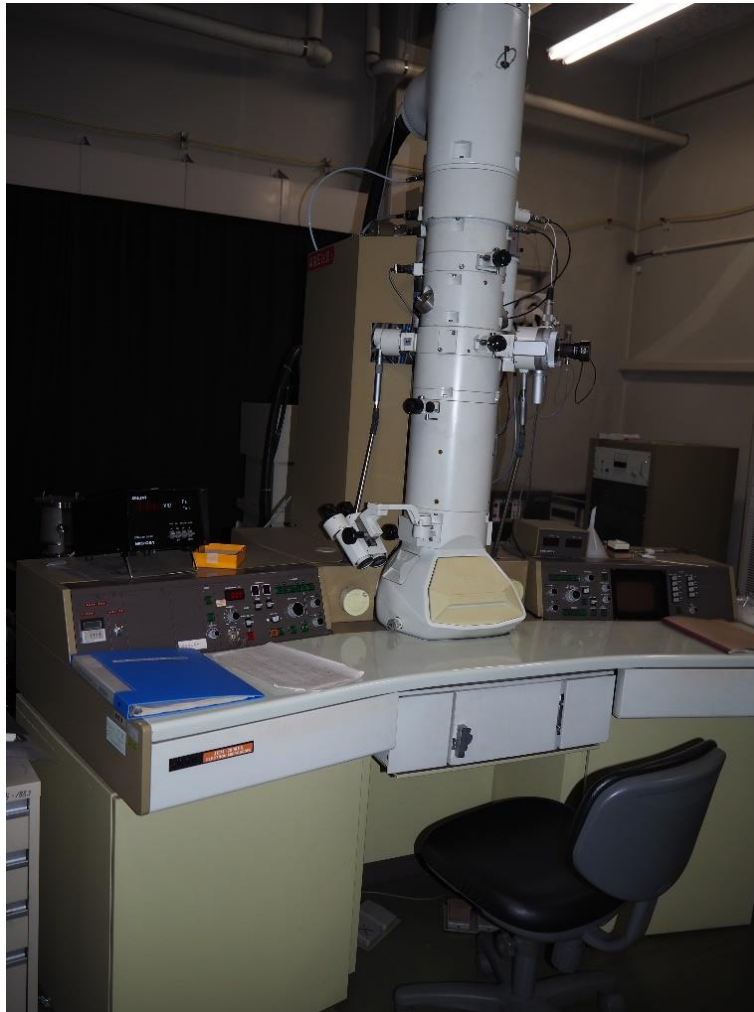


Figure 3.15 Overview of JEOL JEM-2000FX

3.5.4 Aberration-Corrected Electron Microscope

Microstructural observation and Energy dispersive X-ray spectroscopy (EDS) analysis of specimens subjected to ion irradiation were conducted using the JEM-ARM 200FC, an aberration-corrected electron microscope (ARM) with a correction function, as depicted in Figure 3.16.



Figure 3.16 Overview of JEM-ARM 200FC with EDS Analysis

It also enables the observation of element mapping through EDS, allowing for an investigation the concentration of elements in the sample.

The ARM system, operating at 300 kV, enables high-resolution microstructure observation and atomic-scale analysis, thanks to its aberration correction capability. Additionally, it allows for STEM structural observation and EDS mapping, enabling an in-depth investigation into irradiation-induced structural modifications and the distribution of elements within the specimen.

CHAPTER 4. Study on the Mechanism of Hardening in the Initial Stage of Irradiation Under Applied Stress

4.1 Introduction

Zircaloy-2 is located closest to the fuel in BWRs as the fuel cladding tube, which has caused important phenomena, including dimensional changes, increased hardness, and irradiation embrittlement [88, 89]. The operation of a reactor subjects the fuel cladding to hoop stress, resulting from the thermal expansion of the fuel pellet and mechanical-induced stress due to component deformation [10, 88].

During reactor operation, $\langle a \rangle$ type dislocation loops form at relatively low neutron fluences, leading to significant radiation-induced hardening [53, 58, 90-92]. Despite numerous reports confirming the hardening of zirconium alloys under low doses, a comprehensive exploration of the corresponding microstructural changes with increasing doses remains lacking. Additionally, the correlation between irradiation-induced hardening, particularly under applied stress, is not well elucidated. The motion of dislocation loops, including climb induced by applied stress, remains poorly established, although their influence on strengthening is acknowledged. Recognizing the need to understand the effect of external stress on radiation-induced hardening, it becomes imperative to investigate the microstructural evolution and assess the hardening of zirconium alloys during the initial irradiation stage with applied

stress. Such an endeavor is crucial to clarify the relationship between dislocation loops and radiation-induced hardening.

In the context of this study, a simulation of neutron irradiation at 300 °C was conducted through 3.2 MeV Ni³⁺ ion irradiation on Zircaloy-2. This approach enabled microstructural evolution characterizations and hardness tests within the damage range of 0-1 dpa. The study also delved into the effect of applied stress on the radiation-induced hardening of 1 dpa irradiated tensile samples, contributing valuable insights into the alloy's response under complex irradiation conditions.

4.2 Experimental Procedures

The Zircaloy-2 used in this experiment underwent an initial rolling process at RT to produce a thin sheet, which was then punched to obtain Φ3 mm disk specimens and tensile samples. The detailed dimensions of the tensile sample, as discussed in Chapter 3, with a nominal gauge length of 4.9 mm, a gauge width of 1.2 mm. Following mechanical grinding and polishing to achieve a 0.1 mm thickness, all samples underwent an annealing process at 630 °C for 2 hours, followed by air cooling to room temperature.

In the investigation of radiation-induced hardening under stress-free conditions, a consistently electrochemically polished sample underwent multiple irradiation cycles. Nano-indentation test was systematically conducted both before and after each irradiation cycle to evaluate changes in hardness. To comprehend the microstructural evolutions induced by irradiation, TEM specimens prepared

Table 4-1 Summary of Tensile Stress Conditions Applied to Samples.

Temp	Stress /MPa	0	100	150	200	250	350-500
RT		0, 1 dpa		0, 1 dpa		0, 1 dpa	0, 1 dpa
300 °C		0-1 dpa	0, 1 dpa	0, 1 dpa	0, 1 dpa	0 dpa	

4.3 Results and Discussion [93, 94]

4.3.1 Effect of Applied Stress on Hardness and Microstructure at RT

For this study, irradiation under stress conditions required maintaining the applied stress for approximately 1 hour to achieve an irradiation dose of 1 dpa. To ensure the sample did not undergo failure or fracture during the irradiation process, the applied stress level was carefully selected and showed in Table 4-1.

Vickers hardness test was used to determine the effect of external tensile stress conditions on the hardening of unirradiated samples, as shown in Figure 4.2. The red error bars denote the associated standard deviation from the mean for each stress situation, and the black dots reflect the average hardness values acquired from several measurements.

The influence of diverse external tensile stresses on material hardening is negligible at RT. This outcome can be rationalized by the fact that the material remains primarily within the elastic deformation phase, resulting in minimal

work hardening. This conclusion is congruent with the stress-strain curve represented in Chapter 3.

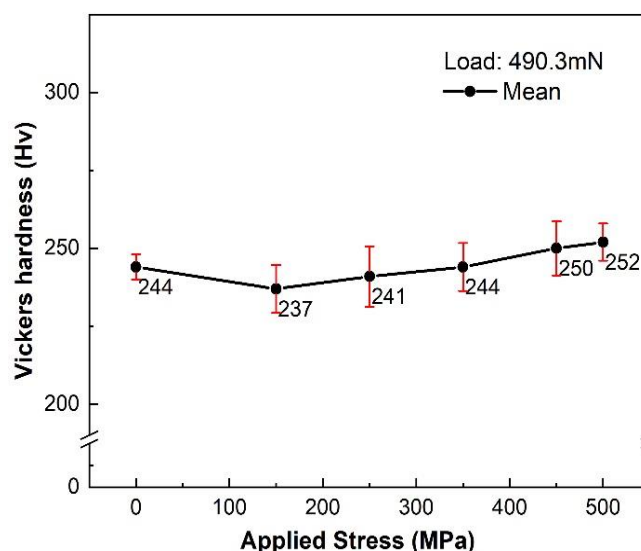


Figure 4.2 Effect of Applied Stress on Vickers Hardness of Zircaloy-2 Following 1-Hour Holding

Figure 4.3 illustrates the stress dependence of microstructure evolution in Zircaloy-2 to a 1-hour holding at RT. The externally applied stress direction is parallel to the observation plane. The micrograph at 0 MPa reveals annealed samples with a pristine interior and an exceptionally low dislocation density. Furthermore, the micrographs depict an assortment of precipitates, present both in the presence and absence of stress. Previous studies on zirconium alloys precipitates suggest that these may correspond to relatively large $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates, indicated by the orange arrows, with a size larger than 30 nm, as well as small $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates, shown as blue arrows [33, 43, 45].

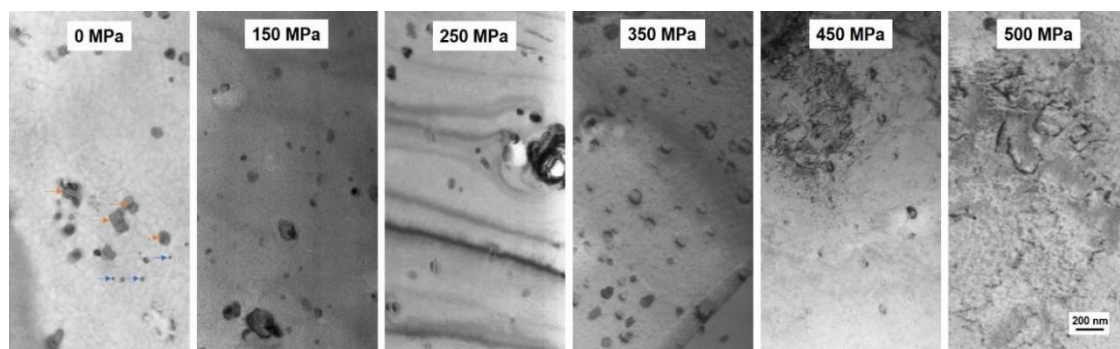


Figure 4.3 Effect of Applied Stress on Microstructure of Zircaloy-2 Following 1-Hour Holding

When the applied stress was below 350 MPa, no dislocation lines were observed in the observation area. However, when the applied stress exceeded 450 MPa, dislocation lines induced by deformation were observed within some grains in the central part of the unirradiated tensile sample. Nevertheless, the density of dislocation lines varied significantly between different locations and within individual grains, which led to no significant increase in hardness values, as shown in Figure 4.2.

The appearance and orientation of dislocation lines are correlated with the hcp structure of zirconium alloys and the direction of applied stress. Furthermore, as the dislocation density increases, different types of dislocation interactions occur, influencing the material's plastic deformation, hardness, and fracture behavior. By further increasing the externally applied tensile stress, plastic deformation occurs within the material, leading to an increased density of internal dislocations. This, in turn, enhances the interaction between dislocation loops generated by irradiation and those formed due to plastic deformation. Such investigations are valuable in understanding the influence of irradiation hardening effects during irradiation.

4.3.2 Dislocation Loop Formation at 300 °C Without Applied Stress

Figure 4.4 shows the dose dependence of TEM microstructures in Zircaloy-2 irradiated at 300 °C to a dose of 1.0 dpa. From 0.05 to 0.3 dpa, dislocation loops were characterized with the $g=(10\bar{1}0)$ vector at close to the $\langle 0001 \rangle$ or $\langle 1\bar{2}1\bar{3} \rangle$ zone axis. According to the invisibility criteria, all the $\langle a \rangle$ loops are visible under this observation condition [35, 95]. The annealed samples exhibited a clean interior with an extremely low dislocation density from the TEM bright field micrograph. After the irradiation at 0.05 dpa, $\langle a \rangle$ loops formed rapidly with a typical size below 4 nm as black dots. With the irradiation dose increased, the loop number density quickly increased. When the irradiation dose reached approximately 0.4 dpa, the microstructure became more complex, with adjacent loops linking together to form a chain-like structure that eventually showed a wavy pattern similar to that observed at 0.6 dpa. Northwood et al. [36] also observed this type of dislocation structure and attributed it to $\langle c \rangle$ type dislocation introduced by deformation before irradiation. Since the samples in this experiment were annealed before irradiation, no such structures were observed in the pre-irradiated samples. Moreover, based on the evolution of the microstructure with doses, it can be inferred that this is caused by the entanglement of $\langle a \rangle$ dislocation loops before the formation of $\langle c \rangle$ loops.

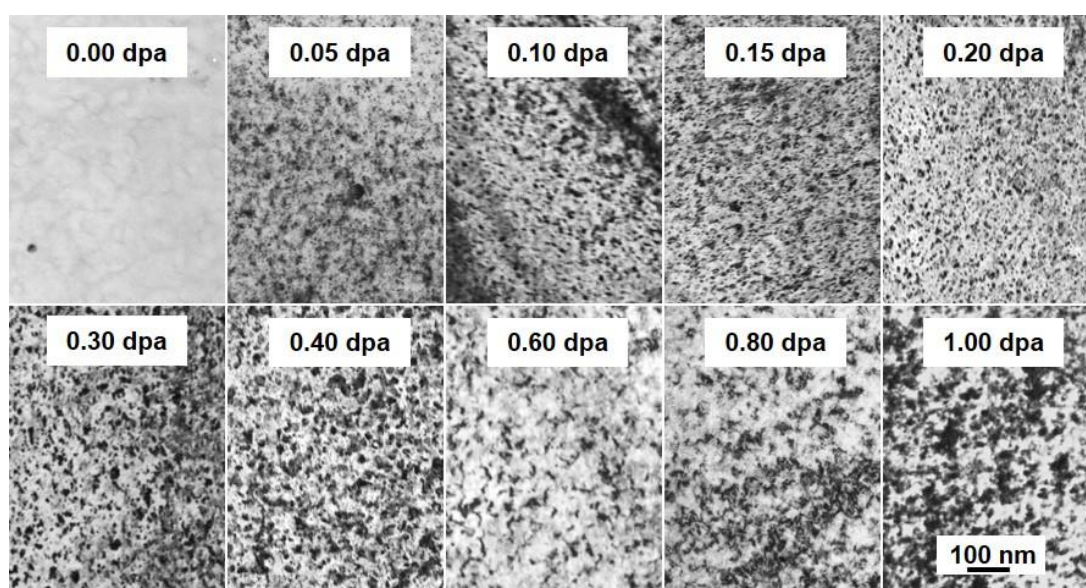


Figure 4.4 Dislocation Loop Formation Following Ion Irradiation to a Dose of 1 dpa at 300 °C

The analysis of $\langle a \rangle$ loops with different irradiation doses was quantitatively conducted and presented in the form of histograms, as shown in Figure 4.5. The average size and standard deviation of the loops were also indicated, respectively. At the initial irradiation stage with 0.05 dpa, the size of $\langle a \rangle$ loops were predominantly less than 10 nm and concentrated around 4 nm. As the dose increased above 0.15 dpa, the number of $\langle a \rangle$ loops smaller than 3 nm decreased sharply, indicating that it was doubtful that any $\langle a \rangle$ loops formed after reaching this dose. Furthermore, at 0.4 dpa, the size distribution of the $\langle a \rangle$ loops shifted, with sizes ranging from 5 to 28 nm, and only a tiny fraction measuring around 5 nm. From this, it can be deduced that when the density of $\langle a \rangle$ loops is significantly high, point defects are more likely to be absorbed by the existing loops rather than initiating nucleation.

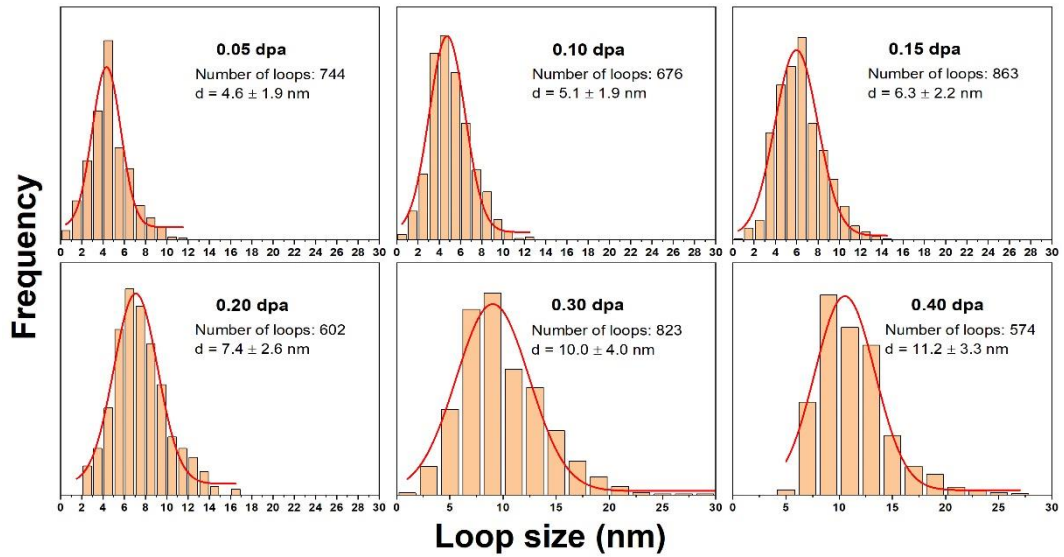


Figure 4.5 Size Distribution of <a> Loops with Different Doses. The Mean Value is Indicated.

The thickness of the observation area was assumed to be 100 nm for the estimation of dislocation loop number density. The dose dependence of dislocation loop density and size is shown in Figure 4.6, along with the corresponding error bars representing the standard deviation. As shown in the figure, the density of dislocation loops reached saturation at 0.1 dpa with a maximum density of $4 \times 10^{22} \text{ m}^{-3}$, which is consistent with the previous deduction that <a> loops no longer nucleated and reached saturation in density at 0.15 dpa. Additionally, with the loop density reaching saturation, the loop size increased to 12 nm until 0.4 dpa. The size of the loops and the dose at which dislocation loops reach saturation were found to be consistent with the previous neutron irradiation results at the same temperature [32, 33, 96]. The density of dislocation loops remained stable until a dose of 0.4 dpa, after which the loops started to entangle.

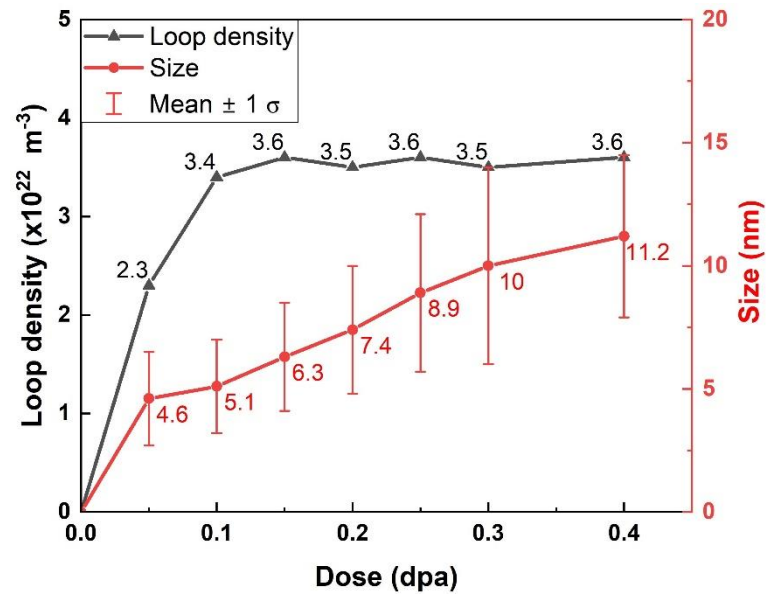


Figure 4.6 Dose Dependence of Dislocation Loop Density and Size in Zircaloy-2
Irradiated at 300 °C

4.3.3 Dose Dependence of Radiation-Induced Hardness Without Applied Stress

Figure 4.7 shows the Load/depth-depth curves of unirradiated and 1.0 dpa irradiated Zircaloy-2 samples irradiated at 300 °C tested by nano-indentation. For detailed insights into specific A and B on the graph, refer to the explanations provided in Chapter 3. Notably, at the same depth, an increase in the L/d ratio is observed, indicating a pronounced hardening in the samples irradiated at 1.0 dpa.

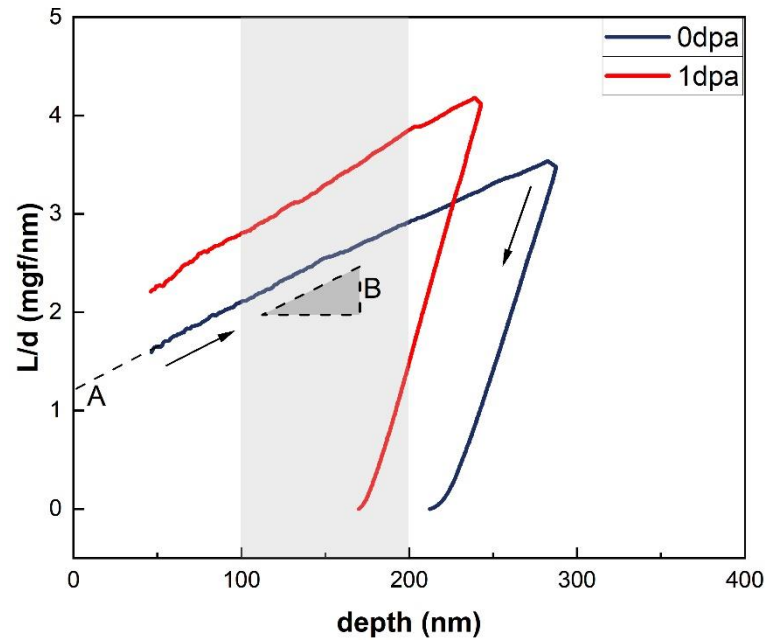


Figure 4.7 Load/depth-depth Curves of Unirradiated and 1.0 dpa Irradiated at 300 °C of Zircaloy-2

The radiation-induced hardening was obtained by comparing B of at a depth of 100-200 nm. The dose dependence of nano-hardness changes after each irradiation up to 1 dpa at 300 °C shown in Figure 4.8. This study performed indentation measurements before and after the irradiation with the same sample. ΔH_v is the difference between the hardness value after irradiation at different doses and the average value before irradiation, which reflects the surface hardening of the sample caused by irradiation. Diamond symbols indicate the hardness data at each test point under different doses in the figure, and the short horizontal lines represent the mean values of the data points at the same dose, with the corresponding error bars representing the standard deviation indicated for each dose. During the initial irradiation stage, the mean hardness value significantly increased. The observed hardening behavior

reached saturation at a dose level of 0.15-0.2 dpa, and the resulting change in ΔH_v remains constant even with the dose further increasing up to 1.0 dpa.

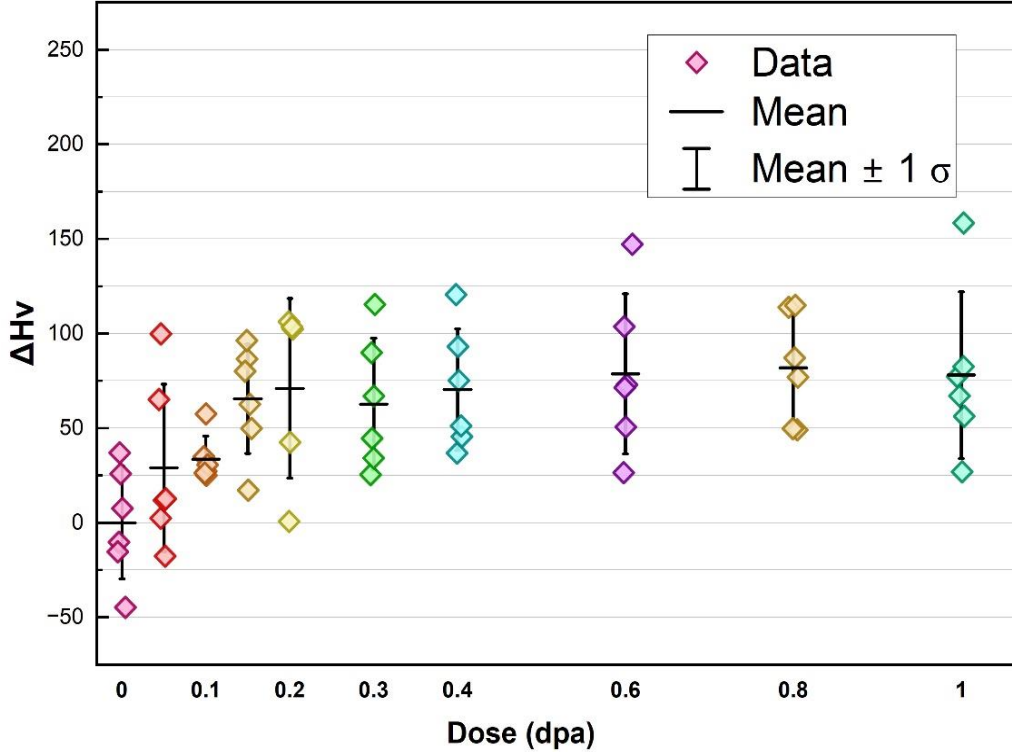


Figure 4.8 Dose Dependence of the Irradiation Hardening in Zircaloy-2 Irradiated at 300 °C

The dose-dependent trend of irradiation hardening aligns with the dose-dependent trend of the dislocation loop number density. Moreover, the dose at which the hardness saturates is close to the dose at which the dislocation loop number density saturates. This suggested that the nucleation and growth of dislocation loops in the early stage of irradiation were one of the leading causes of irradiation-induced hardening. Several models have been proposed to quantitatively understand the radiation-induced hardness in zirconium alloys [58, 97, 98]. The estimation of hardening contribution due to dislocation loops

has been modeled based on the Orowan equation as shown below:

$$\Delta\sigma_y = M\alpha\mu b\sqrt{Nd} \quad (3)$$

where $\Delta\sigma_y$ is the increment of yield strength caused by obstacles. M is the Taylor factor of 3.5 [56, 58, 97]. The obstacle strength factor, represented as α , exhibits significant variations in irradiated zirconium alloys. Different values have been reported, such as 0.3 in Zr-Nb alloys [56, 58], 0.5 [99], and 1.0 considering the role of clusters in irradiation hardening [98]. However, based on previous studies, a typical value of 0.25 has been determined, which aligns well with experimental observations [97, 100]. The μ is the shear modulus of 36.2 GPa for Zircaloy-2 at RT [101]. Burgers vector b for primary prismatic dislocation in zirconium alloys is 0.323 nm [58, 97]. N and d are the number, density, and diameter of the dislocation loops, respectively.

The change in yield strength is also can expressed as [56, 102]:

$$\Delta H_v = \frac{\Delta\sigma_y}{3} \quad (4)$$

where $\Delta\sigma_y$ is in MPa and ΔH_v is in kg/mm².

The estimated values are shown in Table 4-2. Figure 4.9 shows the comparison of radiation-induced hardening between the measured and the estimated values. During the statistical process of dislocation loops, there is a specific statistical error introduced due to the selection of the observation region, which has already been shown in Figure 4.6 and Figure 4.8. Based on the error

propagation formula, the deviation of the results obtained by Equations (3) and (4) is represented as a red band in the figure.

Table 4-2 Characteristics of <a> Loops and a Comparison Between Experimentally Obtained and Estimated Hardness

Dose (dpa)	<a> loops			ΔHV	
	Diameter (nm)	Number density ($10^{22}m^{-3}$)	$\sqrt{Nd}$ ($10^6 m^{-1}$)	Estimated (MPa)	Measured
0.05	4.6	2.3	10.3	35.1	29.0
0.1	5.1	3.4	13.2	44.9	33.6
0.15	6.3	3.6	15.1	51.4	65.4
0.2	7.4	3.5	16.1	54.9	71.0
0.3	10.0	3.5	18.7	63.8	62.7
0.4	11.2	3.6	20.1	68.5	70.3

It can be seen that with the same irradiation dose, the measured value of the hardness change is closer to the calculated contribution of the dislocation loops and follows the same trend with dose dependence. Before the dose increased to about 0.1 dpa, the hardening was pronounced, and the subsequent growth of the dislocation loops led to sustained hardening. At 0.4 dpa, the dislocation loops reached a size after which they started to intersect and

became entangled, resulting in the saturation of the measured hardness. With the increase in dose, the hardness value no longer changed.

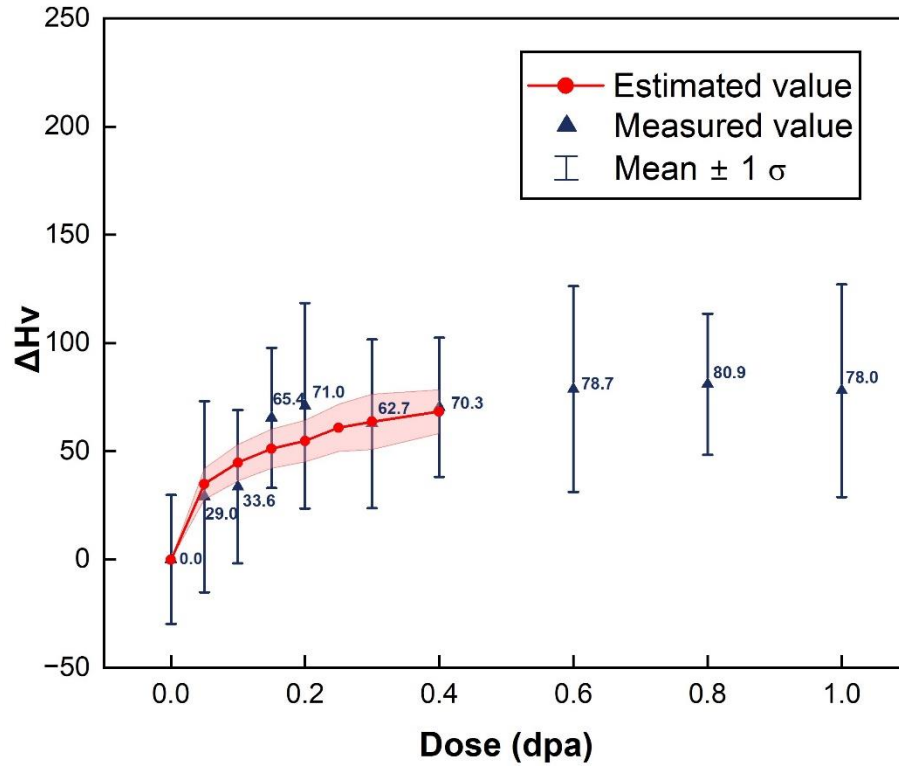


Figure 4.9 Comparison Between Estimated and Measured Values of Hardness

At different doses, the consistency between the measured value and the calculated value of the dislocation loop by the Orowan equation indicates that the hardening of the sample is mainly caused by the behavior of <a> type dislocation loops.

4.3.4 Effect of Applied Tensile Stress on Radiation-Induced Hardening

Figure 4.10 depicts the stress recording process during the irradiation. Figure 4.10(a) shows the plan for the stress control system with load adjustment, employing a loading rate of 10 N/min during the loading process at RT. Once

the applied stress reaches the target value, it will be held constant until the desired irradiation dose of 1 dpa was achieved. Figure 4.10(b)-(f) present the actual stress recording process under different stress conditions during irradiation, providing detailed information about the irradiation conditions, including vacuum, beam currents during irradiation, and the sample displacement at the end of irradiation.

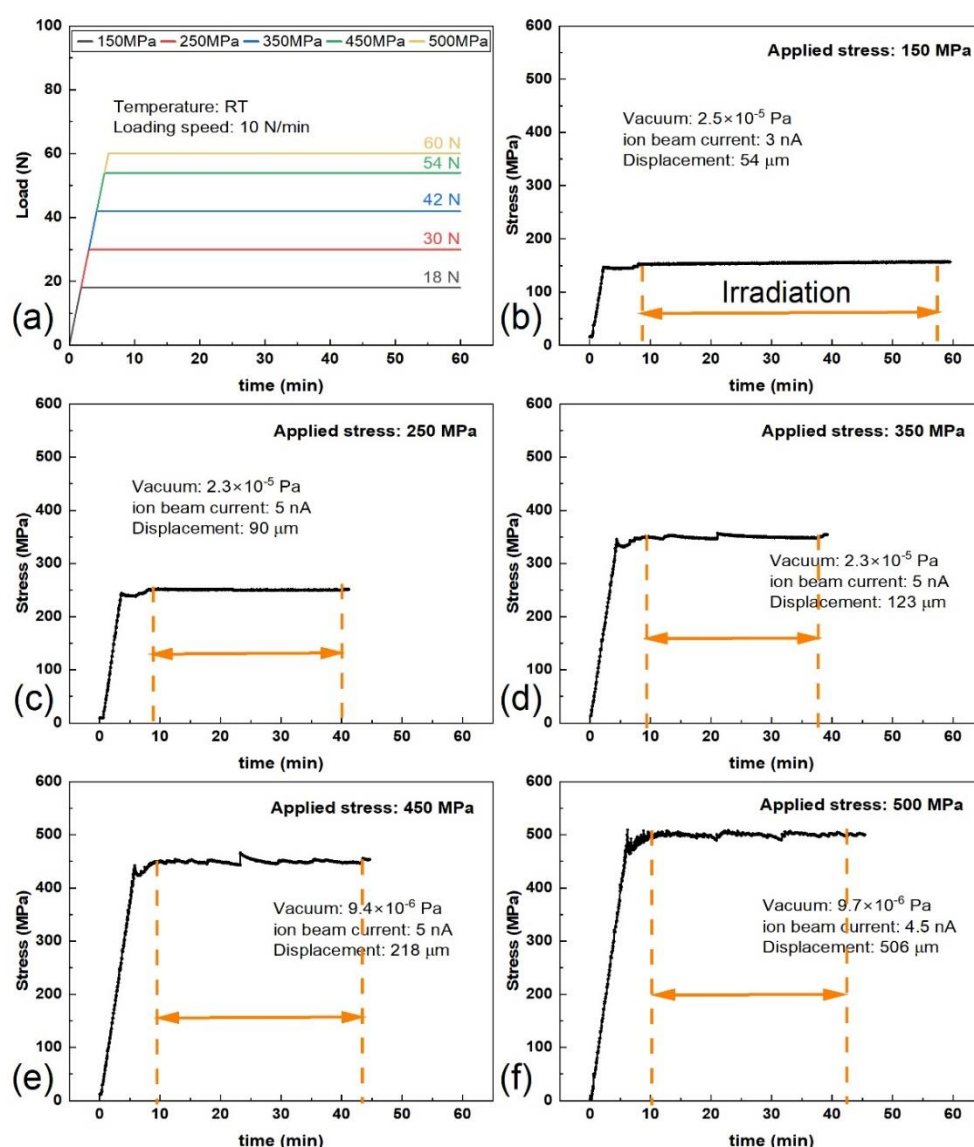


Figure 4.10 (a) Stress Control System, and (b)-(f) Stress Recording with Different Applied Stresses During Ion Irradiation at RT

For samples subjected to lower applied stresses (below 450 MPa), the displacement during irradiation was not significant. However, for samples with 500 MPa of applied stress, the displacement increased rapidly during the irradiation process. Notably, the recorded process corresponds to samples that did not fracture after multiple experiments. Due to the prolonged duration required to maintain 500 MPa applied stress during irradiation, some samples fractured during the irradiation process.

Throughout the irradiation process, minor fluctuations in actual stress are observed, but they consistently remain within 5% of the target value. This recording also indicates that the irradiation heating effect is not significant, as the stress control system is sensitive and would display larger fluctuations in stress if there were substantial changes in sample temperature.

Table 4-3 presents the changes in hardness under different applied stress conditions for both unirradiated and irradiated samples at RT. For the unirradiated samples, the values represent the difference in Vickers hardness tested by Vickers hardness test before and after maintaining the applied stress for 1-hour at RT. On the other hand, for the irradiated samples, the values represent the change in Vickers hardness before and after irradiation, which were obtained from nanoindentation measurements and then converted to Vickers hardness.

Table 4-3 Hardness Test of Unirradiated and Irradiated Samples Under Different Applied Stresses at RT

No.	Applied stress (MPa)	ΔH_v unirradiated	σ	ΔH_v irradiated	σ
T1	150	-6.9	8.7	44.2	41.7
T2	250	-2.5	10.5	43.2	38.5
T3	350	0.0	8.7	55.4	44.3
T4	450	6.3	9.6	48.7	45.3
T5	500	8.6	7.2	58.8	53.3

As a controlled study, the effect of applied stress conditions at 300 °C on the hardness of the unirradiated sample characterized by Vickers hardness test is also shown in Figure 4.11. At 300 °C, the contribution of different applied stresses below 150 MPa to material hardening was insignificant. This could be attributed to the material still being in the elastic deformation stage, and no evident work hardening phenomenon occurred. With the stress larger than 150 MPa, a slight increase in the hardness value was observed, which is consistent with the results of the stress-strain curves. At 300 °C, the application of a stress of 250 MPa resulted in a higher density of dislocation lines, leading to increased deformation resistance and strength. The micrographs in Figure 4.11 also show the numerous precipitates with and without the application of stress.

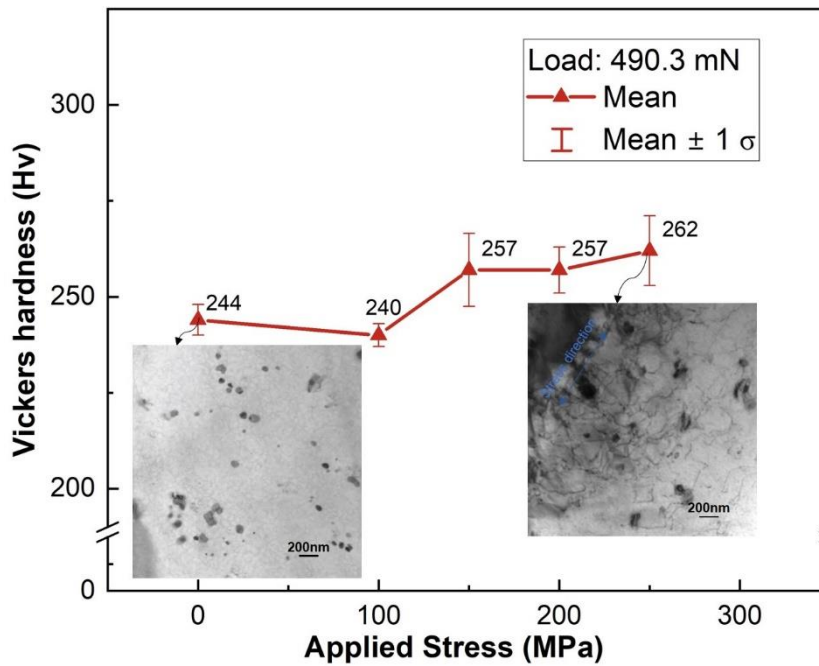


Figure 4.11 Effect of Applied Stress on Vickers Hardness and Microstructure of Zircaloy-2 After Keeping at 300 °C for 1 Hour

Figure 4.12 illustrates the effect of applied stress on the change in Vickers hardness tested by nano-indentation test after irradiation to 1 dpa at RT and 300 °C. The blue and red columns represent the radiation-induced hardening with different applied stress levels after 1 dpa irradiation at RT and 300 °C, respectively. The stress induced hardness changes of unirradiated samples under the same stress and temperature conditions are also shown in white columns for references. The short horizontal lines represent the mean values of the data points at the same dose, with the corresponding error bars representing the standard deviation.

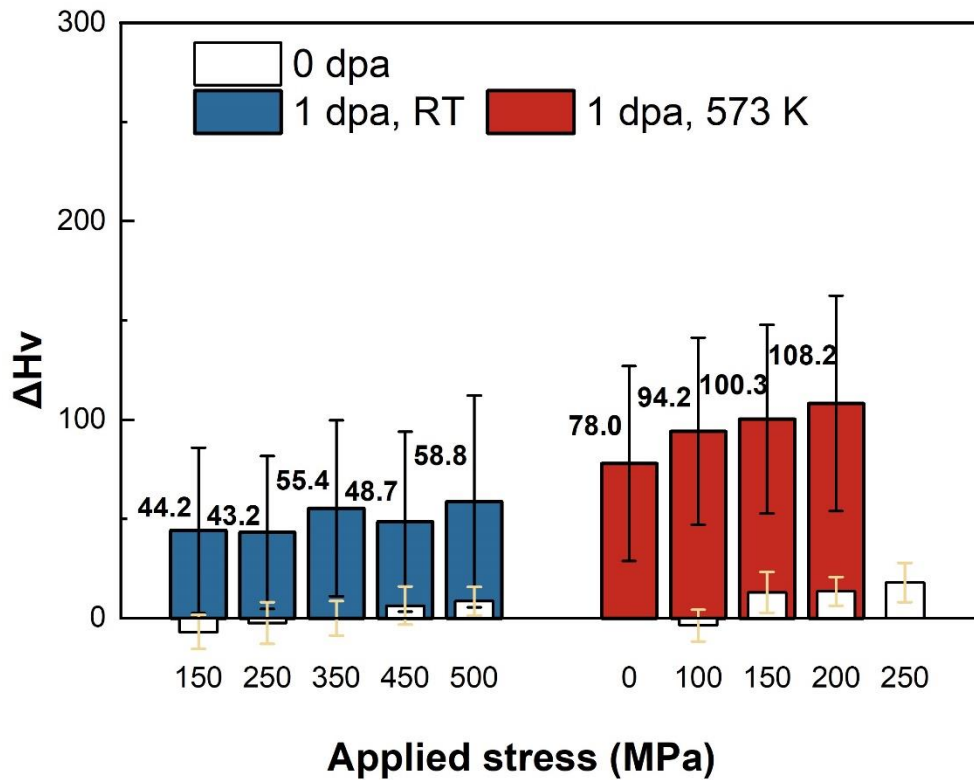


Figure 4.12 The Effect of Applied Stress on the Radiation-Induced Hardness of 1 dpa Irradiated Zircaloy-2

The Figure 4.12 shows that the irradiation-induced hardening is enhanced by the applied stresses, and the stress effect is more significant at 300 °C than at RT. At RT, the irradiation hardening is increased from 44.2 Hv under 150 MPa applied stress to 58.8 Hv under 500 MPa applied stress. While at 300 °C, the irradiation hardening values change from 94.2 Hv under 100 MPa applied stress to 108.2 Hv under 200 MPa applied stress. In comparison to about 80 Hv hardening caused by 1 dpa irradiation at 300 °C without applied stress, the application of stress has a certain effect, which is consistent with the stress changes of the unirradiated sample. However, the net influence of different stresses on irradiation hardening is not significant both at RT and 300 °C.

For radiation conducted under applied stress, material hardening can be divided into several parts: hardening caused by the introduction of dislocations due to applied stress, hardening caused by irradiation-induced $\langle a \rangle$ loops, and hardening caused by the interaction between dislocations introduced by applied stresses and those generated by irradiation.

For the unirradiated sample, no significant hardening occurs at RT due to the elastic deformation of the sample under 500 MPa. The radiation-induced hardening at RT is relatively close but slightly lower than that reported by Byun and Farrell [53] for Zircaloy-4 irradiated to 0.8 dpa by High Flux Isotope Reactor. This may be due to differences in material and irradiation conditions. This also means that the applied stress did not affect the hardening caused by 1 dpa irradiation at RT, which consistently with Vickers hardness test.

For the unirradiated sample at 300 °C, the applied stress with 200 MPa caused an increase in hardness of about 20 Hv. At 300 °C, the change in radiation-induced hardening without applied stress was slightly smaller than that under applied stress, with a difference of about 20 Hv, which is exactly the amount of hardening caused by stress without irradiation. Therefore, it can be concluded that at 300 °C, the interaction between dislocations introduced by applied stresses and those generated by irradiation does not significantly contribute to the hardening when the applied stress is less than 200 MPa. Moreover, the change in hardening due to the applied stress for 1.0 dpa irradiation at 300 °C is not significant. Watanabe et al. [79] investigated the effect of stress on irradiation hardening in Fe-Mn alloys and obtained similar conclusions. They found that the application of stress had no significant effect on hardness increase at 563 K (290 °C). Similarly, Xu et al. [103] studied the mechanical

property changes in Fe-0.6Cu alloy under uniaxial tension stress and concluded that the effect of stress was not clear.

Whether at RT or at 300 °C, the samples remain within the region of elastic deformation under the current stress conditions during irradiation, and no work hardening occurred. And this applied normal stress has induced strain in the material, potentially creating a stress field and thereby influencing the generation of radiation induced dislocation loops. This stress may also play a role in the movement of the dislocation loops and their interactions during subsequent irradiation. To address this, it is crucial to prepare and analyze TEM samples of the irradiated specimens under stress. However, to validate the above conclusions, it is necessary to characterize the irradiation-induced loops and stress-induced dislocations in the tensile samples, a task that will be undertaken in a future study.

4.4 Section Conclusions

The microstructural evolution and radiation-induced hardness of Zircaloy-2 under 3.2 MeV Ni³⁺ irradiation at 300 °C under applied stress were investigated by joint techniques of TEM examination and nano-indentation tests. The contribution of the hardening due to the behavior of <a> loops was evaluated using the Orowan equation and compared with the measured value. The main results are summarized as follows:

1. At low dose levels (below 1.0 dpa), <a> loops were observed to nucleate with a diameter of about 4 nm at doses below 0.05 dpa. As the dose

increased, the size and number density of $\langle a \rangle$ loops increased, reaching saturation density at around 0.1 dpa. These loops intersected with adjacent ones, becoming entangled at doses above 0.4 dpa.

2. Radiation-induced hardening was confirmed in Zircaloy-2 at the early stage of irradiation below 0.1 dpa. After 0.1 dpa, there was a sustained increase in hardness due to the growth of $\langle a \rangle$ loops until the loop size reached a maximum of about 12 nm at 0.4 dpa. The hardness reached saturation with an increase of about 80 Hv at 300 °C without applied stress.
3. The measured values of hardness increase were consistent with the contribution of dislocation loops to hardness as calculated using the Orowan equation. These findings suggest that the hardening of Zircaloy-2 in the initial irradiation stage is mainly due to the presence of $\langle a \rangle$ loops.
4. The applied stress did not have a significant effect on the hardening caused by 1.0 dpa irradiation at RT and 300 °C. However, further characterization of the dislocation loops caused by irradiation and those caused by applied stress is necessary for the irradiated sample with applied stress.

CHAPTER 5. Study on the Precipitate Resolution During High-Dose Irradiation Under Applied Stress

5.1 Introduction

In zirconium alloys, intermetallic second-phase particles play a crucial role, exerting substantial influence throughout both the fabrication process and the operational life of the alloy. Their significance is two-fold: firstly, by restraining grain growth during fabrication, and secondly, by shaping the mechanical properties and corrosion resistance of the alloy throughout its service life. Both alloys contain particles having compositions of $\text{Zr}(\text{Fe}, \text{Cr})_2$, with hcp crystal structure. Additionally, Zircaloy-2 incorporates particles of body-centered tetragonal $\text{Zr}_2(\text{Fe}, \text{Ni})$ [41, 43].

The investigation into amorphous transformations and the depletion of Fe, Cr, or Ni from intermetallic particles in Zircaloy-2 during neutron irradiation was pioneered by Gilbert et al. [42, 44] in 1985. The work highlighted the preferential depletion of Fe from $\text{Zr}(\text{Fe}, \text{Cr})_2$ intermetallic precipitates at irradiation temperatures of approximately 570 K ($\sim 300^\circ\text{C}$), coinciding with a simultaneous crystalline-to-amorphous phase transformation. It was also reported that both the $\text{Zr}(\text{Fe}, \text{Cr})_2$ and $\text{Zr}_2(\text{Fe}, \text{Ni})$ particles remained crystalline at the higher temperature of 675 K ($\sim 400^\circ\text{C}$) and were completely amorphous (without Fe depletion) at the lower temperature irradiation of 350 K (77°C) [104].

In the context of Zirconium alloys, the effects of radiation-induced dissolution of $\text{Zr}(\text{Fe}, \text{Cr})_2$ and $\text{Zr}_2(\text{Fe}, \text{Ni})$ secondary precipitation in the matrix, along with the depletion of Cr and Fe from the precipitates, have been extensively documented by various researchers [43, 45, 105]. The influence of Fe concentration in the matrix is

noteworthy, affecting the diffusional characteristics of vacancies in zirconium alloys and potentially decreasing the magnitude of the irradiation growth rate [50].

Despite numerous reports confirming the radiation-induced secondary precipitation of $\text{Zr}(\text{Fe}, \text{Cr})_2$ and $\text{Zr}_2(\text{Fe}, \text{Ni})$ in zirconium alloys, there has been relatively limited exploration of the effect of applied stress. However, it is crucial to acknowledge that the effect of applied stress is an essential factor that necessary thorough investigation, especially in practical environments.

Recognizing the low rates of neutron irradiation damage, charged particle irradiation, particularly through ion irradiation, has proven to be a potent and versatile tool for studying irradiation effects in materials. This approach has demonstrated the ability to replicate many of the same effects observed under neutron irradiation.

In this study, Zircaloy-2 underwent a 3.2 MeV Ni^{3+} ion irradiation up to 30 dpa at 300 °C and 40 dpa at 400 °C. To comprehensively grasp the effects of applied stress, irradiation was conducted under varying applied stress conditions throughout the entire irradiation process. After irradiation, specimens underwent preparation via a FIB for cross-sectional observation.

The analysis of the irradiated specimens involved a meticulous examination of the dissolution of precipitates and the enrichment of alloying elements due to irradiation. This examination was conducted using spherical aberration (Cs)-corrected STEM in conjunction with X-ray EDS. These advanced analytical tools were employed to unravel the intricate microstructure and elemental distribution changes induced by ion irradiation and applied stress in Zircaloy-2.

5.2 Experimental Procedures

In this experiment, Zircaloy-2 utilized underwent an initial rolling process at RT to produce a thin sheet, subsequently punched to obtain tensile samples. As detailed in Chapter 3, the tensile samples featured a nominal gauge length of 4.9 mm, a gauge width of 1.2 mm, and thicknesses of 0.1 mm and 0.25 mm were used in this part. Following mechanical grinding and polishing, all samples underwent an annealing process at 630 °C for 2 hours, followed by air cooling to RT.

Due to the prolonged duration required for high-dose irradiation, the tensile samples needed to be maintained under specific temperature and stress conditions for 2 or 3 days. Precise control over applied tensile stress and temperature was crucial. Since the stress control system is sensitive to changes in material temperature, the sequence of loading and unloading as well as temperature changes is also very important. Unreasonable conditioning processes can introduce other factors, such as rapid temperature changes that can expose the sample to extreme tensile or compressive stresses, which not only affect the microscopic characterization, but also can lead to fracture or bending in severe cases.

In the high-dose irradiation experiments at 300 °C for the 0.1 mm thick samples, the temperature control system worked well. However, during high-dose irradiation at an elevated temperature to 400 °C, the proportional integral derivative (PID) control system for temperature adjustment became unstable for the 0.1 mm thick samples. The heating voltage and current fluctuated during the irradiation process, and the samples exhibited bending after irradiation, significantly affected the study on the effect of stress. After increasing the thickness to 0.25 mm, the high-dose irradiation temperature control at 400 °C proceeded smoothly. Considering the variability

introduced by the thickness of samples and being mindful of the stability of the temperature control system, a thermocouple was soldered on the backside of the sample during irradiation. This enabled continuous monitoring of temperature variations on the sample surface throughout the entire irradiation process, as introduced in Chapter 3, with all other processing steps remaining identical. For specific irradiation conditions of and the irradiation dose, please refer to Table 5-1.

Table 5-1 Summary of Tensile Stress Conditions Applied to Samples.

Temp	Stress/MPa			
	0	50	100	200
300 °C, 30dpa	○		○	○
400 °C, 40dpa		○	○	

Following irradiation, an in-depth analysis of precipitate dissolution and the enrichment of alloying elements was conducted utilizing EDS analysis. To facilitate this investigation, samples were prepared using the FIB. The sampling direction is visually explained in Figure 5.1, where the red arrow indicating the applied stress direction.

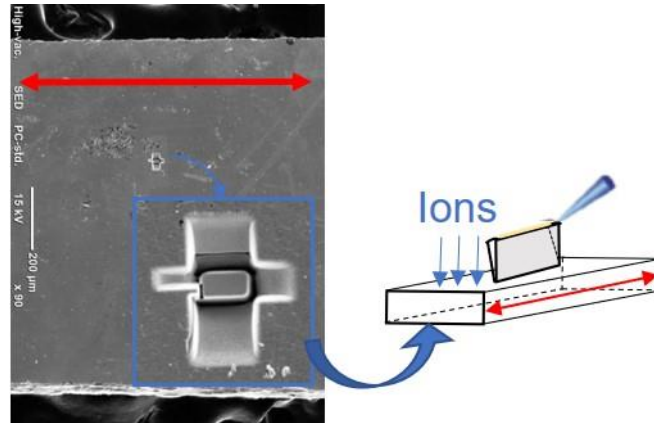


Figure 5.1 Illustration of Applied Stress During FIB Sample Preparation

The EDS mapping analysis is visually depicted in Figure 5.2, showcasing an illustrative example featuring the No.2 of $Zr_2(Fe, Ni)$ precipitate. The analytical process commences by measuring the distance from the sample's surface to the specific precipitate; for instance, the No.2 precipitate measures $1.276 \mu m$ depth in this case. The damage rate was determined at specific depth through SRIM calculation, yielding a value of 0.98×10^{-4} dpa/s. With the irradiation injection time, the corresponding damage dose can be measured, amounting to 29.4 dpa. The analysis culminates with a comprehensive quantitative assessment of the precipitate, as presented in a table, accompanied by an EDS spectrum. This detailed examination delves into the composition of selected elements as Cr, Fe, Ni, Sn, and Zr. After that, the influence of the dose on elemental content in precipitates can be compared.

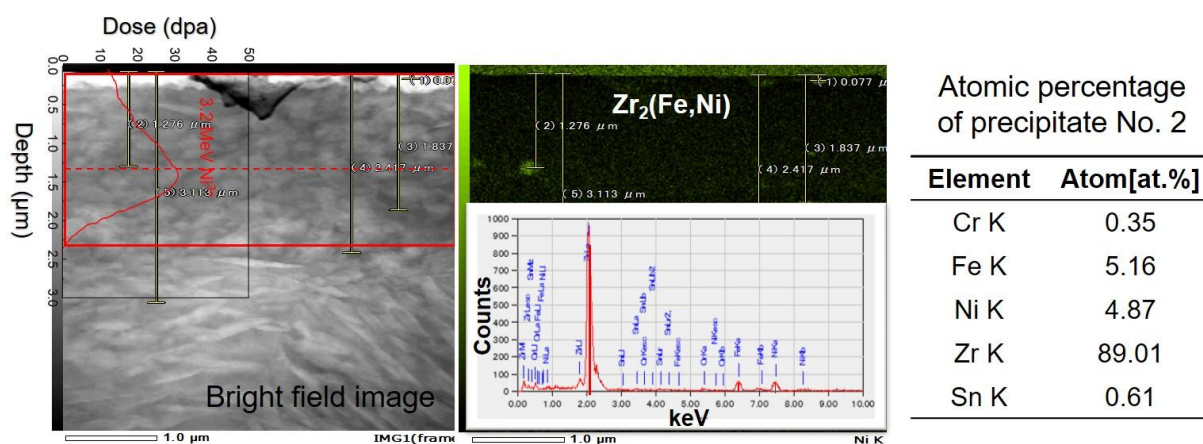


Figure 5.2 EDS Mapping Analysis of Selected Precipitate

5.3 Results and Discussion

5.3.1 Irradiation-Induced Dissolution Under Applied Stress at 300 °C

To achieve an irradiation dose of 30 dpa at 300 °C under stress conditions, it was necessary to maintain the applied stress for a duration exceeding 15 hours. Careful consideration was given to selecting the applied stress level to prevent sample failure or fracture during the irradiation process. To ensure the integrity of the sample, the applied stress was continuously monitored throughout the entire irradiation process. Recognizing the sensitivity of applied stress to temperature variations, it can be reasonably inferred that the temperature was maintained at a specific level as the irradiation commenced. The recorded stress under various stress conditions is presented in Figure 5.3, providing valuable insights into the dynamic relationship between applied stress and temperature during the irradiation experiments.

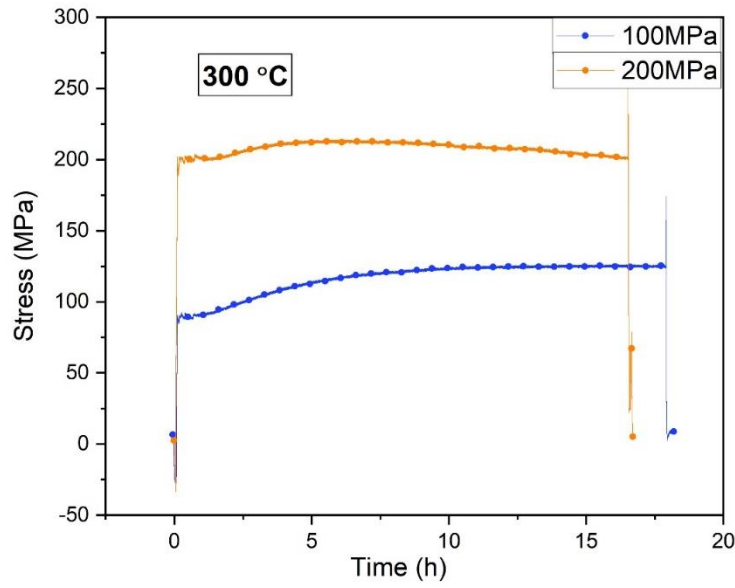


Figure 5.3 Stress Recording During Ion Irradiation at 300 °C up to 30 dpa

After irradiation, EDS mapping was performed from a cross-sectional view in Zircaloy-2 using FIB-prepared samples. Figure 5.4 illustrates the results of EDS mapping for Ni and Fe, emphasizing the $Zr_2(Fe, Ni)$ precipitate. The red box indicates the irradiation area of the sample, while the red dotted line corresponds to the peak damage of 30 dpa. The red arrow indicates applied stress direction. The peak concentration of Ni ions, calculated using SRIM and denoted by the blue dotted line, exhibits consistency with the Ni mapping results. Considering irradiation with 3.2 MeV Ni ions, which may act as impurity ions affecting the material matrix, the maximum concentration distribution of Ni ions at depth by SRIM calculation is approximately 1.7×10^{-6} at%./s. At the peak damage level of 30 dpa, the concentration of Ni ions measures about 0.51 at.% at the peak position at 1.7 μm . This concentration of Ni ions is in close agreement with the mapping analysis and is slightly higher than that of the unirradiated samples. However, the Ni mapping did not show a significant aggregation of nickel ions at this location.

With the limited observation area of samples shown in Figure 5.4, the number of $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates was constrained, making it difficult to determine if precipitate dissolution has occurred.

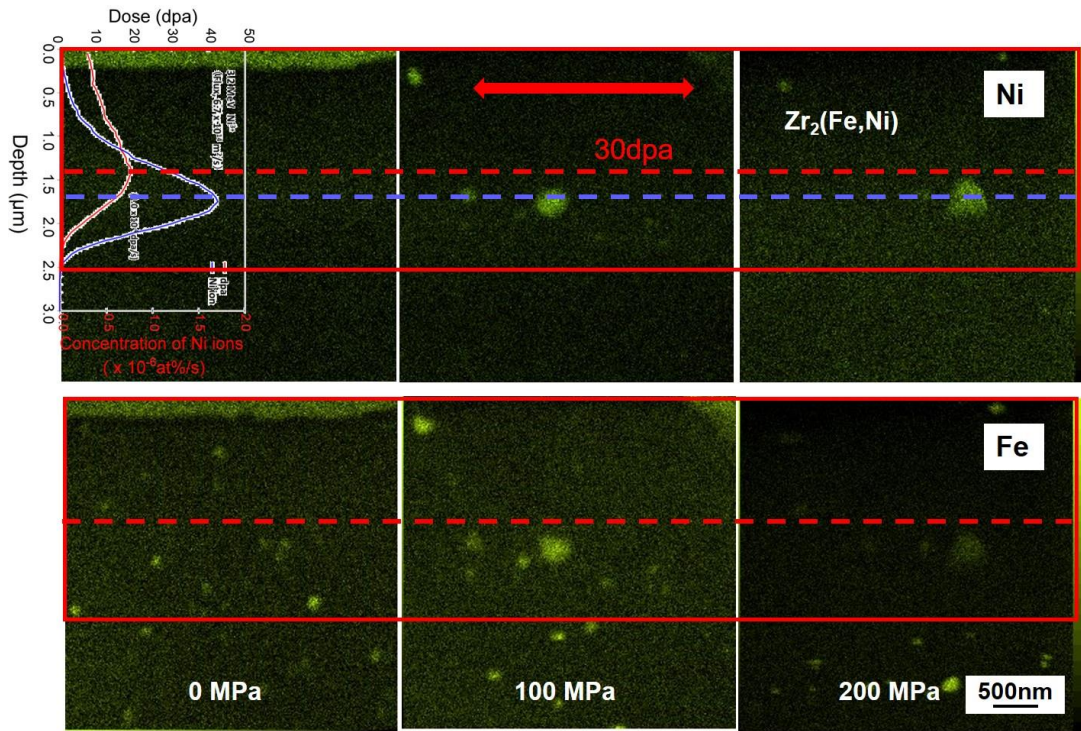


Figure 5.4 EDS Mapping of Ni and Fe in Zircaloy-2 After Irradiated at 300 °C Under Different Applied Stresses

Subsequently, multiple FIB samples were prepared using the analytical method described in Section 5.2 Experimental Procedures, aiming to quantitatively analyze as many $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates as possible. Based on existing findings, it was observed that the dissolution of precipitates is primarily associated with the dissolution of Fe atoms [43, 46]. Therefore, Figure 5.5 illustrates the effect of the dose and applied stress on the elemental content ratios of $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates by calculating the ratio of $\text{Fe}/(\text{Fe}+\text{Ni})$ with different precipitates at different depths. As depicted in the Figure 5.5, the $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates remained nearly stable under irradiation up to

30 dpa at 300 °C, both with and without applied stress. The influence of applied stress on the dissolution rate and behavior of precipitation was not clear.

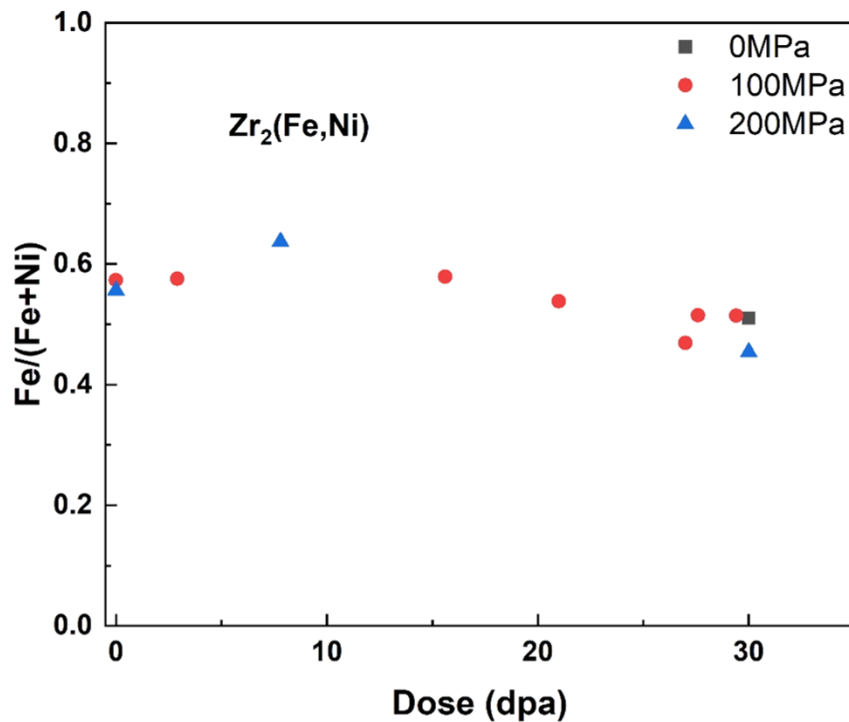


Figure 5.5 Effect of Dose and Applied Stress on Elemental Content Ratios of $Zr_2(Fe, Ni)$

Precipitates in Zircaloy-2 Irradiated at 300 °C

Figure 5.6 illustrates the results of EDS mapping for Cr and Fe, emphasizing the $Zr(Fe, Cr)_2$ precipitate. By using the distribution of Cr mapping, we were able to clearly see the number density of precipitates in the irradiated region was comparable to that in the unirradiated region, but almost all Fe atoms had dissolved out of the precipitate in irradiated area. This phenomenon becomes more pronounced as the stress increases. With an applied stress of 200 MPa, nearly all Fe atoms dissolved out of the $Zr(Fe, Cr)_2$ precipitates during irradiation up to 30 dpa.

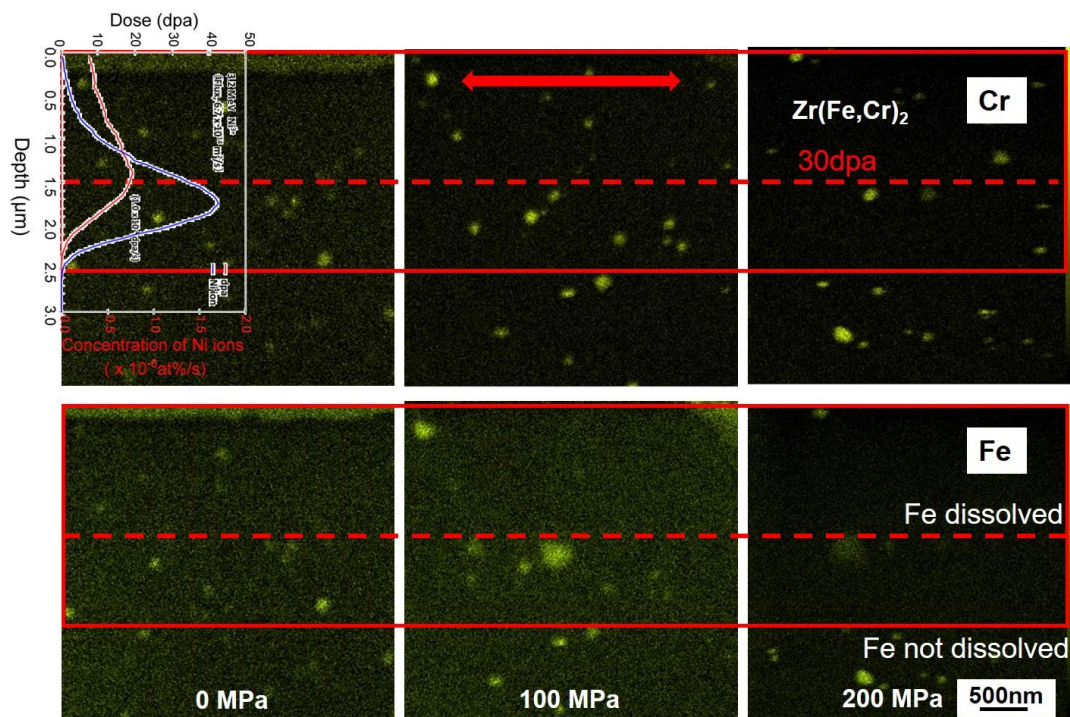


Figure 5.6 EDS Mapping of Cr and Fe in Zircaloy-2 After Irradiated at 300 °C Under Different Applied Stresses

Following the same procedure as before, multiple FIB samples were prepared for the quantitative analysis of as many Zr(Fe, Cr)_2 precipitates as possible. Figure 5.7 illustrates the effect of dose and applied stress on the elemental content ratios of Zr(Fe, Cr)_2 precipitates. Consistent with the mapping results shown in Figure 5.6, Fe atoms were found to dissolve out of the Zr(Fe, Cr)_2 precipitates during irradiation up to 30 dpa. There was a decrease and then an increase in the Fe content in the Zr(Fe, Cr)_2 precipitates under both 100 MPa and no applied stress conditions. However, no increase in Fe content was observed in the irradiated samples under an applied stress of 200 MPa. Considering the possibility of errors in the dose calculation, there may be a slight deviation in the irradiation dose; nevertheless, in any case, the most complete dissolution of Fe atoms from the Zr(Fe, Cr)_2 precipitates was observed with 200 MPa.

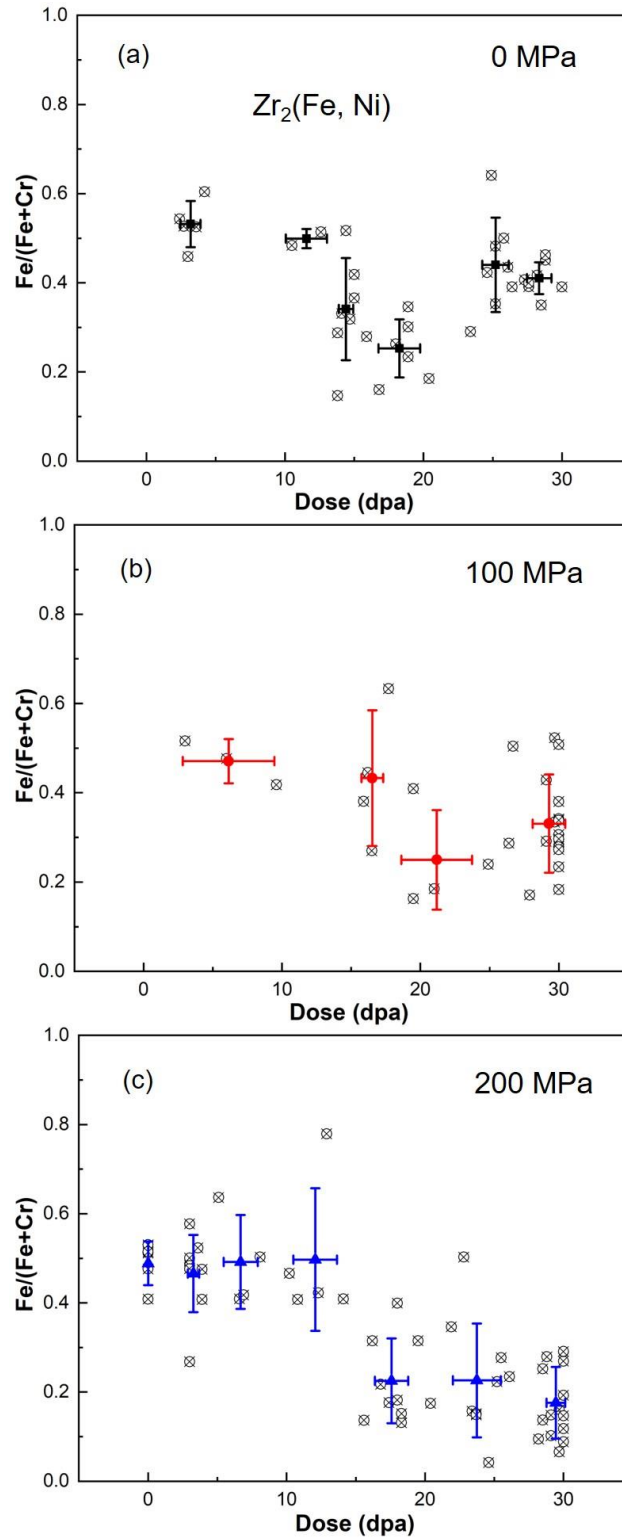


Figure 5.7 Effect of Dose on Elemental Content Ratios of $Zr(Fe, Cr)_2$ Precipitates in Zircaloy-2 Irradiated at 300 °C with Different Applied Stresses: (a) 0 MPa, (b) 100 MPa, and (c) 200 MPa

To eliminate the influence of factors other than ion irradiation on the dissolution of the precipitates, FIB samples were extracted from the backside of all irradiated samples for analysis. Figure 5.8 presents the EDS mapping of Zircaloy-2 after irradiation under 100 MPa. In the figure, at the same depth as the irradiation area, within 2 μm , no Fe atom dissolved out of the precipitate was observed. The distribution of elemental content ratios at different depths in the observation area is displayed in Figure 5.9, with mean values of 0.50 and a standard deviation of 0.05. These values closely resemble those observed in unirradiated samples [43].

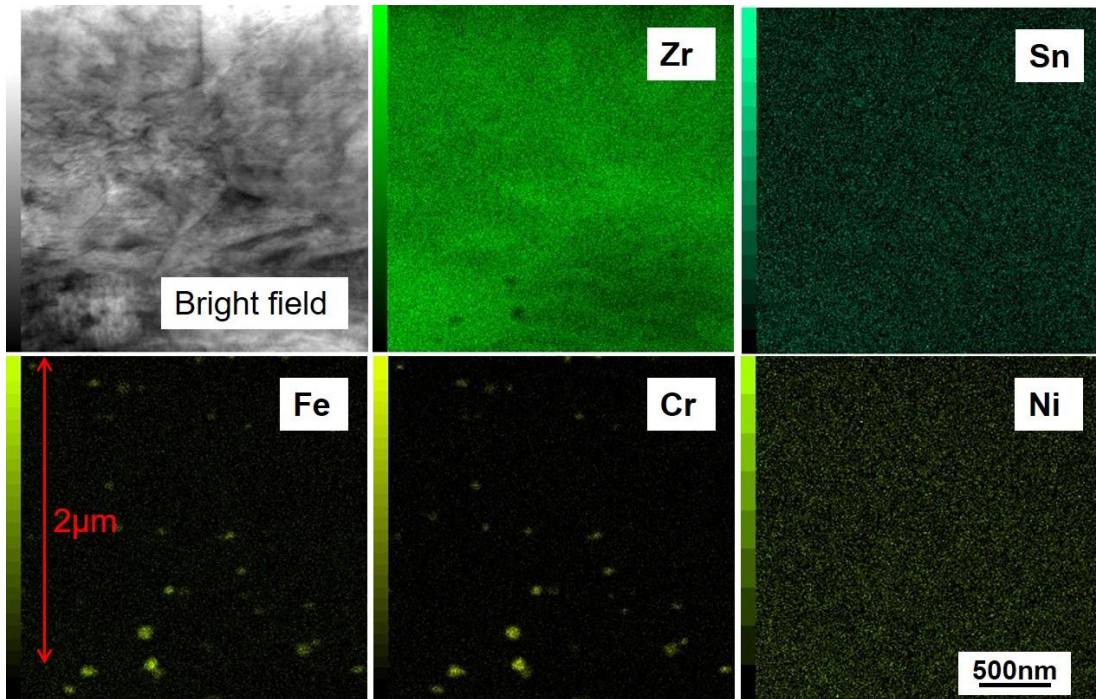


Figure 5.8 STEM-EDS Mapping of the Backside of Zircaloy-2 Irradiated at 300 °C Under Applied Stress with 100 MPa

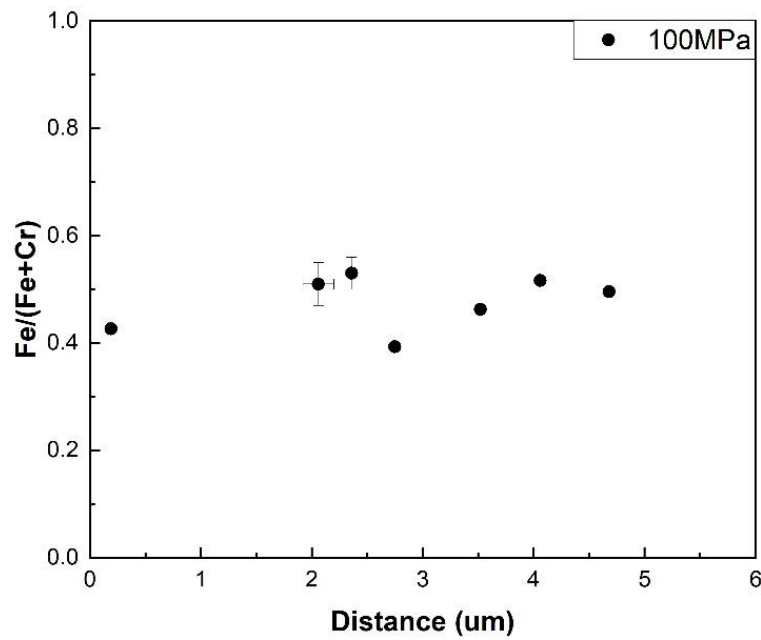


Figure 5.9 Elemental Content Ratio Distribution on the Depth of the Backside of Zircaloy-2 Irradiated at 300 °C Under Applied Stress with 100 MPa

5.3.2 Irradiation-Induced Dissolution Under Applied Stress at 400 °C

For better analysis of precipitate dissolution, as well as later <c> type dislocation loops observation, both temperature and damage dose were increased. To achieve an irradiation dose of 40 dpa at 400 °C under stress conditions with 0.25 mm thick samples, it was necessary to maintain the applied stress for a duration exceeding 45 hours. This period includes 8-10 hours to stabilize the temperature control system and an additional more than 35 hours of irradiation. The applied stress and temperature were continuously monitored throughout the entire irradiation process. The recorded stress and temperature are presented in Figure 5.10, with irradiation under (a) 50 MPa and (b) 100 MPa.

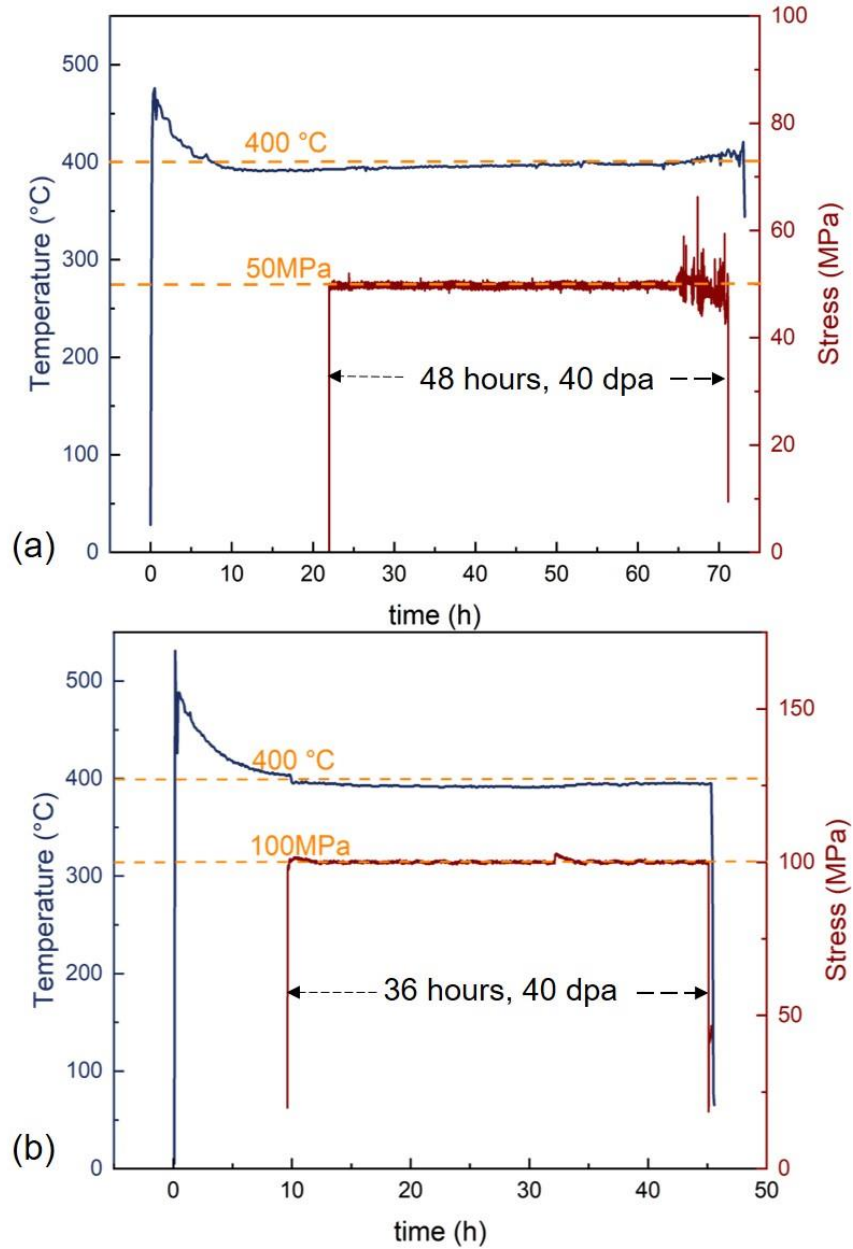


Figure 5.10 Temperature and Stress Recording During Ion Irradiation at 400 °C Under Different Applied Stresses: (a) 50 MPa, (b) 100 MPa

After irradiation, EDS mapping was performed from a cross-sectional view in Zircaloy-2 using FIB-prepared samples. Figure 5.11 illustrates the results of EDS mapping for Fe, Cr, and Ni in Zircaloy-2 after irradiation under different applied stresses. Fe atoms were observed to dissolve from precipitates during irradiation up to 40 dpa at 400 °C

under varying applied stresses.

Similar to irradiation at 300 °C up to 30 dpa, the concentration of Ni ions measures about 0.68 at.% at the peak position at 1.7 μm at the peak damage level of 40 dpa. This concentration is slightly higher than that calculated with irradiation up to 30 dpa. In Figure 5.11, Ni enrichment at the surface was observed, exceeding 15 at.%. Two distinct mechanisms, interstitial mechanisms and vacancy mechanisms, have been identified in stainless steels, providing explanations for the observed nickel enrichment [106, 107]. The interstitial mechanism is particularly favorable for Ni enrichment, attributed to the involvement of undersized atoms. In the case of $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates, Ni atoms undergo dissolution, diffuse to the surface, and subsequently contribute to the reformation of precipitates again. The discussion of Ni dissolved from precipitates in zirconium alloys lacks detailed exploration.

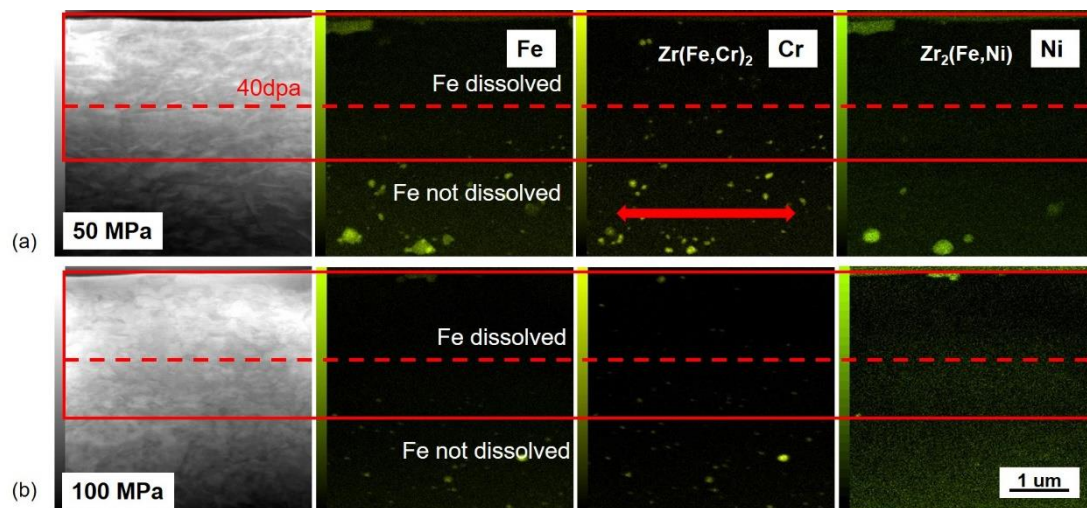


Figure 5.11 EDS Mapping of Fe, Cr and Ni in Zircaloy-2 After Irradiated at 400 °C Under Different Applied Stresses: (a) 50 MPa, (b) 100 MPa

Figure 5.12 illustrates the effect of dose and applied stress on the elemental content

ratios of $Zr_2(Fe, Ni)$ precipitates in Zircaloy-2 irradiated at 400 °C under different applied stresses. As depicted in the figure, the $Zr_2(Fe, Ni)$ precipitates remained nearly stable up to 40 dpa at 400 °C, maintaining the ratio of $Fe/(Fe+Ni)$ at about 0.55, almost the same as in unirradiated samples. This observation also suggests that all of the dissolved Fe atoms shown in Figure 5.11 come from the other types of precipitates.

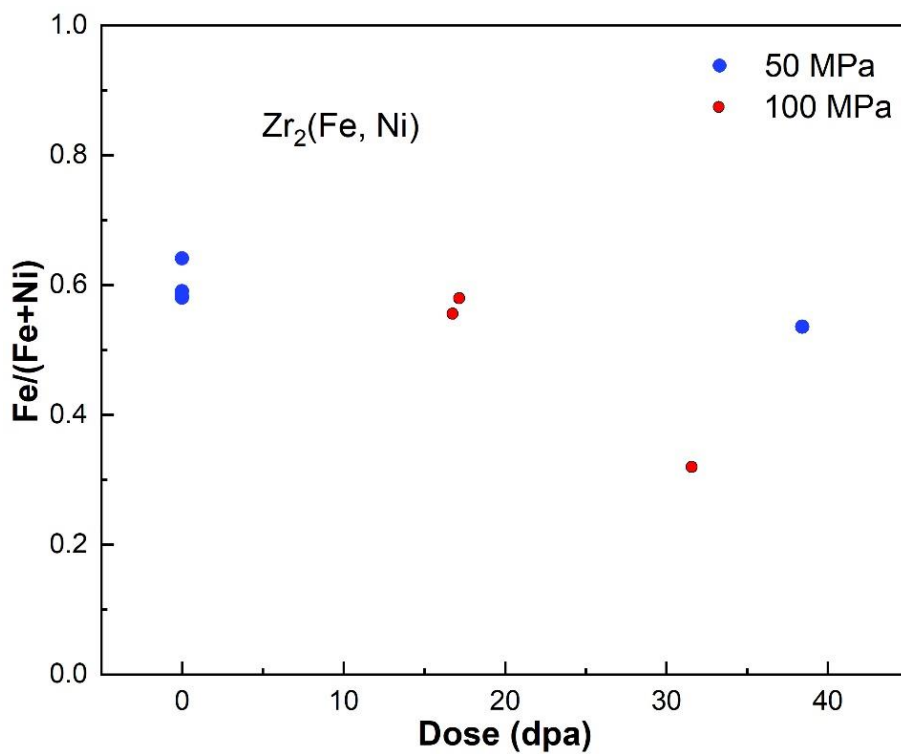


Figure 5.12 Effect of Dose and Applied Stress on Elemental Content Ratios of $Zr_2(Fe, Ni)$ Precipitates in Zircaloy-2 Irradiated at 400 °C

Figure 5.13 illustrates the effect of dose and applied stress on the elemental content ratios of $Zr(Fe, Cr)_2$ precipitates in Zircaloy-2 irradiated at 400 °C under different applied stresses. Fe atoms were found to dissolve out of the $Zr(Fe, Cr)_2$ precipitates during irradiation up to 40 dpa. When compared to the case of irradiation under

applied stress with 50 MPa, a higher applied stress seems to lead to a lower Fe/(Fe+Cr) ratio. However, the effect of applied stress on the precipitation dissolution rate and behavior does not appear to show significant differences.

Irradiation induces high concentrations of vacancies and atom defects. These defects, along with the extended dislocation microstructure formed under irradiation, create spatially fluctuating strain and stress fields. These fields modify the local formation and migration enthalpies of defects, leading to the anisotropy of diffusion. Even in the absence of stress, the diffusion tensor is isotropic [108]. However, with applied stress, it may alter the diffusion tensor which may change the dissolution behavior.

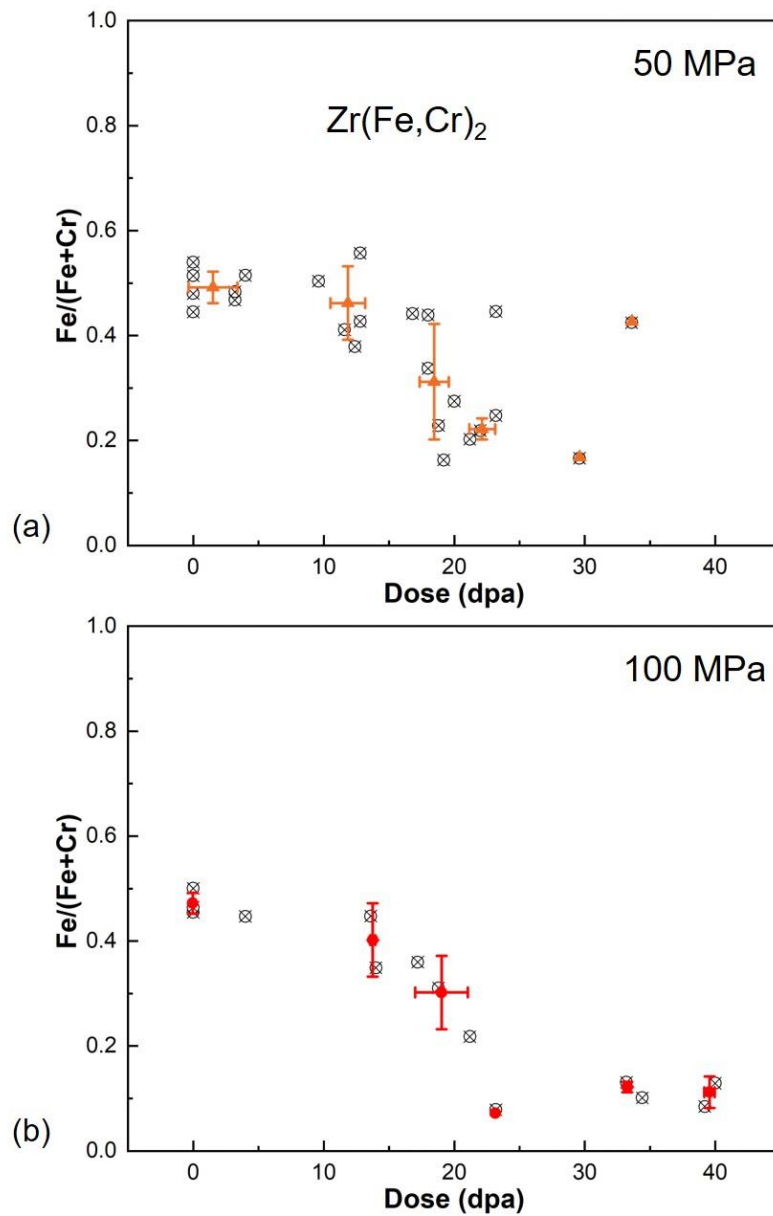


Figure 5.13 Effect of Dose on Elemental Content Ratios of $\text{Zr}(\text{Fe,Cr})_2$ Precipitates in Zircaloy-2 Irradiated at 400 °C with Different Applied Stresses: (a) 50 MPa, (b) 100 MPa

To investigate the effect of different irradiation conditions on precipitate dissolution, samples were chosen under uniform stress conditions of 100 MPa and stress-free conditions, as depicted in Figure 5.14. Hollow circles denote irradiation at 300 °C, while solid circles represent irradiation at 400 °C. The black data points correspond

to irradiation without applied stress, with data for irradiation at 400 °C without stress sourced from published data by Watanabe et al. [43]. The red data points represent irradiation under 100 MPa, accompanied by error bars indicating the standard deviation.

Without considering the phenomenon of an increase in Fe content in SPPs after the decrease, the Figure 5.14 shows that an increase in temperature under both stress conditions significantly enhances precipitate dissolution. For example, with the same irradiation dose as 30 dpa, the Fe content in SPPs at 400 °C is lower than that in samples irradiated at 300 °C. As the temperature rises, the thermal motion of atoms intensifies, may also leading to an increase in the diffusion coefficient, making diffusion easier.

However, at the same temperature, the influence of applied stress is less pronounced.

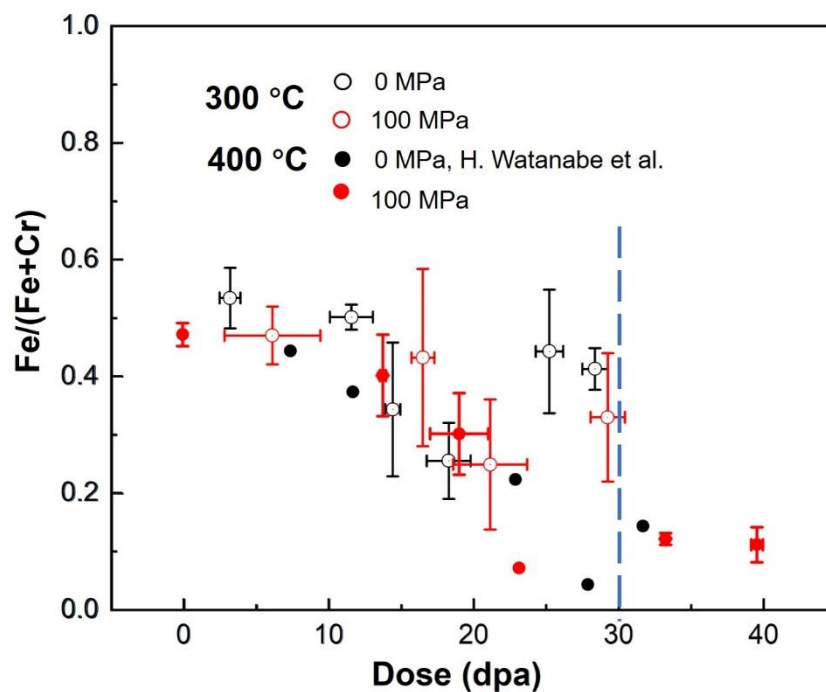


Figure 5.14 Effect of Temperature and Applied Stress on Dissolution of $Zr(Fe, Cr)_2$

Precipitates in Zircaloy-2

5.4 Section Conclusions

The investigation focused on the dissolution of precipitates in Zircaloy-2 subjected to high-dose irradiation with 3.2 MeV Ni^{3+} ions at 300 °C and 400 °C under applied stress. The effect of applied stress and temperature on the dissolution of SPPs was examined. The main results are summarized as follows:

1. At temperatures of 300 °C up to 30 dpa and 400 °C up to 40 dpa, irrespective of the applied stress conditions, Fe atoms dissolved from $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates during irradiation were observed, while $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates remained stable under the same irradiation conditions.
2. A rise in temperature seems to enhance the complete dissolution of $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates, possibly due to the intensification of thermal motion as the temperature rises, leading to an increase in the diffusion coefficient, making diffusion easier.
3. While stress could potentially contribute to a more thorough dissolution of precipitates, which means with smaller ratio of $\text{Fe}/(\text{Fe}+\text{Cr})$. However, this phenomenon was not distinctly observed. Utilizing more advanced analytical tools or intensifying the applied stress might be necessary to emphasize any discernible differences.

CHAPTER 6. Study on C-Component Loops Formation During High-Dose Irradiation Under Applied Stress

6.1 Introduction

The irradiation growth phenomenon is characterized by an elongation along the basal plane of the hexagonal closed-packed structure and a simultaneous shortening along the c-axis, resulting in a constant volume [68, 109]. In the context of irradiation growth in zirconium alloys, a macroscopic elongation along the axial direction of claddings is observed, attributed to the robust texture of the claddings.

As reactors operate, a phenomenon known as 'breakaway growth' accelerates the growth rate after an incubation dose. It has been observed that, in annealed Zircaloy-2 at temperatures between 553 and 673 K (280-400 °C), a transition from saturating growth to accelerating growth rates occurs with increasing dose [66]. This acceleration, breakaway growth, is strongly influenced by irradiation temperature [110], with specimen purity also being a critical factor [111]. The nucleation of c-component dislocation loops is intricately linked to Fe atoms dissolved from SPPs [43]. The studies established a correlation between breakaway growth and the nucleation of c-component dislocation loops formed at high doses [37, 68, 112].

The effect of applied stress on c-component dislocation loops was first explored by Tournader et al. [113] in 2015, focusing on as-received recrystallized Zircaloy-4 irradiated with Zr ions at 573 K (300 °C). While initial applied stress showed no effect on c-component dislocation loops, subsequent stress applied after c-loops formation influenced their growth. Subsequent experiments [114] on recrystallized Zircaloy-4 and M5 revealed a slight effect of applied stress on the c-component dislocation loops

microstructure, aligning with the Stress-Induced Preferential Absorption (SIPA) mechanism.

This chapter delves into the observations of c-component loops induced by 3.2 MeV Ni^{3+} ion irradiation and thoroughly explores their microstructure under the influence of temperature, dose, and applied stress throughout the irradiation process.

6.2 Experimental Procedures

In the experiment studying the formation of c-component loops in Zircaloy-2 irradiated at 300 °C, FIB samples prepared in the previous Chapter 5 were utilized. Additionally, a new set of specimens, prepared by twin-jet, underwent 3.2 MeV Ni^{3+} ion irradiation with the ion injection direction parallel to the c-plane. This differs from the previous irradiation direction, which was nearly perpendicular to the c-plane. The rationale behind this approach is to facilitate the observation of c-component loops with TEM characterization. Ensuring that the crystallographic rotation direction aligns more conveniently with the suitable zone axis allows for the selection of the $g=(0002)$ diffraction vector for c-component loop observation.

For the examination of c-component loops in Zircaloy-2 irradiated at 400 °C in this experiment, all FIB samples used were prepared in Chapter 5.

The entire microstructure evolution was analyzed using conventional transmission electron microscopy, as introduced in Chapter 3.

6.3 Results and Discussion

6.3.1 C-Component Loops Formation at 300 °C Under Applied Stress

Figure 6.1 illustrates the cross-sectional view of Zircaloy-2 irradiated up to 30 dpa at 300 °C under different applied stress conditions. The blue arrow indicates the direction of applied stress, the yellow arrow points to the W-deposition (sample surface), and the yellow arrow's range represents the irradiated area, approximately 2.5 μm . The diffraction patterns during photography are attached in the images. The FIB sample preparation process introduces damage, and even after Ar ion milling, residual damage remains on the sample, complicating observation and characterization. The presence of FIB damage makes it difficult to distinguish between irradiated and unirradiated areas.

In Figure 6.1(a), the sample irradiated under 50 MPa is shown under the $g=(11\bar{2}0)$. Despite the existence of FIB damage, small black dot-like a-component loops can be observed within the irradiated area marked by the yellow arrow. In Figure 6.1(b), a sample irradiated under 100 MPa is intentionally observed under the $g=(0002)$. No c-component loops are generated inside the grains selected under these near two-beam conditions. And no c-component loops were observed in other observation areas under these conditions as well.

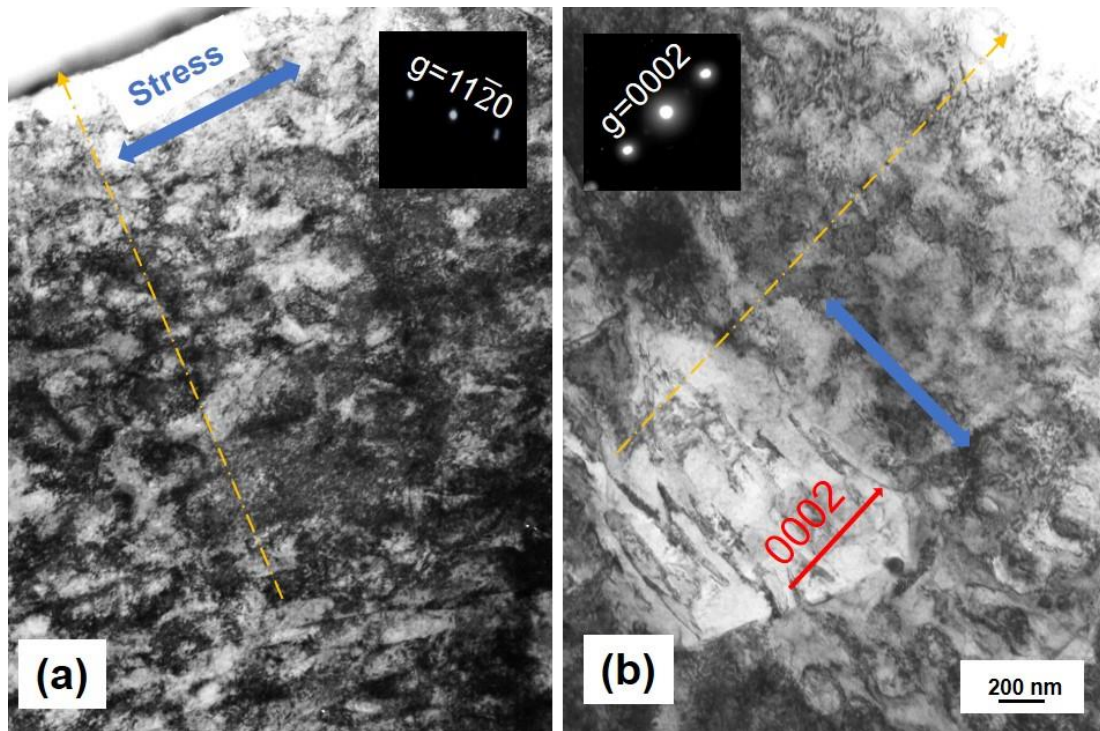


Figure 6.1 Cross-Sectional View of Zircaloy-2 Irradiated with 3.2 MeV Ni^{3+} Ions up to 30 dpa at 300 °C Under Different Applied Stresses: (a) 100 MPa, (b) 200 MPa

In order to clarify whether c-component loops could be generated at 300 °C, higher-dose irradiation was conducted under stress-free conditions. Ion irradiation was performed along the a-axis direction of hcp for the twin-jet-prepared samples, and the irradiation dose was increased to 40 dpa. In the TEM image in Figure 6.2, a short black line perpendicular to $g=(0002)$ is observed in the irradiated region, as indicated by red short arrows. The linear spacing between the generated short black lines is approximately 30 nm, consistent with the characteristics of c-component loops.

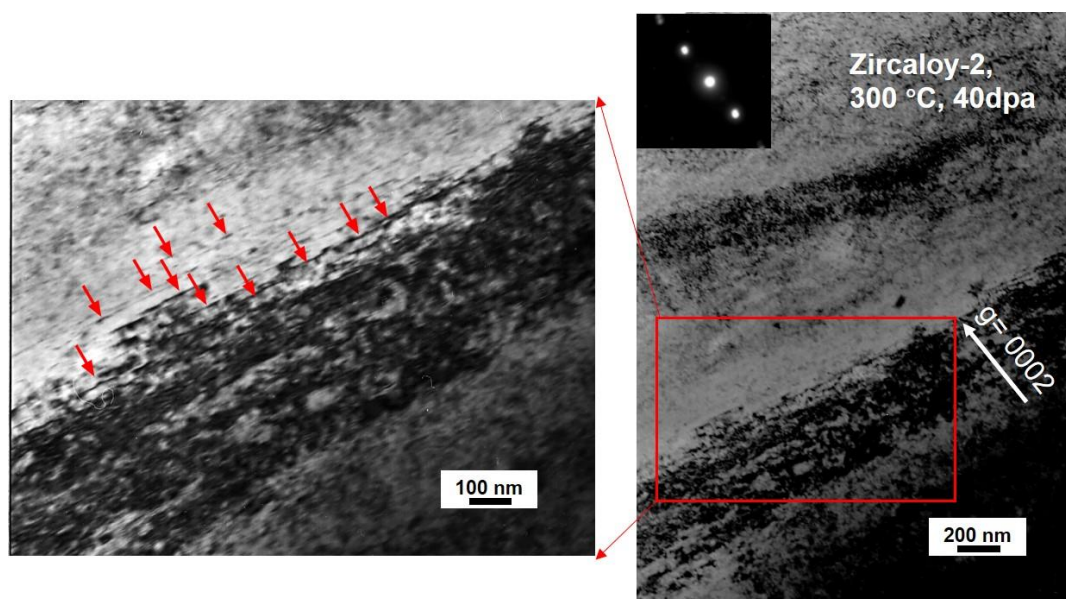


Figure 6.2 TEM Images of Zircaloy-2 Irradiated with 3.2 MeV Ni³⁺ Ions up to 40 dpa at 300 °C

C-component loops were not observed in Zircaloy-2 irradiated under the same conditions at 300 °C up to 30 dpa, despite the clear identification of the dissolution of Fe atoms in precipitates under this condition, as discussed in Chapter 5. However, with the dose increased to 40 dpa, <c> loops were observed. This suggests that c-component loops could be generated at 300 °C with a dose below 40 dpa, but at least higher than 30 dpa with 3.2 MeV Ni³⁺ ion irradiation.

6.3.2 C-Component Loops Formation at 400 °C Under Applied Stress

Figure 6.3 depicts the cross-sectional view of Zircaloy-2 irradiated up to 40 dpa at 400 °C with 50 MPa. The black arrows indicate the direction of ion irradiation, and the blue arrows represent the applied stress direction. W-depo is at the sample surface, and irradiation doses at various depths were calculated using SRIM simulations, and

peak damages were determined. C-component loops were clearly observed with diffraction vector $g=(0002)$, and the spacing between stripes was approximately 25 nm. The appearance and spacing of $\langle c \rangle$ loops remained consistent across various doses. The formation of $\langle c \rangle$ loops required a threshold dose of around 20 dpa, with no apparent $\langle c \rangle$ loops observed below 15 dpa. Higher irradiation temperatures may promote the generation of $\langle c \rangle$ loops with the same dose level.

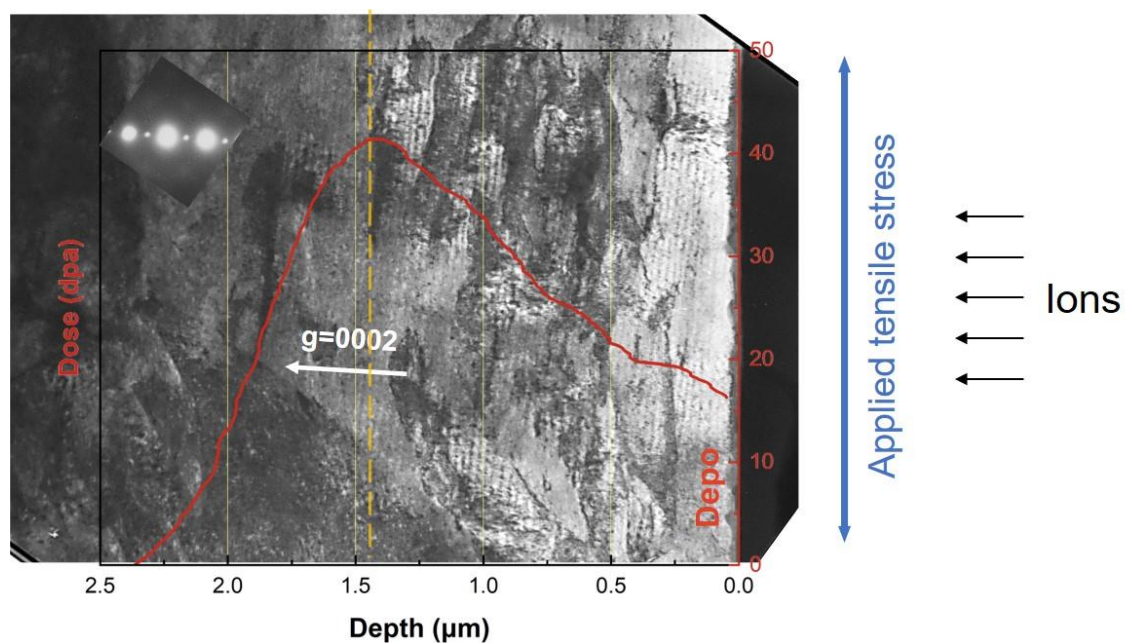


Figure 6.3 Cross-Sectional View of Zircaloy-2 Irradiated with 3.2 MeV Ni^{3+} Ions up to 40 dpa at 400 °C Under 50 MPa

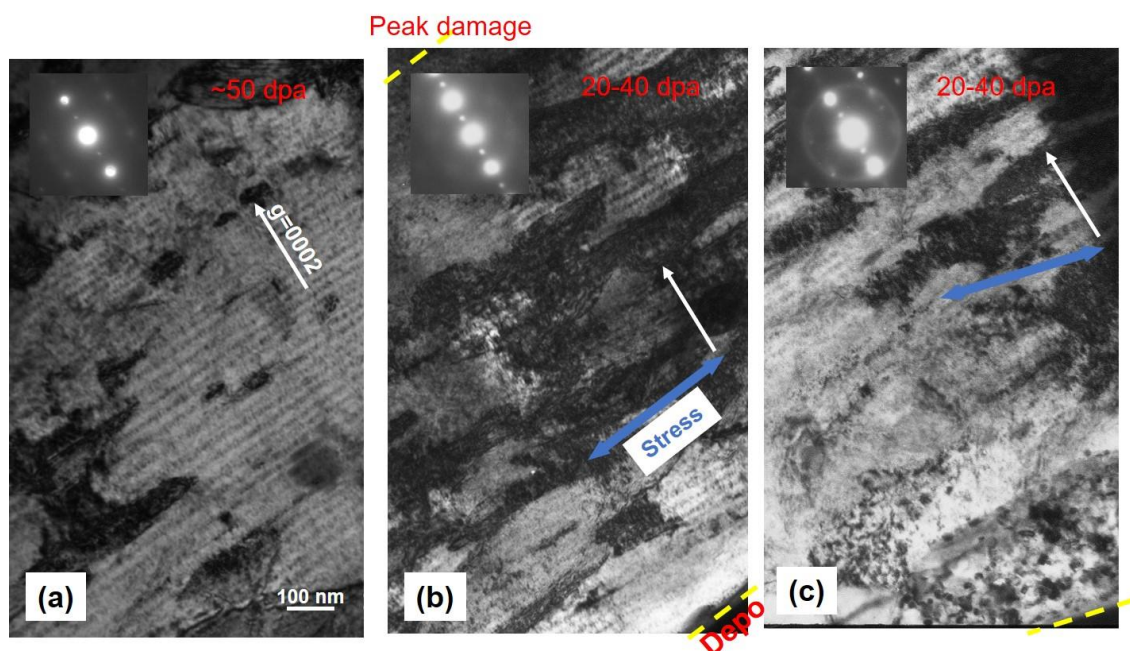


Figure 6.4 Cross-Sectional View of Zircaloy-2 Irradiated with 3.2 MeV Ni³⁺ Ions up to 30 dpa at 400 °C Under Different Applied Stresses: (a) 0 MPa [43], (b) 100 MPa and (c) 200 MPa

Figure 6.4 illustrates the cross-sectional view of Zircaloy-2 irradiated up to 40 dpa at 400 °C under various applied stress conditions. The data for irradiation at 400 °C without stress are sourced from published data by Watanabe et al. [43]. The blue arrow indicates the direction of applied stress, and the yellow dashed line represents the W-deposition (sample surface). In Figure 6.4(a), the observed region has an approximate damage dose of 50 dpa, while in Figure 6.4(b), the observed region has a damage dose ranging from 20 to 40 dpa, with the maximum peak damage reaching 40 dpa. In Figure 6.4(b), the damage dose in the observed region is 20-40 dpa, reaching approximately 40 dpa at the farthest distance from the surface. There was no observable change in the appearance or spacing of the c-component dislocation

loops with varying applied stress.

In consideration of Figure 5.14, at the same irradiation dose, the irradiated samples at 400 °C exhibit lower Fe content in SPPs compared to those at 300 °C. To achieve the same iron content, a higher irradiation dose is required at 300 °C. This also suggests that the Fe in the material matrix may have an influence on the generation of dislocation loops. It is necessary to perform EDS analysis on samples irradiated at 300 °C up to 40 dpa.

6.4 Section Conclusions

The investigation focused on the c-component dislocation loops formation in Zircaloy-2 subjected to high-dose irradiation with 3.2 MeV Ni³⁺ ions at 300 °C and 400 °C under applied stress. The relationship of dissolution of Fe atoms from SPPs to the generation of c-component dislocation loops also discussed. The main results are summarized as follows:

1. The c-component loops could be generated at 300 °C with a dose below 40 dpa, but at least higher than 30 dpa. <c> loops formation required a threshold dose of about 20 dpa at 400 °C.
2. At 400 °C, the applied tensile stress has no significant effect on the formation of <c> loops until 100 MPa.

CHAPTER 7. Summary and Future Work

This study aims to emulate the operating conditions of Zircaloy-2 in BWRs by subjecting it to neutron radiation simulation using 3.2 MeV Ni^{3+} ion irradiation. The experimental setup involves meticulous control over temperature conditions and the application of external stress. The primary objective is to delve into the effects of irradiation, particularly under applied tensile stress, with a specific focus on comprehending the microstructural evolution and macroscopic properties of Zircaloy-2.

The investigation encompasses various facets, including the radiation-induced hardening observed in the initial stages of irradiation, the characterization and phenomena associated with precipitate dissolution, and the overall microstructural evolution occurring during irradiation under applied tensile stress. The key observations derived from these experiments are as follows:

1. At low dose levels (below 1.0 dpa), $\langle a \rangle$ loops with a diameter of approximately 4 nm were observed at doses below 0.05 dpa, reaching saturation density at around 0.1 dpa. These loops grew and entangled with adjacent loops at doses exceeding 0.4 dpa.
2. Radiation-induced hardening was confirmed in Zircaloy-2 at the early stage of irradiation below 0.1 dpa. After 0.1 dpa, there was a sustained increase in hardness due to the growth of $\langle a \rangle$ loops until the loop size reached a maximum of about 12 nm at 0.4 dpa. The hardness reached saturation with an increase of about 80 Hv at 300 °C without applied stress.

3. The measured values of hardness increase were consistent with the contribution of $\langle a \rangle$ type dislocation loops to hardness as calculated using the Orowan equation. These findings suggest that the hardening of Zircaloy-2 in the initial irradiation stage is mainly due to the presence of $\langle a \rangle$ loops.
4. As the irradiation dose increased, at temperatures of 300 °C up to 30 dpa and 400 °C up to 40 dpa, Fe atoms dissolved into Zircaloy-2 matrix from $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates, while $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates remained stable. Higher temperatures seemed to enhance the complete dissolution of Fe atoms from $\text{Zr}(\text{Fe}, \text{Cr})_2$ precipitates.
5. The c-component loops could be generated at 300 °C with a dose below 40 dpa but at least higher than 30 dpa, and a threshold dose of approximately 20 dpa was required at 400 °C.
6. The effect of applied tensile stress on radiation-induced hardening and microstructure evolution of Zircaloy-2 at different damage levels has initially been systematically discussed. Considering our specific experimental conditions, the applied stress up to 200 MPa with tensile samples irradiated at 300 °C and 100 MPa with tensile samples irradiated at 400 °C did not have a significant effect on radiation-induced hardening, precipitate dissolution, and microstructure evolution.

For a comprehensive understanding of the underlying mechanisms governing neutron irradiation-induced changes in zirconium alloys and their effect on irradiation-induced hardening and microstructure evolution under applied stress, it becomes imperative to subject the material to higher stress levels during irradiation. Particularly at 400 °C, where the dissolution process triggers the dissolution of precipitates, although stress might contribute to more thorough precipitate dissolution, this effect is not prominently

evident under the current experimental conditions. Elevating applied stress could lead to more pronounced results in the study of stress effects, and exploring stress direction at a finer scale, such as investigating multiple grains with different orientations, could provide more valuable insights.

Moreover, even if the current effect of stress on dislocation loop generation appears subtle, ongoing research on the effects of stress on other radiation phenomena in zirconium alloys, such as the generation and reorientation of hydrides, as well as its effect on corrosion and creep, remains crucial. Zirconium alloys, serving as materials for cladding tubes, inevitably endure stress environments for prolonged periods. Stress influences various aspects, both at the microscopic level, involving dislocation generation and movement, ion migration effects, lattice deformation and grain orientation, and at the macroscopic level, affecting material mechanical and corrosion properties. Clearly understanding the role of stress is vital for effectively utilizing and advancing zirconium alloys.

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