MICROSTRUCTURAL EVOLUTION OF FERRITIC-MARTENSITIC STEELS
UNDER HEAVY ION IRRADIATION

A Dissertation in
Materials Science and Engineering
by
Cem Topbasi

© 2014 Cem Topbasi

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2014
The dissertation of Cem Topbasi was reviewed and approved* by the following:

Arthur T. Motta  
Chair and Professor of Nuclear Engineering and Professor of Materials Science and Engineering  
Dissertation Advisor  
Chair of Committee

Clifford Lissenden  
Professor of Engineering Science and Mechanics

Zi-Kui Liu  
Professor of Materials Science and Engineering

Clive A. Randall  
Professor of Materials Science and Engineering

Brian D. Wirth  
Special Member  
Governor’s Chair Professor of Nuclear Engineering  
The University of Tennessee

Suzanne Mohney  
Chair, Intercollege Graduate Degree Program in Materials Science and Engineering  
Professor of Materials Science and Engineering and Professor of Electrical Engineering

*Signatures are on file in the Graduate School
ABSTRACT

Ferritic-martensitic steels are primary candidate materials for fuel cladding and internal applications in the Sodium Fast Reactor, as well as first-wall and blanket materials in future fusion concepts because of their favorable mechanical properties and resistance to radiation damage. Since microstructure evolution under irradiation is amongst the key issues for these materials in these applications, developing a fundamental understanding of the irradiation-induced microstructure in these alloys is crucial in modeling and designing new alloys with improved properties.

The goal of this project was to investigate the evolution of microstructure of two commercial ferritic-martensitic steels, NF616 and HCM12A, under heavy ion irradiation at a broad temperature range. An in situ heavy ion irradiation technique was used to create irradiation damage in the alloy; while it was being examined in a transmission electron microscope. Electron-transparent samples of NF616 and HCM12A were irradiated in situ at the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory with 1 MeV Kr ions to ~10 dpa at temperatures ranging from 20 to 773 K. The microstructure evolution of NF616 and HCM12A was followed in situ by systematically recording micrographs and diffraction patterns as well as capturing videos during irradiation.

In these irradiations, there was a period during which no changes are visible in the microstructure. After a threshold dose (~0.1 dpa between 20 and 573 K, and ~2.5 dpa at 673 K) black dots started to become visible under the ion beam. These black dots appeared suddenly (from one frame to the next) and are thought to be small defect clusters (2-5 nm in diameter), possibly small dislocation loops with Burgers vectors of either $\frac{1}{2}<111>$ or $<100>$. The overall density of these defect clusters increased with dose and saturated around 6 dpa. At saturation, a steady-state is reached in which defects are eliminated and created at the same rates so that the defect density is constant. After saturation, defects constantly
appeared and disappeared in a time that is shorter than the time in between frames (normally 34 ms).

The average diameter and size distribution of the irradiation-induced defect clusters did not vary with dose during a single irradiation in the temperature range of 50 to 573 K in NF616, and 20 to 673 K in HCM12A. At 673 K, the defects in NF616 grew and coalesced under irradiation which led to larger average defect sizes and low defect density. At high doses extended defect structures in NF616 formed as short segments aligned along 100 directions.

At 773 K, the frequency of defect formation per unit area was the lowest amongst all irradiations and all the visible defect clusters that formed eventually faded out gradually (in ~28 seconds) leading to no net defect accumulation in NF616 even at the highest irradiation dose of 10 dpa.

Under irradiation, a significant fraction of these defect clusters exhibited sudden one-dimensional jumps (over ~5nm) between 20 and 573 K, that is, some defect clusters move “or jump” along <211> directions which is consistent with the expected Burgers vector direction of (111). Interestingly, at 673 and 773 K, defects in NF616 and HCM12A did not exhibit the sudden jumps and jerks that were frequently observed during lower temperature irradiations.

No resolvable loops, voids or precipitates were formed in NF616 and HCM12A. Furthermore, no significant interaction of the irradiation induced defects with the foil surface, pre-existing dislocation network or grain boundaries was observed between 20 and 773 K.

A simplified rate theory model was developed to describe the initial defect formation processes. The model is based on the reactions between intra-cascade clusters driven by the one-dimensional movement of sub-visible interstitial clusters in their glide cylinder under irradiation after detrapping from interstitial and substitutional solute atoms by cascade impact. Multiple cascade impacts on previously existing clusters allow them to gather clusters during their glide, leading to the formation of TEM-visible (~2 nm) defects. The low dose defect
density approximated by model is in good agreement with the experimental results. In addition, the model rationalizes the threshold dose before which no visible defect clusters were formed.
TABLE OF CONTENTS

LIST OF FIGURES ................................................................................................................. ix

LIST OF TABLES .................................................................................................................. xvi

ACKNOWLEDGEMENTS ........................................................................................................ xvii

Chapter 1  Introduction ........................................................................................................... 1
  1.1  Motivation for the work ................................................................................................. 1
  1.2  Background information on ferritic-martensitic steels .............................................. 4
    1.2.1  Development of ferritic-martensitic steels for conventional power generation industry ................................................................. 4
    1.2.2  Physical metallurgy and constitution of ferritic-martensitic steels .......... 6
    1.2.3  Ferritic-martensitic alloys for future fission and fusion nuclear applications ...................................................................................... 11
  1.3  Goals of the study and approach .................................................................................. 26
    1.3.1  Goals of the study ................................................................................................. 26

Chapter 2  Experimental Procedures ...................................................................................... 29
  2.1  Materials ....................................................................................................................... 29
  2.2  Characterization of the as-fabricated microstructure .................................................. 33
    2.2.1  Sample preparation ............................................................................................... 33
    2.2.2  Microstructure of the alloys ................................................................................. 34
  2.3  In situ irradiation experiment ....................................................................................... 38
    2.3.1  IVEM-TANDEM facility at Argonne National Laboratory ............................... 39
    2.3.2  Characterization of radiation damage using TEM .............................................. 40
2.3.3 Experimental method................................................................. 43
2.3.4 Simulation of primary damage using SRIM software ................. 44

Chapter 3  Microstructural evolution of NF616 and HCM12A under irradiation.... 50
3.1 General Observations in the low temperature regime (20-573 K)......... 51
3.1.1 Initial Defect formation in NF616 and HCM12A ...................... 52
3.1.2 Defect accumulation in NF616 and HCM12A between 20 and 573 K . 63
3.1.3 Defect motion in NF616 and HCM12A between 20 and 573 K ......... 79
3.2 General Observations at elevated temperatures (673-773K)........... 88
3.2.1 Microstructure evolution in NF616 and HCM12A at 673 K.......... 89
3.2.2 Microstructure evolution in NF616 at 773 K ............................. 99
3.3 Comparison of the microstructural evolution in NF616 and model alloy. 105
3.4 Discussion..................................................................................... 111

Chapter 4  Modeling of primary defect formation and accumulation .......... 125
4.1 Summary of previous studies on primary damage formation in Fe....... 126
4.2 Model of Defect Accumulation According to Experimental Observations 128
4.2.1 Simplified model of defect accumulation................................. 130
4.2.2 Evaluation of the minimum number of interstitials in a visible cluster 131
4.2.3 The primary damage................................................................. 131
4.3 Calculation of rate of formation of visible defect clusters ............... 136
4.4 Results ....................................................................................... 140

Chapter 5  Conclusions and future work ............................................. 145
5.1 Summary and conclusions............................................................. 145
5.2 Recommendations for future work

REFERENCES
LIST OF FIGURES

Figure 1-1 The displacement damage and operating temperature regimes for structural materials in current fission (GEN II), proposed fission (GEN IV) and fusion energy systems. Six GEN IV reactor system concepts are SFR, MSR, LFR, GFR, VHTR and SCWR [5]. ........................................ 3

Figure 1-2 Evolution of F-M steels developed for power plants (Reproduced from [8]). .................... 5

Figure 1-3 Fe-Cr-0.1C pseudobinary phase diagram (Reproduced from [4]). ................................. 7

Figure 1-4 SEM image of normalized and tempered NF616 steel [10] ............................................. 10

Figure 1-5 Bright field TEM image of normalized and tempered NF616 steel. Large precipitates on grain boundaries were reported to be M23C6 [9]. ......................................................... 10

Figure 1-6 Schematic of the F-M microstructure observed in NF616 and HCM12A. ......................... 11

Figure 1-7 Typical 1 keV (a,c) and 20 keV (b,d) cascade structure. (a) and (b) show peak damage whereas (c) and (d) show the stable defect structure [15]. ......................................................... 16

Figure 1-8 Interstitial (left) and vacancy (right) type prismatic loops with perfect Burgers vectors [3]. 16

Figure 1-9(a) Swelling rate of austenitic (316) and F-M steels (b) Photograph of austenitic 316 steel in unirradiated and irradiated (1.5x1023 nm2 at 533 °C) condition (Reproduced from [4] and [25]). ......................................................................................... 22

Figure 1-10 Yield stress and ultimate tensile strength of normalized-and-tempered, aged, and irradiated 9Cr steels. Temperature and duration of thermal aging was approximately equal to the irradiation time in reactor [4]. ......................................................................................................................... 22

Figure 1-11 1-D motion of an isolated interstitial loop at 575 K [32]. ................................................. 24

Figure 1-12 BF TEM images of extended defect structures that form in high purity Fe and Fe-8Cr alloys at temperatures of interest [26]. ......................................................................................... 25

Figure 2-1 Schaeffer-Schneider diagram for NF616 and HCM12A alloys (Modified from [36]). ..... 33

Figure 2-2 Optical microscopy images of NF616 and HCM12A showing the tempered martensite microstructure. .................................................................................................................. 35

Figure 2-3 SEM images of prior-austenite grains and the lath structure observed in NF616 and HCM12A. .................................................................................................................. 36
Figure 2-4 Bright field TEM images of elongated laths (top) and the dislocation structure in weakly recovered laths in NF616 and HCM12A (bottom). .................................................................36

Figure 2-5 (a,b) Optical microscopy images of NF616 and model alloy showing the tempered martensite microstructure (c,d) Secondary electron SEM images of prior-austenite grains and the lath structure in the NF616 and model alloy (e,f) Bright field TEM images of elongated lath structure inside prior-austenite grains of NF616 and model alloy. ........................................38

Figure 2-6 (a) Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory and (b) the illustration of the sample area in the microscope [39]. .................................................................40

Figure 2-7 (a) Strong two-beam, (b) s-positive two-beam diffraction conditions used in diffraction-contrast imaging of defects. The curvature of the Ewald sphere is exaggerated for clarity. The open circle represents the objective aperture [40]. .................................................................41

Figure 2-8 DF TEM images of neighboring martensite laths in NF616 imaged with g=<110> (red dots mark the boundary between laths). ........................................................................43

Figure 2-9 SRIM simulation of the interaction of a single 1 MeV Kr ion with the 1000 angstrom thick NF616 foil. Longitudinal and lateral views of the path of the ion (red dots) and the displacements caused (green dots) are shown .................................................................48

Figure 2-10 Damage production cross-section for the 1 MeV Kr irradiation of NF616 calculated by using SRIM. The number of target displacements per ion per angstrom is plotted across the thickness of the sample. ........................................................................49

Figure 3-1 DF TEM image of the initial microstructure of NF616 before irradiation at 298 K. Pre-existing dislocation segments are marked with arrows and the monitored grain is highlighted by dotted line. ........................................................................................................54

Figure 3-2 DF TEM image of NF616 irradiated to 0.001 dpa with 1 MeV Kr ions at 298 K. ..............55

Figure 3-3 DF TEM image of NF616 irradiated to 0.01 dpa with 1 MeV Kr ions at 298 K. ..............55

Figure 3-4 DF TEM image of NF616 irradiated to 0.1 dpa with 1 MeV Kr ions at 298 K. Insets of figures show the close up view of the defect clusters. .................................................................56

Figure 3-5 DF TEM image of NF616 irradiated to 1 dpa with 1 MeV Kr ions at 298 K. Insets of figures show the close up view of the defect clusters. .................................................................56
Figure 3-6 DF TEM images showing the appearance of a defect cluster between consecutive video 
frames (A and B (in 67 ms)) in NF616 irradiated to 0.06 dpa at 298 K. Insets of figures show the 
close up view of the defect clusters. .................................................................58

Figure 3-7 TEM images showing the initial stages of defect accumulation in NF616 at 50, 298 and 
573 K. Insets of figures show the two-beam condition and the close up view of the defect clusters. ..60

Figure 3-8 TEM images showing the initial stages of defect accumulation in HCM12A at 20, 298 and 
573 K. Insets of figures show the two-beam condition and the close up view of the defect clusters. 
........................................................................................................................................61

Figure 3-9 DF TEM images showing the appearance of five defect clusters in NF616 between video 
frames (in 67 ms or less ) at 298 K. The upper video frames are seperated by 67 ms from those 
below. ........................................................................................................................................62

Figure 3-10 BF TEM images showing the appearance of five defect clusters in HCM12A between 
video frames (in 34 ms or less ) at 20 K. The upper video frames are seperated by 67 ms from those below. ........................................................................................................................................62

Figure 3-11 The appearance of defect clusters over several video frames in NF616 under 1 MeV Kr 
irradiation at 298 K. The upper video frames are seperated by 67 ms from those below. ..........63

Figure 3-12 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 50 
K. ........................................................................................................................................66

Figure 3-13 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 473 
K. ........................................................................................................................................67

Figure 3-14 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 573 
K. ........................................................................................................................................68

Figure 3-15 BF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 20 
K. ........................................................................................................................................69

Figure 3-16 DF TEM images of microstructure evolution of HCM12A under 1 MeV Kr Irradiation at 
573 K. ........................................................................................................................................69

Figure 3-17 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 50, 
473 and 573 K ..........................................................................................................................70
Figure 3-18 TEM images of microstructure evolution of HCM12A at 20 and 573 K and NF616 at 50 and 573 K under 1 MeV Kr Irradiation. 0 and 0.1 dpa images of HCM12A were inverted from DF to BF. ..........................................................................................................................71

Figure 3-19 The defect cluster areal density of NF616 as a function of dose at 50, 473 and 573 K. .....73

Figure 3-20 The average defect cluster size of NF616 as a function of dose at 50 K, 473 K and 573 K. .................................................................................................................................................73

Figure 3-21 Size distribution of defect clusters in NF616 irradiated with 1 MeV Kr ions at 50 K as a function of dose, using a bin size of 0.5 nm. The average diameter of defects is shown at each dose.................................................................................................................................................74

Figure 3-22 Size distribution of defect clusters in NF616 irradiated with 1 MeV Kr ions at 473 K as a function of dose, using a bin size of 0.5 nm. The average diameter of defects is shown at each dose.................................................................................................................................................75

Figure 3-23 Size distribution of defect clusters in NF616 irradiated with 1 MeV Kr ions at 573 K as a function of dose, using a bin size of 0.5 nm. The average diameter of defects is shown at each dose.................................................................................................................................................76

Figure 3-24 The irradiation-induced defect structure observed near the edge of the TEM foil in (a) NF616 (this study) and pure Fe [27, 28]. The red arrows shows the direction of the thickness gradient and marks 0.8μ on both images. ......................................................................................................................78

Figure 3-25 Video frames showing the characteristic sudden jumps of defects in NF616 irradiated to ~0.9 dpa with 1 MeV Kr ions at 373 K. red arrows point the initial position (t=0) of the defects in all images. ......................................................................................................................82

Figure 3-26 The successive video frames showing the close up view of the defects in NF616 irradiated to ~0.9 dpa at 373 K. Defect cluters that exhibit jumps are tagged with numbers and red arrows point the initial position (t=0) of the defects in all images. Yellow arrows point the stationary defects in the images......................................................................................................................83

Figure 3-27 The successive video frames showing the close up view of the defects in NF616 irradiated to ~1 dpa at 298 K. Defect cluters that exhibit jumps are tagged with numbers and red arrows point the initial position (t=0) of the defects in all images. Yellow arrows point the stationary defects in the images......................................................................................................................84
Figure 3-28 The successive video frames showing the close up view of the defects in HCM12A irradiated to ~4 dpa at 20 K. Defect clusters that exhibit jumps are tagged with numbers and red arrows point the initial position (t=0) of the defects in all images. Yellow arrows point the stationary defects in the images. ................................................................. 85

Figure 3-29 Jumps of three individual defect clusters observed in NF616 irradiated with 1 MeV Kr ions at 373 K. The average frequencies of defect jumps are noted on the plots. ....................... 87

Figure 3-30 Distribution of defect jump distances in NF616 irradiated with 1 MeV Kr ions at 373 K with a bin size of 1 nm. A total of 52 defects jumps were measured............................................. 88

Figure 3-31 BF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 673 K. .................................................................................................................. 93

Figure 3-32 BF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 673 K. .................................................................................................................. 94

Figure 3-33 The video frames showing the formation and coalescence of defect clusters in NF616 irradiated to ~5 dpa with 1 MeV Kr ions at 673 K. Red arrows point the position of the defects that are tagged with numbers. ................................................................. 95

Figure 3-34 BF TEM images of growth of a defect cluster from 6.8 nm to 19.6 nm over 39 s in NF616 irradiated to ~5 dpa with 1 MeV Kr ions. ................................................................. 96

Figure 3-35 Defect loss to the surface captured by video frames captured with 34 ms interval. Schematic illustration of the initial and final defect configuration is shown (the defect that was lost to the surface is shown in red). ........................................................................ 96

Figure 3-36 Aligned finger defects in (a) NF616 irradiated to 7.4 dpa at 673 K (b) UHP Fe irradiated to 6.5 dpa at 773 K (c) Fe-8%Cr irradiated to 6.5 dpa at 773 K. Note that all the BF TEM images were taken with 110-type g vectors. ........................................................................ 97

Figure 3-37 The defect cluster areal density of NF616 as a function of dose at 50, 473, 573 and 673 K. .................................................................................................................. 98

Figure 3-38 The average defect cluster size of NF616 as a function of dose at 50, 473, 573 and 673 K. .................................................................................................................. 98

Figure 3-39 The appearance of seven defect clusters between video frames (in 67 ms or less) at 773 K. .................................................................................................................. 102
Figure 3-40 The appearance of defect clusters over several video frames in NF616 under 1 MeV Kr irradiation at 773 K. ................................................................. 103

Figure 3-41 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 773 K. ................................................................. 104

Figure 3-42 Two-beam DF TEM images of the gradual disappearance of three defect clusters in NF616 at 773 K. ................................................................. 105

Figure 3-43 DF TEM images of microstructure evolution of NF616 (a-f) and model alloy (g-l) under 1 MeV Kr Irradiation at 50 K. ................................................................. 108

Figure 3-44 DF TEM images of microstructure evolution of NF616 (a-f) and model alloy (g-l) under 1 MeV Kr Irradiation at 473 K. Arrows indicate the resolvable dislocation loops in the model alloy. ................................................................. 109

Figure 3-45 DF TEM images of the interaction of irradiation induced defects with the lath boundary in NF616 and model alloy under 1 MeV Kr Irradiation at 573 K and 473 K, respectively. ............. 110

Figure 3-46 BF TEM images of the extended defects observed in NF616 and Model alloys under 1 MeV Kr Irradiation at 673 K, 298 K and 180 K, respectively. Arrows indicate approximate directions of defect alignment in NF616 and model alloy. ................................................................. 111

Figure 3-47 The threshold dose for defect accumulation of NF616 at 50, 473, 573, 673 and 773 K. ................................. 113

Figure 3-48 The average defect cluster size of NF616 measured at saturation dose at 50, 473, 573 and 673 K. ................................................................. 116

Figure 3-49 The saturation defect cluster areal density of NF616 at 50, 473, 573, 673 and 773 K. ................................. 117

Figure 3-50 The schematic representation of the mechanism for the defect cluster (red loop) motion observed below 673 K using the in situ TEM technique. The traps (solute atoms or complexes) are shown as yellow discs. ................................................................. 121

Figure 4-1 Comparison of defect survival values for cascades in perfect crystal and material with pre-existing defects (i and v denotes interstitial and vacancy, respectively) [15]. ......................... 128

Figure 4-2 SRIM simulation of a Kr ion travelling through the 100 nm-thick NF616 sample. Ion track and displacements created by the ion are highlighted by red and green dots, respectively. Inset shows close-up view of the sub-cascade structure. ................................................................. 132
Figure 4-3 Schematic illustration of an interstitial prismatic loop moving in its glide cylinder while interacting with the defects till it is trapped by the solute atom. Blue region is the attractive interaction volume between the interstitial cluster and the solute atom. .............................................. 139

Figure 4-4 The paths used to calculate formation rate of TEM-visible (80i) clusters. .......................... 140

Figure 4-5 The density of 20i, 40i and 60i as a function of irradiation time in NF616 irradiated with 1 MeV Kr ions. ........................................................................................................................................ 143

Figure 4-7 The density of TEM-visible defects (80i) as a function of irradiation time in NF616 irradiated with 1 MeV Kr ions. ........................................................................................................................................ 144
LIST OF TABLES

Table 1-1 List of candidate in-core materials for GEN-IV reactor systems. P= Primary option, S=
Secondary option (Data from [6]). ........................................................................................................2

Table 1-2 Composition of NF616 and HCM12A alloys provided by the manufacturer ....................5

Table 1-3 Precipitates that form in normalized-and-tempered, aged and creep rupture tested F-M steels
[4]. .........................................................................................................................................................9

Table 1-4 Sequence of events that start with the creation of a PKA [14]. ........................................15

Table 1-5 Comparison of neutron, ion and electron irradiation in metals ........................................19

Table 2-1 Composition of NF616 and HCM12A alloys ....................................................................32

Table 2-2 Nickel and chromium equivalents for NF616 and HCM12A alloys .................................32

Table 2-3 |g.b| values for foil normal n=[111] for loops of the types expected in NF616 and HCM12A
alloys ..................................................................................................................................................43

Table 2-4 Input and output data for the SRIM calculation of 1 MeV Kr irradiation of NF616 ...........47

Table 3-1 The lifetime of various defect clusters in NF616 irradiated at 773 K ............................105

Table 4-1 The energy distribution of PKAs for NF616 irradiated with 1 MeV Kr ions as calculated by
the SRIM code ..................................................................................................................................133

Table 4-2 Fractions of cascade-surviving point defects contained in small interstitial (1 to 20-member)
and vacancy (1 to 9-member) clusters and survival efficiency of point defects, for four different
cascade energy intervals (data from [57]). The energy distribution of PKAs was calculated using
SRIM. ....................................................................................................................................................135

Table 4-3 Average number of interstitial clusters produced in cascades with the given PKA energies
(data from [57]). The energy distribution of PKAs was calculated using SRIM ............................136

Table 4-4 Rate of formation of 20i clusters and the parameters used in calculation .........................137

Table 4-5 Calculation of rate constant (k) and the parameters used in calculation ...........................139
ACKNOWLEDGEMENTS

First and foremost, I would like to thank my thesis adviser, Dr. Arthur T. Motta, for the continuous support and guidance during my years at Penn State. This has been a great learning experience in many ways. Thank you for being a true mentor in guiding me through my thesis work in a way that allowed me to take control of my project.

I would like to thank Dr. Brian D. Wirth for the insightful discussions and suggestions which greatly improved my understanding of my project. Thank you for always finding time to help and making the trip to State College for my defense despite your busy schedule. I would also like to thank his students, Nathan Capps and Aaron Kohnert for their collaboration on the modeling part.

I would like to acknowledge Dr. Zi-Kui Liu, Dr. Clifford Lissenden and Dr. Clive A. Randall. Thank you for your willingness to serve on my thesis committee, and for all of your helpful discussions and feedback.

I would like to thank Dr. Mark Kirk for his guidance in planning and conducting irradiation experiments at Argonne National Laboratory. I feel grateful to have the opportunity to benefit from his priceless experience on the in situ irradiation technique. I would also like to thank Pete Baldo and Ed Ryan of the Argonne National Laboratory for their assistance in running in situ irradiation experiments.

At Penn State, I would like to thank all the past and present members of the Materials for Nuclear Power Group for their help and friendship in and out of the lab. There are too many names to mention separately but I express heartfelt thanks for all of you.

I would like to thank Chris Ulmer for his help for irradiation experiments and for allowing me to use his code for organizing SRIM data.
To my mother and father, Filiz and O. Doğan Topbaşı
Chapter 1

Introduction

1.1 Motivation for the work

Increasing demand for more and cleaner energy in the world draws attention to the next generation fission and fusion nuclear energy systems. These revolutionary concepts offer waste minimization, improved economics, and higher safety standards [1]. Although considerable improvements have been made in fusion energy technology in recent years, key plasma physics issues need to be resolved for nuclear fusion energy systems to be a viable commercial power source. On the other hand, nuclear fission energy systems have proven to be an increasingly reliable source of electricity in the world.

Average capacity factors for U.S. fission reactors increased from 58.6 to 89.6% from 1974 to 2012, in part due to improvements in fuel cladding materials, steam generator and water chemistry control which decreased fuel failure rates [2]. To further improve the efficiency of nuclear systems revolutionary concepts are needed. Six fission energy system concepts that were identified by the U.S. Department of Energy and the Generation IV International Forum are currently under development to enable significant improvements in safety, efficiency, and proliferation resistance [1].

The high energy neutrons produced in the core of fusion and fission reactors have enough energy to displace atoms of structural materials from their lattice sites, thus creating Frenkel pairs (self-vacancy and interstitial pairs), as well as interstitial and vacancy type defect clusters [3]. The damage level in an irradiated material can be specified in terms of displacements per atom (dpa). (1 dpa corresponds to an average of single displacement of all
the atoms in the material from their lattice sites). Only a small fraction of the irradiation induced defects survives the initial cooling of the cascade. The surviving defects can undergo thermally activated recombination and annihilation of these defects at sinks such as grain boundaries, precipitates, and pre-existing dislocations. The interaction of the defects with the pre-existing microstructure can produce significant changes in the properties of structural materials used in nuclear reactors such as: radiation hardening and embrittlement, phase instabilities from radiation-induced precipitation, irradiation creep, high temperature He embrittlement, and volumetric swelling from void formation; all of which can potentially limit the fuel cladding lifetime [4].

Next generation fission and fusion energy systems are planned to operate at considerably higher temperatures and doses compared to the current fission energy systems [5]. The performance of the structural materials under these demanding conditions is crucial in determining the viability of the proposed fusion and fission energy systems.

Several candidate materials have been proposed by the Generation IV International Forum for structural applications in the next generation fission energy systems (GEN IV). Table 1.1 shows the primary and secondary options for candidate materials in the Gas-Cooled Fast Reactor (GFR), Lead-cooled Fast Reactor (Pb-LFR), Molten Salt Reactor (MSR), Supercritical Water Reactor (SCWR), Very High Temperature Reactor (VHTR) and Sodium Fast Reactor (SFR) [6]. Ferritic-Martensitic (F-M) steels are primary options as candidate materials for nuclear fuel cladding for most of these concepts.

<table>
<thead>
<tr>
<th>Reactor system</th>
<th>F–M steel</th>
<th>Austenitic S.S.</th>
<th>ODS steel</th>
<th>Ni-base alloys</th>
<th>Graphite</th>
<th>Refractory alloys</th>
<th>Ceramics</th>
</tr>
</thead>
<tbody>
<tr>
<td>GFR</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>_</td>
<td>P</td>
<td>P</td>
</tr>
<tr>
<td>Pb-LFR</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td>_</td>
<td>_</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>MSR</td>
<td>–</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>SFR</td>
<td>P</td>
<td>P</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>SCWR</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td>_</td>
<td>_</td>
<td>_</td>
<td>_</td>
</tr>
<tr>
<td>VHTR</td>
<td>S</td>
<td>_</td>
<td>_</td>
<td>P</td>
<td>P</td>
<td>S</td>
<td>P</td>
</tr>
</tbody>
</table>

Table 1-1 List of candidate in-core materials for GEN-IV reactor systems. P= Primary option, S= Secondary option (Data from [6]).
F-M steels are also candidate structural materials for future fusion energy system concepts, as first wall and blanket materials in future fusion concepts due to their high irradiation induced void swelling resistance, good microstructural stability, and good thermal properties (expansion coefficient and conductivity) [1, 4]. Operating conditions for F-M steels in these applications are envisioned to be at high temperatures (300-600 °C) and high levels of radiation damage (100-200 dpa), as shown in Figure 1-1 [5].

![Figure 1-1 The displacement damage and operating temperature regimes for structural materials in current fission (GEN II), proposed fission (GEN IV) and fusion energy systems. Six GEN IV reactor system concepts are SFR, MSR, LFR, GFR, VHTR and SCWR [5].](image)

NF616 (ASTM code: P92) and HCM12A (ASTM code: T122) are Third-Generation F–M steels that were originally developed for non-nuclear applications in power generation industry as boiler and turbine materials [4]. NF616 and HCM12A alloys exhibit improvements in creep rupture strength and maximum operation temperatures compared to the previous generations of F-M steels, which makes them promising candidates for in-core applications in SFR and fusion reactor concepts as detailed in Table 1-1 [7]. The properties of
these steels under non-nuclear conditions are well understood, however fundamental aspects of radiation damage in these complex F-M steels need further investigation.

This study shows the results of a systematic research project designed to investigate irradiation induced microstructural evolution in NF616 and HCM12A alloys that may limit the viability of SFR and next generation fusion energy systems. The approach is to develop a fundamental understanding of the radiation damage mechanism in complex F-M steels being considered for in-core applications by using well-controlled in situ heavy ion irradiation experiments coupled with numerical simulation.

1.2 Background information on ferritic-martensitic steels

1.2.1 Development of ferritic-martensitic steels for conventional power generation industry

High-chromium F-M steels were originally developed as boiler and turbine materials in the power generation industry. The original F-M steels were based on Fe-(9-12 %Cr) compositions. Figure 1-2 shows the improvements achieved over the years in creep rupture strength and maximum operation temperatures of F-M steels with alloying. NF616 (9Cr nominal alloy) and HCM12A (12Cr nominal alloy) have increased high temperature strength and maximum operating temperatures over second generation F-M steels, T91 and HT-9, as shown in Figure 1-2. These alloys achieve this through partial substitution of W for Mo and addition of Cu and B. Further improvements in strength were established in fourth generation of F-M steels, NF12 and SAVE12 alloys, by increasing the W and Co concentration in NF616 and HCM12A alloys [4]. The composition of NF616 and HCM12A alloys, as provided by the manufacturer, is given in Table 1-2. Increasing maximum operating temperatures significantly improved the efficiency and reduced the environmental impact of power plants [4].
Table 1-2 Composition of NF616 and HCM12A alloys provided by the manufacturer.

<table>
<thead>
<tr>
<th>Element</th>
<th>NF616 (wt%)</th>
<th>HCM12A (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.109</td>
<td>0.11</td>
</tr>
<tr>
<td>Chromium</td>
<td>8.82</td>
<td>10.83</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.102</td>
<td>0.27</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.0012</td>
<td>0.016</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.194</td>
<td>0.19</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.45</td>
<td>0.64</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.174</td>
<td>0.39</td>
</tr>
<tr>
<td>Niobium</td>
<td>0.064</td>
<td>0.054</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.468</td>
<td>0.3</td>
</tr>
<tr>
<td>Tungsten</td>
<td>1.87</td>
<td>1.89</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-</td>
<td>0.063</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.005</td>
<td>0.001</td>
</tr>
<tr>
<td>Copper</td>
<td>-</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Figure 1-2 Evolution of F-M steels developed for power plants (Reproduced from [8]).
1.2.2 Physical metallurgy and constitution of ferritic-martensitic steels

The primary components of F-M steels are Fe, Cr and C; however interstitial (C, N) and substitutional (Mo, Mn, Cu) solute atoms are added to tailor the properties of the alloys. 9-12Cr F-M steels are produced by high temperature normalizing heat treatment followed by relatively low temperature tempering. At normalizing temperatures (850 to 1200 °C), the alloy microstructure can be ferritic, austenitic or a mixture of both, depending on the composition of the alloy [4]. After normalization, the alloy is air cooled or quenched to room temperature. During cooling, a martensitic transformation takes place whereby austenite transforms to martensite; however delta-ferrite present at high temperatures remains untransformed upon cooling. Figure 1-3 shows the Fe-rich part of the Fe-Cr phase diagram with 0.1% C [4]. It is evident from Figure 1-3 that single phase austenite can be present at normalizing temperatures when Cr content is less than ~12% in Fe-Cr-0.1C alloys. Nevertheless, the single phase austenite region in the phase diagram can be expanded by addition of austenite-stabilizing elements (C, N, Ni, Mn, Cu and Co) and contracted by ferrite-forming elements (Cr, Mo, Nb, V, W, Si, Ti and Al). Because the retained delta ferrite is found to adversely affect strength and toughness of the alloys, the compositions of the 9-12Cr F-M steels are generally designed to obtain fully austenite structure at the normalizing temperature. On the other hand ferrite-forming elements are introduced in the alloy to increase the corrosion resistance [4].
Following normalization treatment and cooling, the alloy is tempered below the ferrite to austenite transformation temperature (around 700 °C) to establish an optimal combination of strength and toughness. Tempering promotes precipitation by increasing the diffusion rate of C and other alloying elements that were initially trapped in the parent austenite phase. Although $\text{M}_2\text{C}_3$ is the main carbide that forms in 9-12 Cr F-M steels, smaller quantities of other carbides, nitrides and Laves phases can form during quenching and tempering [4]. Furthermore, the formation of new phases and changes in the fraction and composition of the existing phases may take place during aging and/or creep straining. Various precipitates observed in normalized-and-tempered, aged, and creep-rupture tested F-
M steels are listed in Table 1-3 [4]. In addition, reduction in the density of dislocations and formation of sub-grain structures occur inside the martensite laths during tempering [4].

Generally, the normalized and tempered 9-12 Cr F-M steels have the typical tempered martensite microstructure. Figures 1-4 and 1-5 show transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of austenized-and-tempered NF616 alloy [8, 9]. Figure 1-4 shows the large prior austenite grains and the fine lath structure within. Figure 1-5 shows sub-grains formed within the elongated martensite laths. The average martensite lath width in NF616 is between 0.37 to 0.50µ, depending on the tempering temperature [8]. A Finer lath structure is reported to improve creep rupture strength of NF616 without any loss of toughness [10].

Figure 1-6 shows a schematic of the representative tempered martensite structure observed in NF616 and HCM12A: sub-cells within the elongated martensite laths with a high density of pre-existing dislocations present a fine and complex microstructure.
Table 1-3 Precipitates that form in normalized-and-tempered, aged and creep rupture tested F-M steels [4].

<table>
<thead>
<tr>
<th>Precipitate Phase</th>
<th>Crystal Structure and Lattice Parameter</th>
<th>Typical Composition</th>
<th>Distribution of Precipitates</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$_{23}$C$_6$</td>
<td>fcc</td>
<td>(Cr$_{16}$Fe$_8$Mo)$_6$C$_6$</td>
<td>Coarse particles at prior austenite grain and martensite lath boundaries and fine intra-lath particles</td>
</tr>
<tr>
<td></td>
<td>a = 1.066 nm</td>
<td>(Cr$<em>{16}$Fe$</em>{10}$Mo$_6$Si$_2$W)$_6$C$_6$</td>
<td></td>
</tr>
<tr>
<td>MX</td>
<td>f.c.c.</td>
<td>NbC, NbN, VN, (CrV)N, Nb(CN) and (NbV)C</td>
<td>Undissolved particles and fine precipitates at martensite lath boundaries</td>
</tr>
<tr>
<td>M$_2$X</td>
<td>Hexagonal</td>
<td>Cr$_2$N, Mo$_7$C and W$_7$C</td>
<td>Martensite lath boundaries (Cr$_2$N and Mo$_7$C); prior austenite grain boundaries (Mo$_7$C); intra-lath (Mo$_7$C and W$_7$C); $\delta$-ferrite in duplex steels [Cr$_2$(CN) and (CrMo)$_2$(CN)]</td>
</tr>
<tr>
<td></td>
<td>a = 0.478 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 0.444 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Z-phase</td>
<td>Tetragonal</td>
<td>(CrV Nb)$_2$N</td>
<td>Large plate-like particles in the matrix after creep straining at 600°C</td>
</tr>
<tr>
<td></td>
<td>a = 0.286 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 0.739 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\eta$-carbide</td>
<td>Diamond cubic</td>
<td>M$<em>6$C (Fe$</em>{10}$Cr$_7$Mo$<em>6$Si$</em>{16}$)C</td>
<td>Prior austenite grain and martensite lath boundaries and intra-lath</td>
</tr>
<tr>
<td></td>
<td>a = 1.07-1.22 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vanadium carbide</td>
<td>f.c.c.</td>
<td>V$_{2}$C$_3$</td>
<td>Low number density in matrix</td>
</tr>
<tr>
<td></td>
<td>a = 0.420 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laves</td>
<td>Hexagonal</td>
<td>Fe$_2$Mo, Fe$_2$W and Fe$_4$(MoW)</td>
<td>Prior austenite grain and martensite lath boundaries and intra-lath; $\delta$-ferrite in duplex steels</td>
</tr>
<tr>
<td></td>
<td>a = 0.4744 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = 0.7725 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chi ($\chi$)</td>
<td>b.c.c.</td>
<td>M$<em>{18}$C or Fe$</em>{35}$Cr$<em>{12}$Mo$</em>{15}$C</td>
<td>Intra-martensite lath; $\delta$-ferrite in duplex steels</td>
</tr>
<tr>
<td></td>
<td>a = 0.892 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 1-4 SEM image of normalized and tempered NF616 steel [10]

Figure 1-5 Bright field TEM image of normalized and tempered NF616 steel. Large precipitates on grain boundaries were reported to be M$_{23}$C$_6$[9].
1.2.3 Ferritic-martensitic alloys for future fission and fusion nuclear applications

Because F-M alloys are being evaluated as core components in sodium cooled fast breeder reactors and potential first wall and breeding blanket materials in fusion energy systems, it is necessary to consider radiation damage. In nuclear fission reactors, neutrons are created by the fission of uranium, whereas in future fusion reactors using deuterium and tritium as nuclear fuel, the neutrons are a product of the deuterium-tritium fusion reactor.

The interaction of the energetic particles originating from fission and fusion reactions with the atoms of the metallic structures may result in transmutation (the change of an atom of one element into atoms of another element), creating elements such as He or increasing the content of higher Z chemical species. In addition energetic particles cause displacement of atoms from their stable positions in the crystalline lattice, thus creating lattice defects. Understanding the fate of these defects is crucial in understanding the microstructure changes experienced by these materials during irradiation. Fusion and fission nuclear energy systems require steels that are resistant to irradiation induced by bombardment from high energy...
neutrons (typically 2 MeV in fission and 14 MeV in fusion) as well as to maintain adequate toughness and strength during service.

The functional lifetime of the structural materials in future fission and fusion nuclear energy systems are determined by the changes in mechanical property and dimensional stability of these materials under operating conditions.

The operation window for F-M alloys in fusion and fission energy systems (Figure 1-1) is determined mainly by radiation embrittlement, irradiation creep, radiation-induced void swelling and compatibility with operating media (i.e water, liquid lithium, liquid sodium, etc.) and high temperature He embrittlement. These property changes are directly related to the evolution of the initial microstructure under irradiation such as defect clustering, solute atom-defect interactions, enhanced diffusion and interaction with the pre-existing microstructure (dislocations, precipitates, grain boundaries).

1.2.3.1 Basics of radiation damage

The primary microscopic events that result from the interaction of radiation with solid are termed radiation damage. The types of radiation that can cause radiation damage include neutrons, ions, electrons and gamma rays, all of which have the potential to displace atoms from their lattice sites with different probabilities. The observable and potentially detrimental changes in properties of metals resulted from the exposure of solids to energetic particles are known as radiation effects [11].

Table 1-4 summarizes the sequence of events that occur under irradiation upon the impact of an energetic particle to the solid [12]. The energy transfer from the incident particle to the target solid atom takes place in $\sim 10^{-3}$ picoseconds [12]. The first atom displaced by the high-energy particle is called the primary knock-on atom (PKA). The PKA recoils with a certain amount of kinetic energy that is lost in a series of collisions with other atoms in the lattice.
The minimum energy required to displace the atoms enough so that they do not return to their initial site is the displacement threshold energy \( (E_d) \). \( E_d \) depends on the crystallographic direction of the displacements since the distance that atom needs to travel in the lattice changes is different in directions. Because of the intrinsic uncertainties of displacement energy measurements and calculations, it is customary to use an average displacement energy on the order of 20-40 eV for many metals [11, 13, 14].

When the PKA energy is high, the number of atoms in a small region take part in the dissipation of energy is such that the very notion of crystalline lattice becomes difficult to define. As the PKA energy is divided between many atoms, a displacement cascade is formed. The region near the cascade also experiences a thermal spike (rise in temperature locally). Molecular dynamics simulations of displacement cascades show that the displacement cascade is in the form of a molten drop during the first few picoseconds [14]. This is followed by the cascade cool down to bulk temperatures and the formation of the final damage state containing a certain number of point defects and point defect clusters. Figure 1.7 displays the results of a molecular dynamics simulation of such a dissipation process at the end of a displacement cascade in iron. The peak damage state and stable defect configuration of 1 keV and 20 keV cascades in iron are shown in Figure 1.7 [14]. The number of point defects produced in the 20 keV cascade is significantly larger, as shown in Figure 1.7.

The FPs, and interstitial and vacancy clusters form in high energy displacement cascades initially accumulate in the lattice. However, because of the close proximity in which these defects are created, they interact with each other, creating defect clusters and/or restoring the undamaged lattice. Recombination of defects causes the final number of interstitials and vacancies to be smaller than the total number of atoms displaced in the cascade. The final damaged state consists of an inhomogeneous distribution of interstitial and vacancy clusters of different sizes. Because the interstitials are energetic atoms, they are expelled from the center of the cascade through replacement collision sequences, and a
vacancy-rich core forms along with an interstitial rich outer rim. This spatial separation between interstitials and vacancies enhances defect clustering, relative to recombination. Figure 1.7 shows the spatial separation of interstitials and vacancies in the stable defect configuration of 1 and 20 keV cascades.

According to the molecular dynamics simulations, the fraction of point defects in clusters increases with cascade energy. In addition high energy cascades exhibit subcascade formation, where the cascade splits up into a group of lower energy subcascades. This phenomenon is more prominent at higher PKA energies. Figure 1-7 shows the peak damage of 20 keV cascade which appears to consist of smaller, lower energy cascades that are smaller whereas 1 keV cascade is in one piece and does not exhibit any subcascade formation.

The depleted zone in the core of high energy cascades can collapse to form vacancy clusters. On the other hand, the mechanism for the formation of intra-cascade interstitial clusters has not been fully established [14]. It is not clear whether the migration and accumulation of interstitials and their clusters during the lifetime of the displacement cascade contribute to the creation of detectable interstitial clusters.

The initial damage in Fe observed by TEM appears as unresolvable white dots in dark-field TEM images and is assumed to consist of nanometer-sized defect clusters, the nature of which is not known (dislocation loops or 3-d clusters, and whether vacancy or interstitial).

The interstitial and vacancy clusters can collapse to form prismatic dislocation loops in bcc Fe, and vacancies can form small voids. Prismatic loops can be visualized as discs formed by aggregation of interstitials or vacancies between lattice planes. Figure 1-8 shows a schematic of the stacking sequence of planes in bcc Fe with the prismatic interstitial and vacancy loops in the middle. The dislocation loops that form in bcc Fe have a perfect Burgers vector, which designates the atomic displacement of the lattice and retains the ABAB stacking sequence in bcc Fe. The perfect Burgers vector configurations in bcc Fe are $\mathbf{b} =$
\( \mathbf{a}_0 <100> \) loops on \( \{100\} \) habit planes and \( \overrightarrow{b} = \frac{1}{2} \mathbf{a}_0 <111> \) loops on \( \{111\} \), where \( \mathbf{a}_0 \) is the lattice parameter.

The mobile defects that escape their collision cascades thermally diffuse through the lattice. These defects may encounter each other, either forming larger defect clusters or annihilating each other. In addition they can be eliminated or captured at pre-existing microstructural features such as dislocations, grain boundaries and solute atoms.

These interactions determine the irradiation effects, i.e., the long-term interactions of defects with the microstructure leading to microstructure changes (segregation, precipitation, dissolution, formation of extended defect structures) and macroscopic effects (void swelling, embrittlement, hardening).

<p>| Table 1-4 Sequence of events that start with the creation of a PKA [14]. |</p>
<table>
<thead>
<tr>
<th>Duration (ps)</th>
<th>Event</th>
<th>Result</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>10^4</td>
<td>Transfer of energy from energetic particle</td>
<td>Primary knock on atom (PKA)</td>
<td>( \sigma(E_n,E) )=cross section for particle energy ( E_n ) to transfer of energy ( E )</td>
</tr>
<tr>
<td>10^4 to 0.2</td>
<td>Slowing down of PKA, generation of a displacement cascade and thermal spike</td>
<td>Recoil atoms and Lattice Vacancies Formation of subcascades</td>
<td>( E_d )=displacement energy ( \nu_{\text{NRT}} )=number of displaced atoms ( T )=energy transferred to recoils</td>
</tr>
<tr>
<td>0.2-3.0</td>
<td>Thermal spike cooldown</td>
<td>Stable Interstitials (SIA) Interstitial clusters Atomic mixing</td>
<td>( \nu(T) )=number of stable point defects ( f )=clustering fraction for cluster size ( j )</td>
</tr>
<tr>
<td>3-10</td>
<td>Cascade cooling to bulk solid temperature</td>
<td>Depleted zone in cascade core</td>
<td>Vacancy loop collapse probability</td>
</tr>
<tr>
<td>&gt; 10</td>
<td>Thermal migration of defects and interaction with sinks</td>
<td>Microstructure evolution (segregation, precipitation, dissolution, hardening, dislocation loop formation, etc..) leading to radiation effects (swelling, embrittlement, hardening, etc.)</td>
<td>( T_{ir} )=irradiation temperature ( E_{mi} )=migration energy for point defect ( i, i=\text{SIA, vacancy.} ) ( K_i )=strength of sink ( j ) for defect ( i ) ( FMD )=Fraction of defects free for long-range migration.</td>
</tr>
</tbody>
</table>
Figure 1-7 Typical 1 keV (a,c) and 20 keV (b,d) cascade structure. (a) and (b) show peak damage whereas (c) and (d) show the stable defect structure [15].

Figure 1-8 Interstitial (left) and vacancy (right) type prismatic loops with perfect Burgers vectors [3].
Defect Production

Since the subsequent microstructural evolution under irradiation depends on the actual number of defects and defect clusters created, it is necessary to estimate the total number of displacements that occur in displacement cascades [11]. Kinchin and Pease [15] were the first to develop a model to estimate the number of displacements generated under irradiation and a modified version of this model, the Norgett–Robinson–Torrens (NRT) model [16] has become the industry standard for the calculation of the number of atomic displacements. According to the NRT model, the number of FPs, $n_{NRT}(E)$, generated by a PKA of energy $E$ is given by

$$n_{NRT}(E) = 0.8 \frac{E}{2E_d}$$  \hspace{1cm} 1-1

where $E_d$ is the displacement threshold energy.

The NRT model does not take into account the variation of displacement energy with crystalline orientation. Nevertheless, it gives an estimate of the total number of atoms displaced by a PKA and provides a useful basis for modeling and comparison.

The damage rate in materials irradiated under different conditions (such as particle type and energy) can be quantified in terms of displacement per atom (dpa) per second, which is essentially the volumetric displacement (displacements per unit volume per second) divided by the atom density:

$$dpa = \int \int n_{NRT}(E)\phi(E_n)\sigma(E_n, E) \ dE \ dE_n \ dt$$  \hspace{1cm} 1-2

where $\phi(E_n)$ is the particle flux and $\sigma(E_n, E)$ is the probability that a particle of energy $E_n$ will scatter elastically and impart a recoil energy $E$ to a struck atom.
The dpa calculated by the NRT formula can be used to compare the level of the radiation damage in a material irradiated by various sources since it is independent of the radiation environment [11].

Nevertheless, dpa only estimates the total numbers of atoms involved in the displacement cascade even though the spatial distribution and number of freely-migrating defects and their clusters are important parameters to investigate radiation damage.

1.2.3.2 Investigation of radiation damage in ferritic-martensitic steels

Since the 1970s, many reactors around the world have been used to irradiate candidate materials for next generation fission and fusion energy systems. Performing irradiations in nuclear reactors involves complications such as space and time limitations, and difficulties in temperature control. The irradiated samples were subsequently subjected to mechanical testing and/or microstructural investigations to study the effects of irradiation. In addition to neutron irradiation, electrons, light ions (p, d, α) and heavy ions (self-ions or heavier) are also used to investigate the radiation damage in materials. These methods are widely available in electron microscopes and accelerators worldwide [4, 17]. Table 1-5 summarizes the properties of fast neutron, ion and electrons irradiations.

Amongst the irradiation sources considered, the lowest energy PKAs are created by electron irradiation. The average PKA energy under electron irradiation is around the displacement energy of Fe even for the PKAs created by electrons with energies on the order of 1 MeV, which means that electron irradiation mostly creates isolated Frenkel pairs. On the other hand, displacement cascades are created in Fe irradiated by fast neutrons and heavy ions. Because of their higher flux and higher interaction cross section, charged particle irradiations generate orders of magnitude higher displacement rates than neutron irradiation, so that damage levels reached in years in a reactor can be achieved in hours or minutes with these techniques. Charged particle irradiated samples are non-radioactive, which makes post
irradiation examination easier. One of the challenges that needs to be taken into account for charged particle irradiations is the limited penetration depth of the energetic particles in the sample. The ranges of the particles of a given energy decrease in the following order: neutrons, electrons, protons, heavy ions. In this case the steep displacement gradients and near surface may affect microstructure development.

A selection of microstructural characterization tools is available to investigate the microstructural changes caused by neutron, electron and ion irradiations. These techniques include transmission electron microscopy (TEM), X-ray scattering, atom probe, field ion microscopy, nuclear reaction analysis, Rutherford backscattering spectrometry, and neutron scattering and spectrometry [18-20].

TEM offers unique opportunities to observe and characterize the irradiation induced microstructure (defect clusters, dislocation loops, precipitates, segregation) in nanometer scale. TEMs interfaced with ion accelerators such as the one used in this work allow monitoring the evolution of the microstructure as it is being irradiated with energetic particles with precise control over the irradiation temperature and dose [13].

<table>
<thead>
<tr>
<th>Table 1-5 Comparison of neutron, ion and electron irradiation in metals</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Typical Flux (particle.cm⁻².s⁻¹)</strong></td>
</tr>
<tr>
<td>Displacement Rate (dpa/s)</td>
</tr>
<tr>
<td>Irradiation time to 1 dpa</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Macroscopic Spatial distribution of damage</td>
</tr>
<tr>
<td>Sample Volume Irradiated</td>
</tr>
</tbody>
</table>
1.2.3.3 Effects of radiation on dimensional stability and mechanical properties of ferritic-martensitic alloys

Previous studies of the effects of irradiation on the physical and mechanical properties of F-M alloys are briefly reviewed in this section.

The agglomeration of irradiation-induced vacancies in steels can cause void swelling which leads to significant dimensional changes of the steels. The swelling rate is defined as $\Delta V/V_0$, where $\Delta V$ and $V_0$ are volume change after irradiation and original volume, respectively. Irradiations conducted at the Experimental Breeder Reactor-II showed the superior void swelling resistance of F-M steels as compared to austenitic steels, as shown in Figure 1-9 [4, 21]. Figure 1-9 shows that the irradiation-induced swelling rate in austenitic steels is one order of magnitude higher than F-M steels at high doses. Therefore, a shift was made to F-M alloys for high dose fission and fusion applications [4, 7].

Irradiation hardening refers to the increase in the yield strength of the steel under irradiation. This is normally associated with a reduction in ductility. Figure 1-10 shows the tensile properties of a F-M steel in as received, aged and irradiated (to ~9 dpa in the Experimental Breeder Reactor-II) condition at 390, 450, 500 and 550 °C [4]. It is evident from Figure 1-10 that irradiation at 390 °C caused an increase in both yield stress and ultimate tensile strength, whereas there was no hardening of aged and irradiated samples at temperatures above 390 °C. Irradiation hardening observed at 390 °C was attributed to the formation of small dislocation loops and precipitates [4].

Allen et al. performed heavy-ion (5.0 MeV Ni) and 2 MeV proton irradiation of HCM12A [22]. Proton irradiation was conducted to doses of 3, 7 and 10 dpa at 673 K and to 3 dpa at 773 K. Hardness measurements performed on the alloy irradiated at 673 K showed an increase of up to 70% in hardness, saturating around 5 dpa [22]. On the other hand, a relatively small increase in hardness was reported for HCM12A irradiated at 773 K to 7 dpa. The hardening of proton irradiated HCM12A was mainly attributed to the formation of
irradiation-induced precipitates and loops [22]. The Ni ion irradiation was performed at 773 K to doses of 5 and 50 dpa. Microstructural analysis performed on the Ni irradiated alloys showed no significant changes in microstructure, although radiation induced loops, voids and precipitates were observed in the proton irradiated HCM12A alloy at 773 K [22].

Furthermore, irradiation induced microstructure evolution may lead to radiation embrittlement which occurs below 400 °C in F-M steels. Radiation embrittlement is the loss of ductility due to the accumulation of irradiation induced defect clusters, dislocation loops and precipitates. Radiation embrittlement is characterized by the increase in a ductile-to-brittle transition temperature (DBTT). DBTT of a metal signifies the temperature at which the fracture energy passes below a pre-determined point and it indicates the transition between low toughness brittle and high toughness ductile fracture regimes [4]. Horsten et al. studied the irradiation behavior of NF616 and HCM12A [23]. NF616 and HCM12A were irradiated in the core of a high flux reactor up to a target dose of 2.5 dpa at 573 K and 2.0 dpa at 343 K. Results of the Charpy tests conducted on NF616 and HCM12A showed ductile-to-brittle transition temperature shifts of 249 K and 225 K, respectively. In addition, HCM12A exhibited more hardening than NF616 [23].
Figure 1-9(a) Swelling rate of austenitic (316) and F-M steels (b) Photograph of austenitic 316 steel in unirradiated and irradiated (1.5x10²³ nm² at 533 °C) condition (Reproduced from [4] and [25]).

Figure 1-10 Yield stress and ultimate tensile strength of normalized-and-tempered, aged, and irradiated 9Cr steels. Temperature and duration of thermal aging was approximately equal to the irradiation time in reactor [4].
1.2.3.4 Effects of radiation on microstructure of ferritic-martensitic alloys

The macroscopic effects of irradiation described above arise from the evolution of the material microstructure under irradiation. Therefore it is essential to investigate the irradiation-induced microstructure evolution to develop a mechanistic understanding of radiation effects. Irradiation-induced microstructural evolution in pure Fe and F-M Fe-Cr alloys were extensively studied in literature since steels used as reactor structural materials are very complex to investigate [3-5, 24-27].

Pure Fe and binary Fe-Cr alloys exhibit a ferritic structure, characterized by large grain size and very low (or zero) density of pre-existing dislocations, precipitates and impurities. Irradiation damage in pure Fe and binary Fe-Cr alloys appeared as small (2–4 nm) defect clusters (assumed to be loops) at early doses. Loops with both $a_0<100>$ and $\frac{1}{2}a_0<111>$ Burgers vectors were identified at low temperatures [24].

The mobility of irradiation induced defects (point defects and their clusters) is crucial to the evolution of microstructure in Fe and Fe based alloys. In high purity Fe, point defects are thermally immobile below 110 K, whereas both vacancies and interstitials are mobile above 230 K [17]. MD studies [28, 29] and TEM [30] investigations showed that interstitial loops in Fe can exhibit fast one-dimensional glide in the direction of their Burgers vector in the absence of applied stress. Figure 1-11 shows a sequence of TEM images of an isolated $\frac{1}{2}<111>$ loop exhibiting continuous movement in its Burgers vector direction [30]. Mobile dislocation loops became immobile below ~450 K, suggesting that efficient trapping of these loops by the interstitial impurities present in the sample [30]. Interstitial solute atoms (C, N, H, He) cause tetragonal distortions in the bcc lattice which greatly reduce the mobility of defect clusters [31]. Furthermore substitutional solute atoms can decrease the mobility of defects depending on the misfit of the substitutional solute atoms with the Fe atoms [32].

Large defect structures (resolvable loops, dislocation tangles, finger loops) develop by the growth and coalescence of small defect clusters and/or unresolvable loops in Fe and its
alloys irradiated to high doses [24]. Jenkins et al. reported formation of high dose extended defect structures earlier and on a larger scale at 573 K than at RT, and in high purity Fe than in Fe–8%Cr [24-26], as shown in Figure 1-12 [24].

Figure 1-11 1-D motion of an isolated interstitial loop at 575 K [32].
Commercial F-M alloys such as NF616 and HCM12A are characterized by a fine lath structure decorated with a high density of pre-existing dislocations and precipitates in contrast to pure Fe and ferritic Fe-Cr alloys [4, 8]. In addition, commercial F-M alloys have a very high density of substitutional and interstitial solute atoms [4]. Although pure Fe and Fe-Cr binary alloys provide significant insight on the microstructural evolution of bcc Fe, the real F-M alloys should be studied to understand the underlying reasons of the superior material properties (mechanical properties, radiation resistance, etc.) of commercial F-M alloys over pure Fe and binary Fe-Cr alloys. However, only a few studies have been performed on the irradiation behavior of current generation F–M alloys.
H. Fukushima et al. reported microstructural evolution of Fe–9%Cr ferritic steel and a Japanese Ferrite Martensitic Steel (JFMS) irradiated with 40 KeV Cu and Fe ions to doses of $8 \times 10^{16} - 8 \times 10^{17}$ ions.m$^{-2}$ at 295 K [33]. Small defect clusters (<3nm) appeared in weak-beam TEM images with a low defect yield (<0.01) which indicates spatial cascade overlap mechanism for the formation of TEM-visible defects [33].

Allen and co-workers reported a study of Ni and proton irradiation of a 12 wt.% Cr F-M steel, HCM12A [22]. The authors found no significant modification in the microstructure of the sample irradiated with Ni ions to 5 dpa at 773 K. On the other hand, an increase in dislocation density was reported for the sample irradiated to 50 dpa [22]. For HCM12A irradiated with 2.0 MeV protons at 673 K to 10 dpa, irradiation-induced precipitates (composition: 50%V, 17%Cr and 12% Nb), 100-type dislocation loops (average size: 34 nm) and voids (average size: 6.2 nm) were reported to form [22].

In conclusion, as this short review show, irradiation-induced microstructure evolution of complex F-M steels is generally unknown and large gaps in knowledge exist in the understanding of microstructure evolution of these F-M steels, which will be addressed in this research project.

1.3 Goals of the study and approach

1.3.1 Goals of the study

The goal of this project is to study the evolution of microstructure in the advanced F-M alloys, HCM12A and NF616, using in situ ion irradiation. The approach adopted in this research project to achieve the stated goals is to perform in situ TEM irradiations of two commercial F-M steels. In situ heavy ion irradiation technique allows monitoring dynamically the evolution of microstructure with precise control over irradiation dose, dose rate and temperature.
We study two third generation F-M steels, NF616 (ASTM code: P92) and HCM12A (ASTM code: T122). Both alloys have the complex and fine tempered-martensite structure which is characterized by fine lath/sub-grain structure and a high density of pre-existing network dislocations within. Both the grain and dislocation structure changes spatially in the sample, therefore following a specific area under irradiation is important to investigate the evolution of the microstructure. In addition irradiation damage in F-M steels may include defect clusters and dislocation loops of vacancy or interstitial nature, voids, second phases, and dislocation tangles and networks all of which adds more complexity to the microstructure. In situ TEM irradiation technique addresses these issues by being able to provide direct observation of such complicated nanometer-scale microstructural features as they form and develop under irradiation.

The key questions to be answered for F-M steels being considered for fission and fusion applications are:

1. How does the F-M microstructure of NF616 and HCM12A evolve with irradiation dose and temperature?
   - What is the threshold dose for the onset of defect accumulation?
   - What are the trends in defect accumulation with dose and temperature?
   - How does the defect size and density vary with temperature and dose?
   - How stable under irradiation are the pre-existing microstructural features (grain boundaries, precipitates, dislocation structure, etc.) that give the F-M steels their desirable mechanical properties and dimensional stability?

2. What is the kinetics of microstructure evolution at different temperature regimes?
   - What is the time dependence of defect formation, elimination and motion at different temperatures?
   - How do defects cluster and react?
3. What is the effect of the initial microstructure of alloys on microstructure evolution under irradiation?

- How does damage evolution correlate with each other and the as-fabricated microstructure? Is there any interaction of the irradiation-induced defects with each other, surface, grain boundaries or precipitates?
- How do the differences in the starting microstructure of NF616 and HCM12A affect microstructure evolution?
- How does the irradiation induced microstructure evolution of NF616 and HCM12A compare with pure Fe, binary Fe-Cr alloys reported in literature?
- How does the irradiation-induced microstructure of NF616 and Fe-9Cr-0.1C model alloy relate?
Chapter 2

Experimental Procedures

This chapter describes the alloys and experimental techniques used in this study. The
first section describes the chemical composition and manufacturing of the alloys studied. The
second section details the characterization of the as-fabricated microstructure of NF616 and
HCM12A by optical microscopy, scanning electron microscopy (SEM) and transmission
electron microscopy (TEM) techniques. Finally, the in situ ion irradiation experiment
technique is presented.

2.1 Materials

In this study, two third generation F-M steels, NF616 (ASTM code: P92) and
HCM12A (ASTM code: T122), were studied [34, 35]. The NF616 and HCM12A alloys were
provided by Sumitomo Metal Industries Ltd. and Japan Atomic Energy Agency through the
University of Wisconsin. Table 2-1 shows the chemical composition of the alloys measured
using inert gas fusion (for oxygen and nitrogen—ASTME 1019-11), combustion infrared
detection (for carbon and sulfur—ASTME 1019-11) and direct current plasma emission
spectroscopy (other elements —ASTME 1097-12). The measurements were performed by an
independent company, Luvak Inc. The results are in good agreement with the compositional
data provided by the manufacturer given in Table 1.2.

The NF616 and HCM12A alloys were produced by a sequence of heat treatments of
normalization, air cooling and tempering treatments. NF616 was normalized at 1343 K for 1
h, air cooled, then tempered at 1043 K for 2 h and air cooled. Similarly, HCM12A was
normalized at 1323 K for 1 h, air cooled, then tempered at 1043 K for 45 min and
air cooled.
The main results of the in situ irradiations of NF616 are compared against a ternary model alloy [36]. The data about the model alloy was provided by Kaoumi et al. from South Carolina University. The ternary model alloy has the same base composition as NF616 and it is designed and specially made to have the starting microstructure of F-M steels without the additional alloying elements. The chemical composition of model alloy is the following (in weight percent): C=0.1%, Cr=9%, Fe=Balance. The model alloy was normalized at 1273 K for 1h, air cooled, then tempered at 1023 K and air cooled [36].

Details of the heat treatments and their effects on the microstructure of NF616 and HCM12A were given in Chapter 1. The normalizing treatment was performed to obtain a fully austenitic microstructure which transforms to martensite upon air cooling. The tempering treatment was performed below the austenite start temperature at which ferrite transforms to austenite on equilibrium heating. The aim of the tempering treatment is to achieve the optimum balance between strength and toughness by modifying the dislocation structure (decrease in dislocation density and formation of dislocation networks), forming precipitates, and sub-grains. The tempering treatment, which was conducted at 1043 K for both alloys resulted in the formation of the sub-grains within martensite laths and growth of \( \text{M}_2\text{C}_6 \) precipitates on grain boundaries. In addition a substantial reduction in the dislocation density of both alloys took place during tempering. For instance, the dislocation density of NF616 can be significantly reduced (up to 73%) by increasing the tempering temperature from 715 to 835 °C which causes enhanced recovery [8]. The rates of all the processes mentioned above are strongly dependent on tempering temperature and duration. These parameters were optimized to obtain good mechanical properties.

Martensitic transformation is a diffusionless shear transformation, during which cooperative motion of a relatively large number of atoms takes place. Each atom is displaced by only a fraction the interatomic spacing and atomic motion is driven by cooling in NF616 and HCM12A.
The constitution of NF616 and HCM12A alloys at room temperature subsequent to the normalization treatments can be predicted from the Schaeffer-Schneider diagram [4, 37]. As indicated Chapter 1, the alloying additions to F-M steels can be categorized as austenite-stabilizers (nickel equivalents) and ferrite-stabilizers (chromium equivalents). The Schaeffer-Schneider diagram predicts the effect of the proportion of ferrite and austenite stabilizers, and therefore the composition of the alloy, on the crystal structure obtained after rapid cooling from normalizing temperatures to room temperature.

The nickel and chromium equivalents for NF616 and HCM12A used in the Schaeffer-Schneider diagram are given by:

\[
Ni \text{ equivalent (wt\%)} = (\%Ni) + (\%Co) + 0.5(\%Mn) + 0.3(\%Cu) + 30(\%C) + 25(\%N) \tag{2.1} \]

\[
Cr \text{ equivalent (wt\%)} = (\%Cr) + 2(\%Si) + 1.5(\%Mo) + 5(\%V) + 1.75(\%Nb) + 0.75(\%W) + 1.5(\%Ti) + 5.5(\%Al) + 1.2(\%Ta) + 1.2(\%Hf) + 1(\%Ce) + 0.8(\%Zr) + 1.2(\%Ge) \tag{2.2} \]

The nickel and chromium equivalents for NF616 and HCM12A calculated by Equations 2.1 and 2.2 are given in Table 2.2. These values can be used to determine the position of NF616 and HCM12A on the Schaeffer-Schneider diagram, as shown in Figure 2-1. For example, Ni equivalent for NF616 can be calculated by plugging in the composition of the alloy (Table 2.1) in Equation 2.2:

\[
Ni \text{ equivalent (wt\%)} = 0.19 + 0 + 0.5(0.44) + 0.3(0.03) + 30(0.114) + 25(0.045) = 4.96 \tag{2.3} \]
Table 2-1 Composition of NF616 and HCM12A alloys.

<table>
<thead>
<tr>
<th>Element\Alloy</th>
<th>NF616 (wt%)</th>
<th>HCM12A (wt%)</th>
<th>Precision (±wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>9</td>
<td>11.09</td>
<td>0.2</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.114</td>
<td>0.108</td>
<td>0.01</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.004</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.045</td>
<td>0.059</td>
<td>0.002</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.006</td>
<td>0.007</td>
<td>0.0005</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>0.013</td>
<td>0.012</td>
<td>0.002</td>
</tr>
<tr>
<td>Boron</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.0005</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.11</td>
<td>0.25</td>
<td>0.005</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.2</td>
<td>0.2</td>
<td>0.02</td>
</tr>
<tr>
<td>Niobium</td>
<td>0.097</td>
<td>0.087</td>
<td>0.005</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.44</td>
<td>0.6</td>
<td>0.02</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.19</td>
<td>0.37</td>
<td>0.005</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.46</td>
<td>0.33</td>
<td>0.02</td>
</tr>
<tr>
<td>Copper</td>
<td>0.03</td>
<td>1</td>
<td>0.002</td>
</tr>
<tr>
<td>Tungsten</td>
<td>1.72</td>
<td>1.68</td>
<td>0.03</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.0033</td>
<td>0.0027</td>
<td>0.0005</td>
</tr>
</tbody>
</table>

NF616 falls in the martensite region whereas HCM12A is positioned in the ferrite/martensite dual phase region in the Schaeffer-Schneider diagram. However, the proximity of the HCM12A to the single-phase martensite region indicates that the alloy microstructure will predominantly consist of martensite with trace amounts of ferrite. Originally, Cu was added to HCM12A to minimize the delta ferrite content in the alloy.

Table 2-2 Nickel and chromium equivalents for NF616 and HCM12A alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>NF616 (wt%)</th>
<th>HCM12A (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni equivalent</td>
<td>4.96</td>
<td>5.69</td>
</tr>
<tr>
<td>Cr equivalent</td>
<td>12.39</td>
<td>14.51</td>
</tr>
</tbody>
</table>

32
2.2 Characterization of the as-fabricated microstructure

The microstructure of as-fabricated NF616 and HCM12A was characterized by light optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM used in this study was a FEI Quanta 200 ESEM, used in both backscatter electron (BSE) imaging and secondary electron (SE) imaging modes. A Hitachi H-9000NAR TEM was used both for the characterization of the as-fabricated alloys and for the in situ irradiation experiments, which will be discussed in Section 2.3.

2.2.1 Sample preparation

The samples for optical microscopy and SEM studies of the alloy microstructure were mechanically polished by successively using 180, 400, 800, 1200-grit paper followed by final polishing with a diamond paste and colloidal silica suspension. The polished samples were etched using a [45% HCl, 20% HNO₃ and 35% H₂O] solution.

The samples for transmission electron microscopy were first thinned to sheets of thickness 80-120 µm using silicon carbide paper. This was followed by mechanical polishing,
and then standard TEM discs (3-mm) were punched from the polished foils. Thin samples (<100 µm) were preferred not only to improve electron transparency, but also to reduce magnetization of the sample in the microscope.

A Struers Tenupol twin-jet electropolishing apparatus was used to electropolish the samples to electron transparency using a 5% HClO₄ and 95% CH₃OH solution cooled down to 233 K by liquid nitrogen. Once prepared, the samples were successively washed with liquid nitrogen-cooled ethanol and methanol to reduce surface contamination and to stop further etching by the residual electrolyte solution. The electro-polished samples were stored in water-free ethanol to maintain surface quality for extended storage periods [38].

2.2.2 Microstructure of the alloys

The microstructure of as-fabricated NF616 and HCM12A after the normalization and tempering treatment is presented in this section. Figure 2-2 shows optical microscopy images of typical tempered martensite structure observed in NF616 and HCM12A at room temperature. The microstructure is confirmed by examination at successively finer scales, including SEM and TEM.

The martensite observed in these alloys is a metastable supersaturated solid solution of carbon in steel. The excess carbon atoms strain the alloy matrix which transforms the bcc structure to bct (body centered tetragonal) structure. Martensite phase takes the shape of elongated laths in order to minimize the interfacial strain between parent austenite and martensite phase. In addition, a fraction of the strain energy is accommodated as dislocations in the microstructure.

Figure 2-3 shows a secondary electron SEM image of NF616 and HCM12A, which reveals prior-austenite grains and the lath structure within. Figure 2-4 shows bright-field TEM images of the elongated laths that form ferrite grains in both alloys after tempering. Carbide precipitation is observed at lath boundaries and at prior-austenite grain boundaries, with larger
precipitates seen at prior-austenite grain boundaries, as shown in Figure 2-4. The laths exhibit a high dislocation density with significant variability between laths. Occasionally, dislocation networks splits the laths and form sub-cell boundaries, as shown in Figure 2-4.

The pre-existing dislocation density in HCM12A, although not quantified, was significantly higher than NF616. This can be attributed to the differences in tempering time and the solute atom concentrations. The tempering time was two times less in HCM12A compared to NF616 (45 min in HCM12A and 90 minutes in NF616). Recovery and precipitation takes place during tempering of F-M alloys and enhanced recovery that occurs over a relatively long time is responsible for the high dislocation density in HCM12A. In addition, reduced precipitation in HCM12A alloys can result in a higher concentration of solutes atoms in the matrix of this alloy.

Figure 2-2 Optical microscopy images of NF616 and HCM12A showing the tempered martensite microstructure.
Figure 2-3 SEM images of prior-austenite grains and the lath structure observed in NF616 and HCM12A.

Figure 2-4 Bright field TEM images of elongated laths (top) and the dislocation structure in weakly recovered laths in NF616 and HCM12A (bottom).
The initial microstructure of the Fe-9Cr-0.1C model alloy was characterized by optical microscopy, SEM and TEM using similar sample preparation techniques to this study [36]. The as-received microstructure of the NF616 and model alloy is shown in Figure 2-5. Figures 2-5(a) and (b) show optical microscopy images of the F-M microstructure observed in both alloys. Figures 2-5 (c) and (d) display secondary electron SEM images of the lath structure inside the large prior austenite grains. The density of precipitates is significantly lower in the model alloy due to the relatively low concentration of carbide stabilizers in this alloy. Figures 2-5 (e) and (f) show TEM images of the similar elongated lath structure observed in NF616 and model alloy. As shown in Figure 2-5, the microstructure of the model alloy replicates the F-M structure (lath/subgrain and prior-austenite grain boundaries) of NF616 reasonably well.
2.3 In situ irradiation experiment

Ion irradiation of free-standing thin films is used to produce irradiation damage on the sample, while it is being examined in a transmission electron microscope (thus an in-situ technique). In situ irradiations provide information on the irradiation-induced defect microstructure and their impact on alloy stability. There are various advantages to the use of in situ heavy ion irradiations for the study of microstructure evolution under irradiation.
As stated above, heavy ion irradiation offers high displacement rates and there is no activation of the sample after irradiation. Furthermore, dose and temperature can be precisely measured and controlled. Observing the damage evolution as it develops allows studying the stability of starting microstructure. In addition, irradiation induced defect microstructure can be quantitatively analyzed by measuring the defect number density and size distributions as a function of dose and temperature. In addition, the interaction of defect clusters with each other and with pre-existing microstructure can be studied by following the kinetics of defect accumulation during irradiation. Heavy ion irradiation offers high displacement rates and there is no activation of the sample after irradiation. Finally, dose rate, ion type and ion energy can be varied, which allows a full exploration of a range of irradiation conditions.

2.3.1 IVEM-TANDEM facility at Argonne National Laboratory

In situ heavy ion irradiations of NF616 and HCM12A alloys were performed using the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory. The IVEM-Tandem is a 300-kV Hitachi H-9000NAR interfaced with ion accelerators where in situ ion beam studies involving ion damage can be conducted [39].

The TEM voltages range from 100 to 300 KeV. In this study, the TEM was operated at 200 KeV for the electrons to stay well below the threshold displacement energy for iron. The maximum point-to-point resolution at 300 KeV is 0.25 nm with a line resolution of 0.14 nm even with the ion beam line attached to the TEM column [39]. The single-charged ion beams range in mass from protons to gold with energies from 40 to 500 keV. The energy of double-charged ion beams can reach 1 MeV for some ions.

Figure 2-6 shows a picture of the IVEM and a schematic illustration of the specimen area inside the microscope. Figure 2-6(a) shows the Hitachi H-9000NAR and its associated ion beam line linked to a 2-MeV tandem ion accelerator and a 0.65-MeV ion implanter which are located on the upper floor of the building. Figure 2-6(b) shows the schematic of the
sample area of the IVEM. The IVEM has a side-entry stage with a slightly expanded objective pole piece to provide room for the ion beam line [39]. The ion Faraday cup assembly shown in Figure 2-6(b) allows record the ion dose [39]. The angle between the ion beam and the electron beam axis is 30°, allowing continuous observation of the sample as the beam is hitting it. The high angle of incidence is very beneficial in irradiations of F-M alloys since tilting these samples more than 20-30° is usually not practical due to their ferromagnetic nature. Heating/cooling specimen holder allows in situ experiments in the temperature range of 20-1200 K. The sample temperature is measured using a thermocouple attached to the specimen cup.

![Figure 2-6 (a) Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory and (b) the illustration of the sample area in the microscope [39]](image)

**2.3.2 Characterization of radiation damage using TEM**

In this study, the TEM is used to investigate formation of radiation damage in the form of dislocation loops, defect clusters, voids and irradiation-induced second phases. In addition the evolution of the pre-existing microstructure such as modifications in the pre-
existing dislocation network and the possible amorphization of the previously existing precipitates were systematically investigated.

Irradiation induced defects are imaged based on their strain fields in TEM using diffraction contrast. To utilize diffraction contrast, the sample is tilted to a slightly s-positive (positive deviation from the Bragg condition) 2-beam diffraction condition. The deviation parameter, s, is the distance of a given reciprocal lattice point g from the Ewald sphere. Bright field (BF) and dark-field (DF) TEM images were formed by selecting the transmitted or diffracted beams with the help of an objective aperture. The Ewald sphere construction for s=0 (strong) and the s-positive two-beam diffraction conditions are shown schematically in Figure 2-7. In each case, the schematic of the Ewald sphere is shown together with a schematic diffraction pattern (DP) showing the position of the relevant Kikuchi lines, and an actual diffraction pattern [40].

Imaging under s-positive two-beam diffraction condition presents considerable advantages compared to the strong (at Bragg condition) two-beam diffraction condition [40].
Figure 2-8 shows DF TEM images of neighboring laths in NF616 imaged using g=<110>. Due to the small variation in the orientation of the laths, the lath on the left was imaged under a strong two-beam condition whereas the lath on the right was imaged under slightly s-positive two-beam condition. The image peak widths are broad under strong two-beam conditions (see dislocations in the left lath in Figure 2-8) but much sharper and confined to the physical size of the dislocations under s-positive two-beam conditions (see dislocations in the right lath in Figure 2-8). Therefore, the contrast obtained with slightly s-positive two-beam condition is better suited to image small defect clusters and dislocation loops that form under irradiation, as detailed in [40].

In this study, dislocation loops and defect clusters were imaged using slightly s-positive two-beam diffraction conditions. TEM images were recorded in dark-field and bright field with operating diffraction vectors known to image most of the irradiation-induced dislocation loops in NF616 and HCM12A under the g=<110> diffraction condition.

Dislocation loops from a particular family of Burgers vectors are expected to form with equal probability in all equivalent orientations. Thus, for a given two-beam imaging condition, only a fraction of the defects potentially imaged with that condition are visible, depending on the specific g.b visibility criterion [40]. It is important to note that no correction was made to the measured defect density values to take into account the multiplicity of orientation. According to the g.b invisibility criterion, only half of the ½<111> loops and two-thirds of the <100> loops can be imaged when using a 110-type g vector as shown in Table 2-3. Thus the reported densities in this study are low by a factor of 2 to 3. However they will be lower by the same factor in all micrographs, assuming that the defects are of the same type.
Figure 2-8 DF TEM images of neighboring martensite laths in NF616 imaged with $g=\langle 110 \rangle$ (red dots mark the boundary between laths).

Table 2-3 $|g.b|$ values for foil normal $n=[111]$ for loops of the types expected in NF616 and HCM12A alloys.

<table>
<thead>
<tr>
<th>$g/b$</th>
<th>$1/2 &lt; 111 &gt;$</th>
<th>$1/2 &lt; \bar{1}11 &gt;$</th>
<th>$1/2 &lt; 1\bar{1}1 &gt;$</th>
<th>$1/2 &lt; 1\bar{1}1 &gt;$</th>
<th>$&lt; 100 &gt;$</th>
<th>$&lt; 010 &gt;$</th>
<th>$&lt; 001 &gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>111</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>110</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

2.3.3 Experimental method

A series of 1 MeV Kr ions in situ ion irradiations of electron-thin NF616 and HCM12A alloys were conducted between 20 K and 873 K under a typical flux of $5 \times 10^{11}$ Kr ions.cm$^{-2}$.s$^{-1}$. The microscope was operated at 200 keV thus no displacement damage in Fe is expected from the electron beam. The vacuum in the TEM was better than $10^{-7}$ torr to minimize sample degradation during irradiation.
The irradiation induced microstructure evolution of the alloys was observed under particular diffraction conditions. Great care had to be taken to consistently adjust the imaging conditions because of sample magnetism. In the course of the irradiation, specific areas were identified and followed throughout the experiment and irradiation was paused frequently to perform detailed microscopy of the defects formed. Two-beam TEM images were recorded at regular dose intervals.

In addition to taking systematic micrographs and diffraction patterns, in situ video recording of microstructural evolution of NF616 and HCM12A was performed using a video-rate camera coupled to the TEM. High quality videos with time resolution of 34 or 67 ms were used to investigate dynamic processes, such as defect creation, elimination and jump characteristics that occur under irradiation.

Defect clusters were manually counted and measured from the TEM images using ImageJ [41]. The defect cluster size was taken as the maximum dimension of the defects on dark-field TEM images. Occasionally, when the defect contrast was such that defect identification was uncertain, the feature was counted as 1/2 defect. The error bars shown in the defect densities relate directly to this uncertainty in defect identification.

Note that identical in situ irradiation setup (microscope, ion type, ion energy, etc.) were used by Kaoumi et al. to study microstructure evolution in the model alloy, thus enabling direct comparison of the results obtained in model alloy with those of NF616 [36].

2.3.4 Simulation of primary damage using SRIM software

The doses in displacements per atom (dpa) values were calculated using the Stopping and Range of Ions in Matter (SRIM) code in order to quantify the dose in dpa in NF616 and HCM12A under 1 MeV Kr irradiation [42]. SRIM is a Monte Carlo calculation which calculates the interactions of an incident ion with the solid comprising of stationary target atoms. The trajectories of the individual projectile and recoiled target atoms are monitored.
and stored in output files [42]. The input parameters for the SRIM are: The atomic and mass number for incident and target atoms, initial energy of the incident ion, displacement energy of the target atom, angle of the incident ion beam, and thickness of the target material. SRIM considers two-body collisions to simulate the interactions between the projectile and target atoms in an amorphous solid.

The incident ions interact with solid atoms via a universal interatomic potential which is a function of ion energy, and the masses and atomic numbers of the atoms in solid. The potential is of the form:

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \psi \left( \frac{r}{a} \right)$$  \hspace{1cm} 2.4

where $Z_1$ and $Z_2$ are the atomic numbers of the incident ion and the solid atoms, $r$ is the interatomic distance, $e$ is the elementary charge, $\Psi$ is the universal screening function and $a$ is the empirical screening length.

$a$ is given by:

$$a = \frac{0.8854 a_{\text{Bohr}}}{Z_1^{0.23} + Z_2^{0.23}}$$  \hspace{1cm} 2.5

where $a_{\text{Bohr}}$ is the Bohr radius. $\Psi$ is determined by empirical fitting of the calculated interatomic potentials of 521 randomly selected combinations and is given by:

$$\psi \left( \frac{r}{a} \right) = \sum_{i=1}^{4} A_i \exp \left[ -B_i \psi \left( \frac{r}{a} \right) \right]$$  \hspace{1cm} 2.6
where A, and B, are constants that are valid for all ion-target combinations. Using this potential, SRIM enables to determine the path of the projectile and recoil target atoms, distribution of the displaced atoms, the ion ranges in the sample and energy loss of the incident ions due to electronic stopping [42].

The doses in displacements per atom (dpa) and range of Kr ions in NF616 and HCM12A alloys were calculated using the SRIM code, using displacement energies of 40 eV for Fe and Cr and 28 eV for C [14]. The input and output data for these calculations are listed in Table 2-4. There are two main options in SRIM code to calculate ion-induced displacement damage: (1) “Ion Distribution and Quick Calculation of Damage”, and (2) “Detailed calculation with full damage cascades” [42]. The “Detailed calculation with full damage cascades” is recommended by the authors of the SRIM code [42] for better accuracy and it was used to calculate displacement damage in this study. This option allows following every single recoiling atom until its energy drops below the lowest displacement energy of the target atom. The “Ion Distribution and Quick Calculation of Damage” option is based on the Kinchin-Pease formalism [15]. More recently Stoller and co-workers have compared the displacement calculations generated using molecular dynamics simulation of cascades [43], SRIM full cascades (FC) option and SRIM Kinchin-Pease (KP) option. The authors find difference in the SRIM-KP calculations and MD of ~10-20% but a factor of two difference with SRIM-FC, which they attribute to a problem with the displacement calculation method in SRIM. They recommend using the damage energy (after subtracting electronic loss) to calculate dpa. One issue is how to do this consistently for a polyatomic solid. In using FC option, the polyatomic nature of the material is explicitly considered, whereas using the KP option would not take this into account.

We performed a SRIM simulation of a composition similar to that of the steels used, and found that FC option gives a result about 50% higher than KP. Because our results are
reported using FC option, it should be noted that for comparison with MD or KP option, a factor of 1.5 should be subtracted.

Figure 2-9 shows a SRIM simulation of the trajectory of a 1 MeV Kr ion in NF616 and the point defects created by the ion. It is important to note that SRIM simulates the initial damage and it does not take into account any annealing and recombination of defects. Approximately 95% of the incident Kr ions go through the sample, as estimated using SRIM. The displacement cascade damage (green dots in Figure 2-9) created by a single Kr ion indicates sub-cascade formation. SRIM gives information about the number and energy of the PKA’s generated by each ion through the thickness of the sample. SRIM calculations were performed with $10^4$ ions for good statistics and on average; ~56 PKAs were created for each incident ion.

Table 2-4 Input and output data for the SRIM calculation of 1 MeV Kr irradiation of NF616.

<table>
<thead>
<tr>
<th>Input</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Target composition (wt%)</td>
<td>C:0.1, Cr:9, Fe:Balance</td>
</tr>
<tr>
<td>Type of calculation</td>
<td>Detailed calculation with full damage cascades</td>
</tr>
<tr>
<td>Stopping power version</td>
<td>SRIM-2008</td>
</tr>
<tr>
<td>Thickness (Å)</td>
<td>1000</td>
</tr>
<tr>
<td>Displacement Energy (eV)</td>
<td>Fe:40, Cr:40, C:28</td>
</tr>
<tr>
<td>Ion type</td>
<td>Kr</td>
</tr>
<tr>
<td>Ion energy (MeV)</td>
<td>1 MeV</td>
</tr>
<tr>
<td>Ion beam angle of incidence</td>
<td>15 Deg.</td>
</tr>
<tr>
<td>Number of ions</td>
<td>10000</td>
</tr>
<tr>
<td>Output</td>
<td></td>
</tr>
<tr>
<td>Average vacancies/ion</td>
<td>2347.2</td>
</tr>
<tr>
<td>Backscattered ions</td>
<td>6</td>
</tr>
<tr>
<td>Transmitted ions</td>
<td>9543</td>
</tr>
<tr>
<td>Average sputter (atoms/ion)</td>
<td>Fe:3.14, Cr:0.3572, C:0.0068 (total: 3.502)</td>
</tr>
</tbody>
</table>

In addition, SRIM software was used to calculate the ion beam-induced damage in NF616 and HCM12A in terms of dpa. The damage production cross-section for the 1 MeV Kr irradiation of NF616 is shown in Figure 2-10. The damage production estimated by SRIM varies weakly along the depth direction within the foil due to the high energy of Kr ions.
Thus, depth-averaged values obtained from SRIM are used. The average number of displacements per ion per angstrom, $K_{\text{avg}}$, is determined to be ~2.4 from the SRIM output.

The dose rate (in dpa.s$^{-1}$), $k$, in the electron transparent samples of NF616 and HCM12A can be estimated by:

$$k = \frac{\phi K_{\text{avg}}}{N_{\text{at}}}$$  \hspace{1cm} (2.7)

where $\phi$ is the ion flux [ions.s$^{-1}$.cm$^2$] and $N_{\text{at}}$ [Å$^{-1}$.cm$^2$] is the atomic density.

“Detailed Calculation with full Damage Cascade” SRIM calculation performed for $10^4$ Kr ions resulted in the dose rate of $1.44 \times 10^{-3}$ dpa/s for a flux of $5 \times 10^{11}$ ions.cm$^{-2}$.s$^{-1}$. The results obtained for HCM12A were identical to those obtained for NF616 and the small composition differences do not significantly change the result.

Figure 2-9 SRIM simulation of the interaction of a single 1 MeV Kr ion with the 1000 angstrom thick NF616 foil. Longitudinal and lateral views of the path of the ion (red dots) and the displacements caused (green dots) are shown.
Figure 2-10 Damage production cross-section for the 1 MeV Kr irradiation of NF616 calculated by using SRIM. The number of target displacements per ion per angstrom is plotted across the thickness of the sample.
Chapter 3

Microstructural evolution of NF616 and HCM12A under irradiation

In this chapter, the results of the in situ irradiations of NF616 and HCM12A are presented. The irradiations were performed with 1 MeV Kr ions between 20 and 773 K to investigate the microstructure evolution of these alloys in different temperature regimes.

The results include diffraction patterns and TEM images captured at specific doses, as well as video frames extracted from the in situ irradiation videos. NF616 and HCM12A alloys have pronounced \{111\} texture so that generally grains oriented close to zone axis [111] were available for examination.

As stated above, for each in situ irradiation experiment, we set up s-positive 2-beam conditions to image nanometer-sized defects to minimize the dynamical contrast effects seen in strong (s=0) two-beam images. This is established by simply tilting the foil just sufficiently away from Bragg condition until the image loses most of its dynamical features. 110-type g-vectors were consistently used to obtain dark and bright field images so as to enable direct comparison between images captured at different temperatures and doses.

Quantitative analysis was performed on TEM images and video frames to determine defect size and density by manually counting a total number of \(\sim 2 \times 10^4\) defect clusters using ImageJ software. Similarly, the jump distance and direction of specific defect clusters were individually determined by conducting frame-by-frame analysis of videos before and after the motion. The detailed analysis performed on TEM micrographs and video frames leads to the following general results about the microstructure evolution of NF616 and HCM12A alloys, which will be discussed in greater detail throughout this chapter.
3.1 General Observations in the low temperature regime (20-573 K)

The following statements are valid for NF616 and HCM12A irradiated between 20 and 573 K to ~10 dpa. As the irradiation starts, there is a period during which no changes are visible in the microstructure. After a threshold dose, around 0.1 dpa in this temperature regime, black dots start to become visible under the ion beam. These black dots appear suddenly, (from one frame to the next) and are thought to be small defect clusters (2-5 nm in diameter), the nature of which (whether dislocation loops or 3-d clusters, and whether vacancy or interstitial) cannot be resolved. It is possible that these are small dislocation loops with Burgers vectors of either \( \frac{1}{2}\langle 111 \rangle \) or \( <100> \) as reported by Jenkins et al. [25, 26, 44]. Of these two types the \( \frac{1}{2}\langle 111 \rangle \)-type loops are reported to be more mobile than \( <100> \) type loops [24].

The overall density of defect clusters increases with dose and saturates around 6 dpa. At saturation, a steady-state is reached in which defects were eliminated and created at the same rates so that the defect density does not vary. In general, although the saturation densities were similar in this temperature range, they were slightly higher at lower temperatures.

After saturation, frame-by-frame analysis of videos taken during irradiation shows that these defects continuously appear and disappear in a time that is shorter than the time in between frames (normally 34 ms). It is also observed that under irradiation a significant fraction of these defect clusters exhibited sudden one-dimensional jumps (over ~5nm), that is, some defect clusters move “or jump” along specific directions. For the jumps examined, the defect motion was regularly in an apparent \( <211> \) direction, which is consistent with the expected Burgers vector direction of (111).

At the end of each irradiation an examination of the sample was performed using under focus/over focus contrast to detect possible void formation. The result was that no voids were observed in any of the irradiations.
When the beam is turned off defect formation stops and the existing defects do not disappear or indeed move, so that the defect cluster distribution that was present before the beam was turned off remains frozen. This indicates that these small defect clusters, once formed, are thermally immobile, at least in the temperature regime (20-573K). In this temperature regime, the average diameter and size distribution of the irradiation-induced defect clusters did not vary with dose during a single irradiation with temperature for various irradiation campaigns. Once the black dots formed, no significant growth was observed during the irradiation period. The defect cluster density or average size also did not vary with foil thickness, indicating that the foil surface did not play a major role in the defect accumulation process.

In fact the pre-existing microstructure appeared to have little effect on the damage accumulation process. Finally the irradiation-induced defect clusters showed no interaction with the pre-existing material microstructural features such as grain boundaries, carbides etc. The average cluster diameter was similar for both alloys and although the foil thickness was not determined in each case, it is thought that the defect cluster density was similar in both as well. Also no irradiation-induced precipitates or second-phases were observed in NF616 and HCM12A in this temperature range.

In the following sections, the general observations highlighted in bold are presented in greater detail in the order above.

3.1.1 Initial Defect formation in NF616 and HCM12A

In this section, the observations of the primary black dot formation in NF616 and HCM12A between 20 and 573 K are discussed. TEM images and in situ irradiation videos captured during irradiation were used to investigate the kinetics of defect formation at low doses.
A detailed low dose irradiation experiment was performed in NF616 at room temperature (RT), to determine the starting dose for defect accumulation and to investigate the possibility of collapse of individual cascades into TEM-visible defect clusters at room temperature. Irradiation was paused at low doses (10^{-3}, 10^{-2}, 10^{-1} dpa) during the RT irradiation of NF616, whereas the stops were at relatively high doses (10^{-1}, 2\times10^{-1}, 8\times10^{-1} dpa) during the other irradiations of NF616 and HCM12A, as discussed in Section 3.1.1.1.

3.1.1.1 Defect formation in NF616 irradiated at room temperature to low doses

Primary radiation damage formation in NF616 at RT was studied by irradiating the material to low doses (10^{-3}, 10^{-2}, 10^{-1}, dpa). This was done by lowering the ion beam intensity ~4 times to precisely control fluence and to ensure sample stability during irradiation at very low doses. Figure 3-1 shows a two-beam dark-field TEM image of the sub-grain followed throughout the irradiation. The inset of Figure 3-1 shows the 110-type g vector used to capture the dark-field TEM images throughout the irradiation. There were pre-existing dislocation segments in the monitored grain, as indicated by the arrows in Figure 3-1.

Figures 3-2, 3-3, 3-4 and 3-5 show a series of two-beam dark-field TEM images of the same area in NF616 captured at 10^{-3}, 10^{-2}, 10^{-1} and 1 dpa at room temperature. There were no visible defects at 10^{-3} and 10^{-2} dpa; on the other hand, defects appeared as small dots in two-beam dark-field images at 10^{-1} dpa, the defect had an average diameter of 3.2 nm. The density of defects increased at 1 dpa, as shown in Figure 3-5, although the diameter remained constant.

The nature and Burgers vectors of these nanometer-sized defects could not be determined because of the difficulties in performing detailed microscopy on a ferromagnetic sample with fine grain structure, but earlier work showed that dislocation loops, presumably of interstitial type, with \frac{1}{2}a_0\langle111\rangle and a_0\langle100\rangle Burgers vectors can form in Fe–Cr alloys under irradiation at room temperature [26, 45]. As stated in Chapter 2 (see Table 2-2), when
using a 110-type g vector for imaging only half of the \( \frac{1}{2}<111> \) loops and two-thirds of the \(<100>\) loops can be imaged, according to the g.b invisibility criteria. Thus the real defect density is likely 2-3 times than observed higher. It is not possible to distinguish uncollapsed defect clusters from dislocation loops in this size range using TEM; therefore these defects are referred to as defect clusters throughout the text.

Figure 3-1 DF TEM image of the initial microstructure of NF616 before irradiation at 298 K. Pre-existing dislocation segments are marked with arrows and the monitored grain is highlighted by dotted line.
Figure 3-2 DF TEM image of NF616 irradiated to 0.001 dpa with 1 MeV Kr ions at 298 K.

Figure 3-3 DF TEM image of NF616 irradiated to 0.01 dpa with 1 MeV Kr ions at 298 K.
Figure 3-4 DF TEM image of NF616 irradiated to 0.1 dpa with 1 MeV Kr ions at 298 K. Insets of figures show the close up view of the defect clusters.

Figure 3-5 DF TEM image of NF616 irradiated to 1 dpa with 1 MeV Kr ions at 298 K. Insets of figures show the close up view of the defect clusters.
The TEM-visible defects in NF616 formed only under the ion beam: no defect formation was observed under the sub-threshold (200 keV) electron beam alone. The defects appeared between one frame and the next. Successive video frames in Figure 3-6 show the sudden appearance of one of the very first defects in NF616 under irradiation at 298 K. The 3.4 nm diameter defect cluster formed at 0.06 dpa in less than 67 ms (time resolution of the movie). The fact that defects formed only under irradiation and in 67 ms or less, indicates that defect creation is governed by the ion beam at 298 K. Because approximately 2 ions were incident per 1 nm$^2$ at 0.06 dpa, it is evident that multiple cascade impacts were required for the defect creation process to take place.
3.1.1.2 Defect formation in NF616 and HCM12A between 20 and 573 K at low doses

The results of low dose irradiations of NF616 and HCM12A between 20 K and 573 K are presented in this section. Figures 3-7 and 3-8 show the microstructure of NF616 and HCM12A at 0 and ~0.1 dpa at various temperatures. It should be noted that although micrographs are not shown at doses lower than 0.1 dpa in some cases, the dose for visible
defect formation could be determined more or less precisely because the sample was observed throughout the irradiation, so that the irradiation could be stopped if defects appeared.

For all irradiations, a threshold dose was required for the observation of visible clusters, i.e. the defects were not immediately observed at the start of irradiation, again indicating that multiple cascade impacts onto previous cascades or onto pre-existing defects is necessary for defect accumulation. The onset of defect accumulation in both alloys between 20 and 573 K started between 0.01 and 0.1 dpa. This is in agreement with the results of the detailed room temperature irradiation of NF616 given in the previous section.

During irradiations performed at temperatures of 20 and 573 K, 2-5 nm defects spontaneously appeared between video frames. Figures 3-9 and 3-10 show the video frames that capture the sudden appearance of five defect clusters during the irradiation of NF616 at 298 K and HCM12A at 20 K. Defect formation was observed from one frame to the next (67 ms or less), possibly in time frames comparable to the time required for cascades to cool (1-5 ps). Occasionally, the contrast of newly formed defects increased in succeeding video frames, corresponding to a time interval of ~0.2 s. As an example, Figure 3-11 shows TEM images that display an increase in defect contrast after their initial formation at 298 K. The increase in contrast can likely be attributed to the absorption of free TEM-invisible defects that were in the close vicinity of the recently formed defects. Jenkins et al. reported similar increase in the contrast of defect clusters over time periods as long as 0.2s in pure Fe and Fe-Cr alloys irradiated in situ with 100 or 150 keV Fe and Xe ions [25].
Figure 3-7 TEM images showing the initial stages of defect accumulation in NF616 at 50, 298 and 573 K. Insets of figures show the two-beam condition and the close up view of the defect clusters.
Figure 3. TEM images showing the initial stages of defect accumulation in HCM12A at 20, 298, and 573 K. Insets of figures show the two-beam condition and the close-up view of the defect clusters.
Figure 3-9 DF TEM images showing the appearance of five defect clusters in NF616 between video frames (in 67 ms or less) at 298 K. The upper video frames are separated by 67 ms from those below.

Figure 3-10 BF TEM images showing the appearance of five defect clusters in HCM12A between video frames (in 34 ms or less) at 20 K. The upper video frames are separated by 67 ms from those below.
3.1.2 Defect accumulation in NF616 and HCM12A between 20 and 573 K

This section reports the results of accumulation of radiation damage in NF616 and HCM12A between 20 and 573 K. Figures 3-12, 3-13 and 3-14 show sequences of images taken during irradiation of NF616 at 50, 473, and 573 K. Similarly, Figures 3-15 and 3-16 show the microstructure evolution in HCM12A under irradiation at 20 and 573 K. All these micrographs were taken using 110-type g vectors in two-beam bright-field and dark-field TEM images as shown in Figures 3-12, 3-13, 3-14, 3-15 and 3-16. Pre-existing dislocation networks, grain/sub-grain boundaries and precipitates in the monitored grains, as shown in Figures 3-12(a), 3-13(a), 3-14(a), 3-15(a) and 3-16(a). Note that at 50 K, the first DF
TEM image was recorded at 0.4 dpa due to a change in the local diffraction conditions which required a change in the irradiation location of the sample.

Typically, defect accumulation was monitored in smaller regions in HCM12A compared to NF616 because HCM12A has a significantly higher density of pre-existing dislocations which hinder the observation of small irradiation-induced defects in their close vicinity. Therefore areas with relatively low pre-existing dislocation density were selected to monitor microstructure evolution under irradiation. This resulted in selecting thinner parts of the foil to observe damage accumulation in HCM12A. It is evident that by selecting a thinner region, the dislocation density in the monitor volume can be reduced; however the trade-off in observing thinner regions under irradiation is that, in general, the regions close to the foil edge are mechanically less stable and bending may occur in these regions under irradiation.

The initial stages of defect accumulation in NF616 and HCM21A are given in Section 3.1.1. In all irradiations of NF616 and HCM12A, defects appeared as white dots in DF TEM images (or black dots in BF TEM images) and the overall concentration of visible defects increased steadily with dose until reaching saturation. Close up images of defect accumulation in NF616 at 50, 473 and 573 K are shown in Figure 3-17 to allow comparison between images taken under similar diffraction conditions. At low doses, the areal density of defect clusters was highest at 50 K, as shown in Figure 3-17. The areal number density of defect clusters increased with dose saturating around ~6 dpa at 50, 473 and 573 K, as quantified below.

Figure 3-18 shows close up images of the irradiated microstructure of HCM12A at 20 and 573 K, and NF616 at 50 K. The irradiated microstructure of HCM12A was similar to that of NF616 in this temperature range: black dots, 2-5 nm in diameter, which started to form at cascade overlap doses and their density increased with dose until saturation.

Dynamic observations of microstructure evolution in both alloys show that defect clusters constantly appear and disappear during irradiation between 20 and 573 K. It was
possible to observe this dynamic flickering on and off of defect clusters because this dynamic appearance and disappearance of defect clusters continued beyond the saturation dose but stopped as soon as the ion beam was turned off. All the observed defect appearance and disappearance events occurred instantaneously (i.e. between frames (34 ms or less)) in NF616 and HCM12A in this temperature range.

No resolvable loops, voids or irradiation-induced precipitates were observed during irradiation in this temperature range. Also, no interaction of the irradiation induced defects with the pre-existing microstructure (dislocation network, grain boundaries) in the form of denuded zones, or dislocation climb was observed during irradiation in the temperature range between 20 and 573 K.
Figure 3-12 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 50 K.
Figure 3-13 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 473 K.
Figure 3.14 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 573 K.
Figure 3-15 BF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 20 K.

Figure 3-16 DF TEM images of microstructure evolution of HCM12A under 1 MeV Kr Irradiation at 573 K.
Figure 3-17 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr irradiation at 50, 473 and 573 K.
Figure 3-18 TEM images of microstructure evolution of HCM12A at 20 and 573 K and NF616 at 50 and 573 K under 1 MeV Kr Irradiation. 0 and 0.1 dpa images of HCM12A were inverted from DF to BF.
The areal density of defect clusters in NF616 irradiated at 50, 473 and 573 K were measured manually from the micrographs using ImageJ. The results are plotted in Figure 3-19 as a function of dose. Note that, the areal density [nm$^{-2}$] can be converted to a volumetric density [nm$^{-3}$] if the foil thickness is known. Assuming a foil thickness of 100 nm, the top density of 4.6 x 10$^{-4}$ nm$^{-2}$ would become 4.6 x 10$^{-6}$ [nm$^{-3}$]. In the manual counting of defects, when the defect was not clearly identified, the feature was counted as 1/2 defect. Since no correction was made to the measured defect density values to take into account the invisibility criterion, the reported defect densities are low by a factor of 2 to 3. Assuming that the defects are of the same type the actual densities would be 9.2 to 13.8 x 10$^{-6}$ nm$^{-3}$. Figure 3-19 shows a steady increase in defect density with saturation occurring around 6 dpa at all temperatures. It is also clear from the Figure 3-19 that the saturation defect density decreases slightly with increasing temperature. Note that error bars refer to the uncertainty in defect identification.

Figure 3-20 shows the measured average defect cluster diameter as a function of dose at 50, 473 and 573 K. The average defect cluster diameter values and defect size distributions are shown only above 2.5 dpa because below this value few defects exist to give proper statistics. As shown in Figure 3-20, the average defect size does not change significantly with dose at 50, 473 and 573 K. The defect cluster size distributions are plotted in Figure 3-21, 3-22 and 3-23 for the 50, 473 and 573 K irradiations, respectively. The defect cluster size distributions vary little during irradiation, especially after saturation, that is the defect size distribution reaches a steady-state. No significant change is seen between the defect cluster size distributions at 50 K and 573 K.
Figure 3-19 The defect cluster areal density of NF616 as a function of dose at 50, 473 and 573 K.

Figure 3-20 The average defect cluster size of NF616 as a function of dose at 50 K, 473 K and 573 K.
Figure 3-21 Size distribution of defect clusters in NF616 irradiated with 1 MeV Kr ions at 50 K as a function of dose, using a bin size of 0.5 nm. The average diameter of defects is shown at each dose.
Figure 3-22 Size distribution of defect clusters in NF616 irradiated with 1 MeV Kr ions at 473 K as a function of dose, using a bin size of 0.5 nm. The average diameter of defects is shown at each dose.
Figure 3-23 Size distribution of defect clusters in NF616 irradiated with 1 MeV Kr ions at 573 K as a function of dose, using a bin size of 0.5 nm. The average diameter of defects is shown at each dose.

The wedge shape of the TEM foil near the edge allowed to investigate the effect of the foil thickness gradient on microstructure evolution. Figure 3-24 shows two regions near foil edge to show the effect of thickness on defect structures observed in NF616 (this study) and pure Fe [25, 26] under heavy ion irradiation. Both alloys were prepared using the same electropolishing procedure, so that the thickness gradient near the edge is expected to be
similar. The arrows on Figure 3-24 show the direction of the thickness gradient, and a fixed distance of 0.8µ was marked on images to better display changes in the irradiation-induced microstructure evolution with thickness in Fe and NF616. The defect density is not seen to change with foil thickness in NF616 while it changes sharply in pure Fe.

Figure 3-24 (a) shows the microstructure of NF616 irradiated to 3.3 dpa at 372 K. In the irradiated area there were pre-existing dislocation lines and tangles in the microstructure that should be differentiated from radiation damage. The irradiation-induced defects appear as white dots distributed throughout the thickness gradient with no detectable denuded zone near the edge. No interaction of defects occurred even in the thicker parts of the foil. Note also that the defect size remained constant through the thickness gradient.

In contrast Figure 3-24 (b) shows the microstructure of pure Fe irradiated to 3.3 dpa at RT [25, 26]. The Fe was annealed before irradiation to obtain a dislocation-free sample, so that the microstructure consists only of irradiation-induced defects. It is evident from Figure 3-24 (b) that the damage structure along the thickness gradient was inhomogeneous: There is a clear denuded zone near the edge (partially shown in the image) formed by the escape of <111> clusters from the foil. On the other hand, strings of defects formed in thicker areas, indicating defect cluster interaction and coalescence do not occur in NF616.
Figure 3-24: The irradiation-induced defect structure observed near the edge of the TEM foil in (a) NF616 (this study) and pure Fe [27, 28]. The red arrows show the direction of the thickness gradient and marks 0.8 μm on both images.
3.1.3 Defect motion in NF616 and HCM12A between 20 and 573 K

Detailed and extensive kinetic information of visible defect motion was obtained during in situ irradiation. Frame-by-frame analysis of the videos taken under the electron and ion beams was used to discuss the influence of this defect motion on microstructure evolution.

Defect motion was examined by forming stacks of video frames in ImageJ. Stacks are ordered sequences of extracted video frames and ImageJ allows to save the initial and final position of defects on stacked images. This data was used to determine the defect jump distance. The position of still features near the mobile defect clusters such as other clusters, grain boundaries or dislocations were used as a reference to determine the very limited motion of clusters, which is on the order of a few nanometers. Thus, the systematic and careful frame-by-frame analysis allowed to clearly differentiate defect jumps from TEM foil drift. In addition defect jump directions were determined on images and matched with specific crystallographic directions using the selected area diffraction pattern of the monitored grain.

A high fraction of defect clusters in NF616 and HCM12A exhibited sudden one-dimensional jumps and jerks under the ion beam between 20 and 573 K. Figure 3-25 shows successive frames extracted with 1 second intervals from a video of the irradiation of NF616 in the IVEM, at a dose of ~0.9 dpa with 1 MeV Kr ions at 373 K. Three defect clusters marked with red arrows, exhibit sudden jumps, as shown in Figure 3-25. These jumps were consistently observed in NF616 and HCM12A for irradiations performed below 573 K. An in-depth frame-by-frame analysis was performed by extracting 29 (or 19, depending on the time resolution of movies) video frames per second to investigate the kinetics of defect motion. The total number of video frames recorded in the time period to reach 1 dpa is approximately 20166 (for 29 fps videos) and 13212 (for 19 fps videos). Note, however that high quality in situ irradiation videos were not always available, due to the changes in the local diffraction conditions during irradiation. Figure 3-26 shows close-up views of the
sudden jumps of the specific defects marked in Figure 3-25 captured with 34 ms intervals. Similarly, Figures 3-27 and 3-28 show a close-up view of sudden jumps of three defects clusters in NF616 at 298 K and in HCM12A at 20 K, respectively. Note that the red arrows in Figures 3-26, 3-27 and 3-28 mark the initial position of the defects and yellow arrows mark the stationary defects in the close vicinity of displaced ones. Thus the yellow arrows connect two dots (since the cluster did not move) while the red arrows connect a cluster to an empty space showing it moved. As stated previously these defect jumps occur extremely quickly in 34 ms or less over distances of 3-9 nm which indicates velocities that exceed ~260 nm.s\(^{-1}\).

The fact that defect jumps were observed at 20-50 K in HCM12A and NF616 indicates that thermal motion is not the mechanism by which the of point defects and their clusters move. In addition, defect clusters in NF616 and HCM12A were immobile at all temperatures when the ion beam was turned off, which again indicates that the motion was driven by the ion beam. This is further confirmed by post-irradiation isochronal annealing of NF616. In this experiment, NF616 was irradiated to 3 dpa at 298 K, followed by successive annealing at 373, 473, 573 and 673 K with a hold time of ~20 min at each step. There was no detectable defect motion or growth throughout the annealing, indicating that neither thermal motion, nor the field of dislocations or image forces caused the clusters to move in the absence of the ion beam.

Previous studies showed that heavy ion beam beam-induced defect jumps occur in pure Fe and binary Fe-Cr alloys at 298 K and 573 K [25]. Different from NF616 and HCM12A alloys, the defect motion in pure Fe and binary Fe-Cr alloys were reported to occur thermally and/or under electron beam [25, 30, 32]. One-dimensional jumps and jerks of defect clusters were seen in Fe and Fe-Cr alloys, triggered by sub-threshold (200 kV) electron beam at RT and 573 K, although the frequency of defect jumps observed under the electron beam was significantly lower than the jumps observed when the ion beam was on [25]. The frequency of defect jumps was increased by focusing the electron beam, and interestingly, the
jump distance stayed the same when the electron beam was focused [25]. This difference indicates a role of interstitial and substitutional solutes in restraining defect cluster motion.

Detailed TEM analysis showed that the jumps captured in the videos were one-dimensional and occurred in one of the <211> directions in grains oriented close to (111). Insets of Figures 3-26, 3-27 and 3-28 show the <110> (g-vector) and <211> directions. Note that red arrows mark the initial positions of the defects on images and the motion is in the approximate <211> direction at all cases. Jumps occurred in + and – directions along <211>, and occasionally defects exhibited back-and-forth motion between along <211>. Previous studies on ion and electron beam-induced motion of small defect clusters (<~10 nm) have shown that mostly clusters with Burgers vector of ½<111> undergo one-dimensional discrete jumps towards their Burgers vector in pure Fe and simple Fe-Cr alloys [25, 30]. In our case, it was not possible to accurately determine the jump direction in our experiments, since both likely Burgers vectors (<100> and ½<111>) project over the <211> direction.
Figure 3-25 Video frames showing the characteristic sudden jumps of defects in NF616 irradiated to ~ 0.9 dpa with 1 MeV Kr ions at 373 K. Red arrows point the initial position (t=0) of the defects in all images.
Figure 3-26 The successive video frames showing the close up view of the defects in NF616 irradiated to ~0.9 dpa at 373 K. Defect clutters that exhibit jumps are tagged with numbers and red arrows point the initial position (t=0) of the defects in all images. Yellow arrows point the stationary defects in the images.
Figure 3-27 The successive video frames showing the close up view of the defects in NF616 irradiated to ~1 dpa at 298 K. Defect clusters that exhibit jumps are tagged with numbers and red arrows point the initial position (t=0) of the defects in all images. Yellow arrows point the stationary defects in the images.
Individual defect clusters were followed in captured video frames to determine the direction, frequency and distance of defect jump distances. The distance and frequency of defect jumps were measured throughout the lifetime of the defect clusters in TEM-images, which is the time between the appearance and disappearance of these defect clusters in videos captured during irradiation. Note that only a fraction of defect clusters disappear under irradiation. The frequency of defect jumps is the average number of one-dimensional jumps that a defect cluster exhibited during irradiation per unit time. The to-and-fro motion of defect clusters was quantified by labeling the jumps as + or – along <211>, according to their direction.

Figure 3-29 shows the irradiation-induced one-dimensional jumps of three defect clusters in NF616 irradiated to ~1dpa at 373 K. The frequency of defect jumps shown in Figure 3-29 ranges from 0.06 to 0.1s\(^{-1}\). The different defect clusters displayed diverse behavior under irradiation. The number of defect jumps for each individual cluster changes...
considerably and a fraction of defect clusters did not exhibit jumps at all. Jenkins et al. reported similar results for Fe and Fe-Cr alloys regarding the motion of defect clusters: Under heavy ion irradiation defects exhibited one-dimensional jumps with varying frequency and a significant percentage of clusters were immobile [25, 26].

The distribution of defect jump distances observed in NF616 irradiated with 1 MeV Kr ions at 373 K is shown in Figure 3-30. The calculated average jump distance is found to be ~5 nm. Jumps smaller than ~2 nm could not be quantified because of the resolution limit of the captured video frames. Furthermore, about 50% the jumps were in the arbitrarily chosen “+” direction, which indicates the one dimensional jumps occur in both possible directions with equal probability. This also indicates that the direction of jumps are not towards the hole in the wedge-shaped foil (+ direction), that is, in the direction of the thickness gradient.
Figure 3-29 Jumps of three individual defect clusters observed in NF616 irradiated with 1 MeV Kr ions at 373 K. The average frequencies of defect jumps are noted on the plots.
Figure 3-30 Distribution of defect jump distances in NF616 irradiated with 1 MeV Kr ions at 373 K with a bin size of 1 nm. A total of 52 defects jumps were measured.

### 3.2 General Observations at elevated temperatures (673-773K)

The results of the irradiations of NF616 and HCM12A conducted at elevated temperatures (673-773 K) are given in this section. The maximum irradiation temperatures of NF616 and HCM12A were, respectively, 773 and 673 K. Significant difference in defect accumulation behavior and morphology are seen at these higher temperatures, which is why they are shown in a separate section. The initial defect formation process observed at these elevated temperatures was similar to that one observed at lower temperatures, i.e., 2-5 nm defects formed only under the ion beam once the threshold dose for defect accumulation was reached. However, the dose for the onset of defect accumulation shifted by more than order of magnitude higher doses at 673 K in both alloys.

Detailed analysis of the videos taken during irradiation show that the TEM-visible defects constantly appear and disappear in a time that is shorter than the time in between video frames (normally 34 ms), in agreement with the lower temperature irradiations. Interestingly, at 673 and 773 K, defects in NF616 and HCM12A did not exhibit the sudden jumps and jerks that were frequently observed during lower temperature irradiations.
At 673 K, large finger-shaped defects were formed in NF616 whereas small defect clusters, identical to those formed at low temperatures, were observed in HCM12A irradiated to high doses at this temperature. At 673 K, the defects in NF616 grew and coalesced under irradiation which led to large average defect sizes and low defect density. At high doses extended defect structures in NF616 formed as short segments aligned along 100 directions.

At 773 K, defects in NF616 appear at high doses (~3-4 dpa) and the frequency of defect formation per unit area was the lowest amongst all irradiations. A fraction of these defect clusters grew in size for several seconds but the visible defect clusters eventually faded out gradually (in ~28 seconds) different from the defects observed at lower temperatures. As a result, there was no net defect accumulation in NF616 even at the high irradiation dose of 10 dpa at 773 K.

No resolvable loops, voids or precipitates were formed in NF616 and HCM12A irradiated at elevated temperatures. Furthermore, no significant interaction of the irradiation induced defects with the foil surface, pre-existing dislocation network or grain boundaries was observed at either irradiation temperature.

3.2.1 Microstructure evolution in NF616 and HCM12A at 673 K

In this section, the microstructure evolution observed in NF616 and HCM12A at 673 K are given. Figures 3-31 and 3-32 show sequences of two-beam bright field images of HCM12A and NF616 taken with 110-type g-vectors at 673 K.

The dose required for the onset of visible defect accumulation increased with temperature in both alloys. Contrasting to the low temperature regime (50-573 K), where defects were visible at doses around 0.1 dpa, (Section 3-2), at high temperatures defects appear at doses that are higher by more than order of magnitude. The microstructure of either alloy irradiated to 2.5 dpa at 673 K does not reveal any irradiation-induced defects, as shown
in Figures 3-31 and 3-32. Defect accumulation started just above 2.5 dpa in both alloys. The overall concentration of visible defects increased steadily until reaching saturation. This is shown in Figures 3-31 and 3-32.

As stated above, during high temperature irradiation defect clusters in NF616 and HCM12A did not exhibit the cascade-induced sudden jumps and jerks that were frequently observed between 20 and 573 K. This observation is in agreement with the in situ heavy-ion irradiations of pure Fe and Fe-8%Cr binary alloys with at 773 K reported by Jenkins et al. These authors attributed the lack of jumps in these materials to the high fraction of <100> loops present at this temperature, since ½<111> loops exhibited sudden jumps more frequently than <100> loops, as stated earlier in the text [25]. It is possible that the same explanation applies in this case.

Once the threshold dose for defect accumulation is reached, the defect cluster accumulation observed in HCM12A at 673 K was similar to that observed at low temperatures, in that the density of 2-5 nm defect clusters increased steadily till saturation and there was no visible change in defect size. In addition there was no noticeable interaction of defect clusters with each other or with the existing dislocations, as illustrated in Figure 3-31.

The irradiation-induced microstructure evolution of NF616 at 673 K (Figure 3-32) can easily be distinguished from the one observed in HCM12A (Figure 3-31) by means of the noticeable increase in the defect cluster size. Furthermore, it is evident from the sequence of micrographs given in Figure 3-32 that the defect cluster density is much lower at 673 K than the 50-573 K irradiations. This can be attributed to the merging and coalescence of defects at 673 K. Figure 3-33 shows a series of video frames showing the formation and coalescence of defect clusters during irradiation at 673 K. Note that the red arrows point to the position of defects tagged as 1 and 2 in each frame. Figure 3-33(a) and Figure 3-33(b) show the formation of defect cluster 1 in the vicinity of defect cluster 2. The formation of defect 1 occurred as usual between frames (<34ms). After the formation of defect cluster 1, both
defects exhibit little change in their contrast for ~17 s. Subsequently, a gradual growth of defect 1 and corresponding shrinkage of defect 2 took place over the subsequent 135 s, as shown in Figure 3-33(c-k). Finally, defect 1 absorbed defect 2 completely, as shown in Figure 3-33(k) and Figure 3-33(l). The fact coalescence of the two defects occurred gradually, indicates that thermal processes are significant at this temperature. The final defect diameter in Figure 3-33(l) is 17 nm, which is approximately 3 to 4 times larger than the average diameter of defects measured at 50-573 K (and consequently 10-20 times larger in volume). In addition growth of defects by absorption of TEM-invisible defects was observed. Figure 3-34 shows video frames captured during irradiation of NF616 to ~5 dpa with 1 MeV Kr ions. The size of the arrowed defect in Figure 3-34 increased from 6.8 nm to 16.1 nm in 39s.

Occasionally, during irradiation at 673 K large defects in NF616 were lost, presumably by gliding out of the foil. Figure 3-35 shows BF images of such a defect that was lost to the foil surface between video frames. The finger shaped defect that appeared to be positioned on top of two smaller defects disappeared between frames as illustrated in Figure 3-35. The schematic in Figure 3-35 shows the initial and final configuration of defects. Defect loss to the surface was only observed under the ion beam and between captured frames (34 ms or less). This suggests that cascade-induced detrapping of defect clusters could cause the observed effects.

At the highest dose reached (7.4 dpa), large finger-shaped defects appeared in NF616, which were mostly oriented along two families of defects. Similar, (but far more orderly) extended defect structures were observed in pure Fe and Fe-Cr alloys, as shown in Figure 3-36 (alignment indicated with arrows). The common feature observed in NF616, binary Fe-Cr and Fe is the orthogonal alignment of finger shaped defects. Jenkins et al. characterized the finger defects as interstitial loops with $\vec{b} = a_0<100>$. It is evident from Figure 3-36 that defects in Fe-Cr alloys formed on a finer scale and at higher doses than those in pure Fe [24], likely because of the effect of solutes in reducing thermal migration of defects.
Figures 3-37 and 3-38 show the defect density and average defect cluster plots shown in Section 3.1.2 with the addition of the 673 K irradiation data. Figure 3-37 shows the shift of onset of defect accumulation at 673 K. In addition the defect density was 8-12 times lower at high doses at 673 K. It is also evident from Figure 3-38 that the average defect size at 673 K was largest amongst all irradiations.

It is possible to estimate the total number of interstitials in clusters by taking into account the measured average defect size and density values at a specific temperature. The ratio of the total number of interstitials in clusters at 573 K (6.8 dpa) to 673 K (4.9 dpa) can be calculated as follows [46]:

\[
\frac{n_{573K}}{n_{673K}} = \frac{9_{573K}\pi d_{573K}^2 b}{4V_a} \left/ \frac{9_{673K}\pi d_{673K}^2 b}{4V_a} \right. = \sim 1.4
\]

where \( n_i \) is the density of interstitial clusters at temperature \( i \), \( d_i \) is the average diameter of interstitial cluster at temperature \( i \), \( V_a \) is the atomic volume ,and \( b \) is the magnitude of the Burgers vector of \( \frac{1}{2}<111> \). The significantly lower number of interstitials at 673 K can be attributed to the enhanced mobility of defects at 673 K which can result in loss of defects to fixed sinks, such as foil surface.
Figure 3-31 BF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 673 K.
Figure 3-32 BF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 673 K.
Figure 3-33 The video frames showing the formation and coalescence of defect clusters in NF616 irradiated to ~5 dpa with 1 MeV Kr ions at 673 K. Red arrows point the position of the defects that are tagged with numbers.
Figure 3-34 BF TEM images of growth of a defect cluster from 6.8 nm to 19.6 nm over 39 s in NF616 irradiated to ~5 dpa with 1 MeV Kr ions.

Figure 3-35 Defect loss to the surface captured by video frames captured with 34 ms interval. Schematic illustration of the initial and final defect configuration is shown (the defect that was lost to the surface is shown in red).
Figure 3-36 Aligned finger defects in (a) NF616 irradiated to 7.4 dpa at 673 K (b) UHP Fe irradiated to 6.5 dpa at 773 K (c) Fe-8%Cr irradiated to 6.5 dpa at 773 K. Note that all the BF TEM images were taken with 110-type g vectors.
Figure 3-37 The defect cluster areal density of NF616 as a function of dose at 50, 473, 573 and 673 K.

Figure 3-38 The average defect cluster size of NF616 as a function of dose at 50, 473, 573 and 673 K.
3.2.2  Microstructure evolution in NF616 at 773 K

The highest irradiation temperature of NF616 was 773 K, and the results are shown in this section. Higher temperature irradiations have to be very carefully conducted because of vacuum problems causing sample degradation. In this particular irradiation, Moiré fringes formed and degraded the quality of the sample but did not interfere with imaging of the radiation damage. The same irradiation-induced 2-5 nm defects appeared spontaneously during the irradiation. The defects started to appear at high doses (~3-4 dpa) and the frequency of defect formation per unit area was the lowest of all irradiations.

Figure 3-39 shows the appearance of seven defect clusters in NF616, which, as usual, appeared between video frames (in 67 ms or less) during irradiation at 773 K. A fraction of these defect clusters exhibited an increase in contrast after they were formed. The contrast of defect clusters captured in videos was accurately monitored by differentiating the changes in the contrast of defect clusters from the overall changes in the contrast of the images. Figure 3-40 shows the enhancement in the contrast of two defect clusters over ~0.2s. Similar observations were made during low temperature irradiations, as discussed in Section 3.1.1.

Figure 3-41 shows the sequence of 2-beam DF images of NF616 irradiated to a maximum dose of 10.1 dpa at 773 K. Low-dose images are not shown, due to the local changes in diffraction conditions at the beginning of irradiation. Interestingly, the irradiation-induced defects formed in NF616 appeared suddenly (as in low temperatures) but were not stable, fading out gradually and eventually disappeared completely. This resulted in no net defect accumulation in NF616 irradiated at 773 K to 10.1 dpa so that the microstructure was essentially unchanged, as shown in Figure 3-41. The gradual fading of defects was also observed under thermal conditions by turning the ion beam off after the defect was formed and observing it in the microscope. This indicates that thermal processes of defect migration and absorption are responsible for the disappearance in contrast.
The gradual elimination of defects is most likely not due to defect loss to the surface, since the area monitored under irradiation was estimated to be fairly thick (60-100 nm). Also the observed slow fading away is not consistent with defect loss to a surface.

This gradual disappearance of defects was not at all observed in irradiations of NF616 and HCM12A, in the temperature range between 20 and 573 K, defect elimination occurring between successive video frames (normally 34 ms).

Figure 3-42 are video frame sequences that show three defects in NF616 over 30-75s under irradiation at 773 K. It is evident from Figure 3-42 that the contrast of defect clusters decreased gradually, whereas the nearby dislocations maintained the same level of contrast throughout the irradiation. The lifetime of defects similar to those shown in Figure 3-42 were measured by extracting frames from videos recorded with a time resolution of 19 frames per second. Analysis of video frames allowed to measure the lifetime of defects, that is the time between they appear and completely disappear in video frames. Table 3-1 lists the lifetime of nine defects in the order as they appeared in in situ irradiation at 773 K. The defect lifetime was between 11 and 73 seconds and the average was calculated as 28s.

These observations fit quite well with pervious observations reported on 9 and 12Cr F-M steels with similar composition and starting microstructure to NF616 and HCM12A [4]. These steels were irradiated at the Experimental Breeder Reactor-II (EBR-II) and were subjected to mechanical testing and microstructure analysis after irradiation [4]. Figure 1-10 shows the yield stress and ultimate tensile strength of normalized and tempered, thermally aged, and irradiated 9Cr F-M steel irradiated to 9 dpa. It is evident from Figure 1-10 that no changes in mechanical properties were observed above 720 K. The 9Cr F-M steel was further irradiated in the EBR-II to 9-13 dpa at 663, 773 and 823 K. Klueh et al. performed TEM analysis of the samples subsequent to the irradiations [4]. The microstructure of the sample irradiated at 663 K contained a high density of dislocation loops and tangles. On the other
hand samples irradiated at 773 and 823 K showed no apparent change in the microstructure compared to the unirradiated sample, in good agreement with our results [4].
Figure 3. g) The appearance of seven defect clusters between video frames (in 67 ms or less) at 77.3 K.
Figure 3-40 The appearance of defect clusters over several video frames in NF616 under 1 MeV Kr irradiation at 773 K.
Figure 3-41 DF TEM images of microstructure evolution of NF616 under 1 MeV Kr Irradiation at 773 K.
Figure 3-42 Two-beam DF TEM images of the gradual disappearance of three defect clusters in NF616 at 773 K.

Table 3-1 The lifetime of various defect clusters in NF616 irradiated at 773 K.

| Defect lifetime (s) | 11 | 73 | 24 | 12 | 32 | 23 | 8 | 29 | 43 |

3.3 Comparison of the microstructural evolution in NF616 and model alloy

In this section, the results of the microstructure evolution in Fe–9Cr-0.1C model alloy [36] and NF616 (this study) under 1 MeV Kr irradiation are presented. The data about the
model alloy was provided by Djamel Kaoumi from South Carolina University. Model alloy has a similar F-M microstructure as NF616 without the additional interstitial and substitutional solute atoms, as shown in Figure 2.5. It is important to note that, identical sample preparation (mechanical polishing, electropolishing, etc.) and in situ irradiation setup (microscope, ion type, ion energy, etc.) were used in both studies to enable direct comparison, as detailed in Chapter 2.

Figures 3-43 and 3-44 show series of two-beam DF TEM images of the specific areas in NF616 and model alloy followed under irradiation at 50 K and 473 K, respectively. The microstructural evolution in NF616 and model alloy at 50 K showed strong resemblances at low doses, as shown in Figure 3-43. The irradiation induced damage in NF616 and model alloy appeared at cascade overlap doses and it was in the form of white dots in DF TEM images. Defects remained in constant size up to 8.2 and 2 dpa in NF616 and model alloy, respectively. In addition, saturation of homogeneously distributed defect clusters was observed in NF616 and model alloy. Defects in both alloys were constantly created and eliminated during irradiation which continued well above the saturation dose. In addition, a significant fraction of defect clusters in model alloy exhibited sudden jumps over 2-10 nm under the ion beam similar to the jumps observed in NF616, as discussed in Section 3.1.3. Preliminary comparison of defect jump measurements (not shown) yielded smaller jump distances for NF616.

Figure 3-44 shows the irradiation induced microstructural evolution in NF616 and model alloy at 473 K. Interstitials and vacancies are thermally mobile in pure Fe at 473 K. The initial damage development in NF616 at 50 K and 473 K was quite similar. There was an increase and saturation of defect clusters in NF616 with no apparent change in the size of defect clusters. On the contrary defect clusters in model alloy started to increase in size around 1 dpa possibly by absorption of point defects and coalescence of defect clusters. Resolvable dislocation loops started to appear in model alloy around 2-3 dpa and interaction
of these loops resulted in the formation of dislocation tangles at high doses, as shown in Figure 3-44(g-l).
Figure 3-43 DF TEM images of microstructure evolution of NF616 (a-f) and model alloy (g-l) under 1 MeV Kr Irradiation at 50 K.
Figure 3-44 DF TEM images of microstructure evolution of NF616 (a-f) and model alloy (g-l) under 1 MeV Kr Irradiation at 473 K. Arrows indicate the resolvable dislocation loops in the model alloy.
Figure 3-45 show dark-field images of grain boundaries which separate neighboring laths in NF616 and model alloy irradiated to doses of ~10 dpa. Although the NF616 was irradiated at 573 K and model alloy was irradiated at 473 K. Two-beam dark-field images of the laths oriented close to (111) zone axis were taken with 110-type g vectors in both alloys to allow direct comparison. The microstructural evolution in NF616 irradiated at 573 K did not vary from that observed at 50 K and 473 K. While in the model alloy, an apparent denuded zone is observed, no such denuded zone was observed in NF616. Four detailed grain boundary studies in NF616 and HCM12A samples irradiated between 473-673 K and no denuded zones were observed.

![Figure 3-45 DF TEM images](image)

*Figure 3-45 DF TEM images of the interaction of irradiation induced defects with the lath boundary in NF616 and model alloy under 1 MeV Kr Irradiation at 573 K and 473 K, respectively.*

Figure 3-46 shows high-dose defect structures observed in NF616 at 673 K and model alloy at 298 and 180 K. Gradual coalescence of defect clusters in NF616 at 673 K resulted in the formation of finger shaped defects that appeared to align vertically, as shown in Figure 3-46(a). Figures 3-46(b) and (c) show the strings of defects formed in model alloy at 298 K and 180 K, respectively. Initially uniformly distributed defect clusters (black dots in DF TEM images) merged and formed segments of defects at high doses in the model alloy. These segments evolved into strings in model alloy. Strings of defects aligned cooperatively
approximately parallel to \(<110>\) directions between 50 K and 573 K. At 50 K and 180 K, defect strings developed further into complex structures which consisted of rafts linked to each other with segments of defects, especially in the relatively thick parts of the sample. Hernandez-Mayoral et al. reported formation of large resolvable loops and strings with \(\frac{1}{2}<111>\) Burgers vectors [26]. There was no evidence of void formation or precipitation in NF616 and model alloy irradiated to 7-10 dpa between 50 K and 673 K.

Figure 3-46 BF TEM images of the extended defects observed in NF616 and Model alloys under 1 MeV Kr Irradiation at 673 K, 298 K and 180 K, respectively. Arrows indicate approximate directions of defect alignment in NF616 and model alloy.

3.4 Discussion

In this section, we detail the experimental observations and discuss them with a view to developing the model discussed in Chapter 4. In the heavy ion irradiations of bcc Fe, most point defects and their clusters are created in cascades created by energetic ions [3, 14]. The widely accepted picture of the distribution of defects in the final state of a cascade includes a vacancy-rich core surrounded by interstitials. In fcc materials such as Cu and Ni, the vacancy-rich core of individual cascades was reported to create vacancy-type defects, that are visible in TEM even at doses below 0.0001 dpa, i.e., at doses which formation of defects by point defect migration and growth from a variety of displacement cascade events is not likely.
On the contrary, single cascade events in bcc Fe initiated by high energy neutrons or ions do not reveal any TEM-visible damage [27, 45], which was attributed to the relatively low intra-cascade clustering in Fe [14]. Although collapse of individual, isolated cascades to visible defects in Fe did not occur under heavy-ion irradiations, visible damage was observed at relatively high irradiation doses. The results of our in situ irradiation experiments are in agreement with this picture.

The fact that the formation of observable defect clusters requires a finite irradiation dose, indicates that some cascade overlap and/or time for defect diffusion and reaction is necessary for TEM visible defect formation. Furthermore, analysis of the frame-by-frame videos taken during irradiation between 20 and 773 K showed that defects that were not present in a given frame were visible in the next, indicating that they were created in 34 ms (or 67 ms, depending on the time resolution of videos) or less. This is many orders of magnitude shorter than the time required for thermal diffusion to take place. In all the irradiations TEM-visible defect formation was only observed when the ion beam was hitting the sample. In addition defect creation took place athermally (at 20-50 K), in fact with the highest efficiency, in NF616 and HCM12A. This indicates that defect creation in these alloys is mainly a cascade-governed process. Taken as a whole, these observations suggest that TEM-visible defects form by the impact of cascades upon an area that already contains a critical density of sub-visible defects.

Figure 3-47 shows threshold dose for defect accumulation of NF616 between 50 and 773 K. The significant increase in threshold dose for defect accumulation between 573 and 673 K can be explained by the ability of defect clusters to move and annihilate damage at the high temperature. The lack of defect mobility at low temperatures may assist in establishing the critical background density of sub-nm defects necessary for the formation of visible defect clusters by a subsequent impact. At high temperatures, the sub-visible clusters of vacancies and interstitials may have enhanced mobility in the early stages of the cascade, before they
were trapped by the interstitial and substitutional solute atoms. The increase in the mobility of the interstitial and/or vacancies and their clusters can enhance absorption of vacancies by interstitials since these defects are spatially separated in the cascade. MD simulations showed that vacancy clusters are formed near the cascade core whereas; interstitials are positioned near the outer rim of the cascade [14]. This mentioned boost of intra-cascade recombination/absorption during the early stages of the cascade may result in a decrease in the clustering of cascade damage compared to the low temperatures. For that reason, the average size of sub-visible defect clusters created in cascades at high temperatures (≥673 K) can be smaller compared to the ones formed in the low temperature regime (20-573 K).

Figure 3-47 The threshold dose for defect accumulation of NF616 at 50, 473, 573, 673 and 773 K.

Although it is not possible to perform inside-outside contrast to determine the nature of the small defects formed in NF616 and HCM12A, it is expected, (based on previous results from the literature), that these defect clusters are interstitial. The defects in Fe and ferritic alloys produced by heavy ion and neutron irradiations were characterized as interstitial using TEM [26, 45], and sub-nm vacancy clusters were in the form of nano-voids or loosely packed vacancy sponges as detected by positron annihilation studies [14, 45, 47]. This is consistent with the MD studies which predicted a significantly higher fraction of intra-cascade clustering
of interstitials compared to vacancies [14]. In addition MD simulations showed that nanometer-sized interstitial clusters, containing as many as 100 interstitials exhibit fast one-dimensional motion in the direction of their Burgers vector with very low migration energies that are comparable to single interstitial migration energies [3, 48]. Therefore, mobile and sub-visible interstitial clusters may escape their collision cascade and interact with other defects created in other cascades. On the other hand, vacancy clusters need ~50 vacancies to collapse into a loop. The uncollapsed clusters do not glide in their glide cylinder and remain as relatively immobile three-dimensional vacancy clusters [26].

What is the process that enables formation of TEM-visible defects in NF616 and HCM12A? As displacement cascades are generated in the material, their defect debris includes interstitial clusters in the sub-visible range, which can enhance microstructural evolution by eliminating the cluster nucleation phase. The TEM-invisible interstitial clusters with Burgers vector of \( \frac{1}{2}a_0<111> \) grow during irradiation by absorption of smaller clusters through one-dimensional motion in the direction of their Burgers vector. However, the defect motion is discontinuous since interstitial and substitutional solute atoms can trap defect clusters and immobilize them. On the other hand, the shockwave created by cascades induced by high energy Kr ions may have enough energy to de-trap clusters, and allow unrestricted defect clusters to interact with the defects in their glide cylinder until they are trapped again. This motion allows interstitial loops to gather other interstitials along the way, absorb vacancies, or get annihilated at the sinks such as surface, grain boundaries and dislocations. According to the proposed mechanism, interstitial clusters with Burgers vector of \( \frac{1}{2}a_0<111> \) undergo a finite number of coalescence events which will eventually form defects that are observable in TEM (>2 nm).

Our observations between 20 and 573 K are consistent with the previous in situ heavy ion irradiation studies of Fe and binary Fe-Cr in this temperature regime. These studies showed the presence of a balanced population of interstitial clusters with Burgers vector of
½<111> and <100> in Fe-Cr [26]. Formation of clusters with Burgers vector of <100> is rather complicated since they are predicted to be sessile even at small sizes. Marian and Wirth proposed a mechanism for the formation and growth of defect clusters with <100> Burgers [29]. According to this mechanism, the <100> cluster nuclei form through the direct interaction of mobile and sub-visible ½<111> clusters of similar size through the following reaction [29]:

\[
\frac{1}{2}[111] + \frac{1}{2}[\bar{1}\bar{1}\bar{1}] \rightarrow [100]
\]

The reaction given in Equation 3-1 is a strain field mediated action but it can be activated by the thermal part of the cascade. Initially, the intersection of two ½ a₀<111>- type defect clusters forms a <100>{110} junction, which grows until the whole cluster is transformed. With increasing defect cluster size, <100>{110} cluster rearrange itself to form pure-edge <100> 100 defect clusters [29]. The defect clusters with a₀<100> Burgers vectors are reported to have relatively low mobility and they reach TEM-visible size by absorption of small clusters with ½ a₀<111> Burgers vectors [29].

There is no qualitative difference in defect accumulation in NF616 and HCM12A between 20 and 573 K. Figure 3-48 shows the average defect size (measured at saturation dose) at 50, 473, 573 and 673 K. First, the similarity of the defect size distributions between 20 and 573 K indicates that the role of temperature and cluster mobility is limited in this temperature range. In the low temperature regime (20-573 K), defect clusters are not influenced by thermal defect migration that would make them grow or shrink. They are, rather created and eliminated directly in the cascade events. Similarly, the dynamic observations of spontaneous defect cluster appearance and disappearance emphasize the cascade-driven defect appearance/disappearance processes. Another observation that highlights the restricted defect motion in NF616 is the little interaction between the defect
clusters and the pre-existing microstructure between 20 and 573 K. There were no denuded zones near the defect sinks such as grain boundaries, dislocations or foil edge. On the other hand, large defect structures such as rafts and resolvable loops formed in model alloy between 50 K and 473 K by coalescence of defect clusters and absorption of point defects of the same nature [36]. In addition the decrease in the density of defects between 50 K and 473 K was more pronounced in the model alloy compared to NF616. This can be attributed to the higher mobility of defects in model alloy in this temperature range which can result in a high rate of recombination and defect loss to the sinks. In accordance, the defect-denuded zones along the grain boundaries were observed only in model alloy [36], indicating the enhanced transport of defects to sinks in model alloy. Many of the differences in the microstructural evolution of NF616 and model alloy [36] including the formation of denuded zones, effect of temperature on average defect size and defect density can be rationalized within the framework of the trapping of defects by interstitial and substitutional solute atoms, which will be discussed in the next chapter.

![Figure 3-48 The average defect cluster size of NF616 measured at saturation dose at 50, 473, 573 and 673 K.](image)
Defect density saturation between 20 and 673 K observed in NF616 and HCM12A around 6 dpa can occur when the rate of defect cluster formation is equal to the rate of defect cluster elimination. Figure 3-49 shows the saturation value of defect density between 50 and 773 K. The possible mechanisms that can explain the disappearance of defect clusters under irradiation include loss to the foil surface and shrinkage to TEM-invisible sizes due to absorption of vacancies by interstitial clusters.

The defect cluster density can reach a level that the probability of a cascade induced shock wave can sweep some of these defect clusters a larger fixed distance and ultimately toward the surface. However, defect loss to surface does not appear to be the dominant defect elimination mechanism in NF616 and HCM12A since there was no apparent variation of defect density with thickness. In addition frames extracted from irradiation videos showed that defect clusters appeared at the very edge of the foil and survived multiple cascade events. This can be attributed to the low mobility of defects in NF616 and HCM12A. Contrarily, defect-denuded zones and dependence of defect size on foil thickness were observed in pure Fe irradiated with heavy ion to similar doses [25, 26].

![Figure 3-49 The saturation defect cluster areal density of NF616 at 50, 473, 573, 673 and 773 K.](image)
Therefore, it is more likely that an absorption mechanism driven by the limited defect motion is active in NF616 and HCM12A. According to this mechanism, interstitial defect clusters that exhibit cascade-induced motion can gather vacancies as they glide between traps, which can result in the decrease of the interstitial clusters size. The shrinkage of interstitial clusters by absorption of vacancy clusters can make them disappear from the TEM images if the final size is smaller than \(\sim 2\) nm. In this case, the TEM-invisible defect clusters would remain in the sub-visible range and interact with the interstitial and vacancy clusters that would either make them grow to TEM-visible sizes or they may shrink further, leading to the complete elimination of the interstitial clusters. This can explain saturation behavior and the continuous appearance/disappearance of defect clusters that continued after saturation in NF616 and HCM12A.

The visible motion of defect clusters in NF616 and HCM12A between 20 and 573 K was in the form of sudden jumps and jerks. On the other hand, at 673 and 773 K defects in NF616 and HCM12A did not exhibit these jumps. The fact that defect jumps were only observed under the ion beam and jumps were exceptionally fast (exceeding 250 nm.s\(^{-1}\)) indicate that the cascade-induced shockwave created in the first picoseconds of the ion impact governs the defect motion in NF616 and HCM12A below 573 K. It is important to note that high rates of defect jumps were observed at 20-50 K with a high rate, which supports the cascade-induced defect motion mechanism since point defects and their clusters are thermally immobile at this temperature.

The defect cluster motion observed in NF616 and HCM12A under irradiation exhibits similarities to the one-dimensional defect motion in pure Fe and binary Fe-Cr alloys which was reported to occur thermally [30] or athermally (electron and ion beam-induced) [25]. The differences in the present observations with those reported in pure Fe and Fe-based commercial alloys can be ascribed to solute effects. For example pure Fe and model alloys were reported to exhibit discrete jumps under sub-threshold electron beam alone.
Correspondingly, the average jump distance of defects decreases with increasing solute atom content. Jump distance was reported be ~100 nm for high purity Fe, <30 nm for the low-purity Fe \[49\], and <10 nm for NF616 and HCM12A (this study).

There is a very high density of substitutional (Cr, Mo, V, P, Si, Ni, Mo, Al, W, Mn) and interstitial (C, N) solute atoms in NF616 and HCM12A. The interstitial solute atoms cause tetragonal distortions in bcc lattice and greatly reduce defect cluster mobility \[30, 31, 50\]. In addition substitutional solute atoms decrease the mobility of defects in Fe to a lesser extent, depending on the misfit of the solute atom with the matrix \[49\]. Furthermore, substitutional and interstitial solute atoms form mixed interstitial/substitutional atom atmosphere which can effectively pin the irradiation-induced defects. Certain combinations of interstitial and substitutional solute atoms were associated with anisotropic strain fields in bcc lattice, leading to strong elastic interactions between defects and solute atoms. Likewise, the pre-existing dislocation network in F-M steels is pinned by the solute atom atmosphere which greatly reduces the recovery processes (cross-slip and climb) at high temperatures, giving F-M alloys desirable elevated temperature properties. However, the high concentration of numerous alloying additions makes it hard to evaluate the individual and combined effect of the solute atoms on defect mobility.

The cascade-induced sudden motion of defects observed during in situ irradiations is analogous to the motion of sub-visible defect clusters with \(\frac{1}{2}a_b<111>\) Burgers vectors described earlier in this section. The one-dimensional intermittent defect jumps in NF616 and HCM12A observed under irradiation suggest a mechanism by which the initially trapped defect clusters are set free by the necessary energy provided by the cascade impact. Once de-trapped, the defect clusters move with low activation energies within the glide cylinder until reaching the next trap in its glide cylinder. Figure 3-50 shows the experimental setup for the in situ observations of sudden jumps and jerks in NF616 and HCM12A. The defect cluster (red loop) exhibits a jump between two traps (yellow discs), possibly solute atoms or
complexes. Although the glide cylinder along <111> direction is tilted in this grain orientation (close to [111] zone axis), the projection of the defect motion appears one dimensional on the TEM screen as shown in Figure 3-50.

Interestingly there no sudden defect jumps were observed at 673 K. The absence of one-dimensional defect motion can be attributed to the sessile <100> type defect clusters that predominantly form at high temperatures in Fe [24]. This is at first puzzling, since the theory of isotropic elasticity favors formation of \( \frac{1}{2}a_0<111> \) defect clusters over \( a_0<100> \) defect clusters due to their smaller Burgers vector. However, an anisotropic elasticity study conducted by Dudarev et al. showed that formation of \( a_0<100> \) defect clusters become increasingly favorable above 573 K due to spin fluctuations in Fe at elevated temperatures [51]. Although defect clusters with \( \bar{b} = a_0<100> \). are immobile, they have a strong strain field (\( G.b^2 \) is large) that allows them to interact strongly with the defects in the close vicinity and absorb them.

While both <100> and \( \frac{1}{2} <111> \) defect clusters are pure-edge prismatic in nature, the <100> 100 loops necessitate a larger jump distance than <111> 111 loops. Marian and Wirth reported a high migration energy that exceeds 2.5 eV for <100> loops. Thus <100> loops stay as immobile if not de-trapped by very high energy cascades during irradiation [29].
At 673 K, even though defects in NF616 appear to be created in cascade events, they can grow and coalesce. The larger average defect size and the lower defect density can be attributed to the coalescence of defects and enhanced elimination of the defects at the surface due to this increased mobility, especially in the sub-visible scale. This indicates less efficient trapping of defects by interstitial and substitutional solute atoms. The fact that there was no noticeable interaction of these relatively mobile defects with grain boundaries (no denuded zones) or with the pre-existing dislocation network (no climb) at 673 K, suggests that they have little long range motion.

The microstructure evolution in HCM12A at 673 K exhibited strong similarities to the lower temperature irradiations of NF616 and HCM12A. Once the threshold dose for
defect accumulation was reached, 2-5 nm defects were formed and accumulated with minimum interaction with each other and with the pre-existing microstructure. Constant defect size in HCM12A suggests more efficient trapping of defects in this alloy compared to NF616. The differences in the concentration of interstitial and substitutional solute atoms in the alloy matrix of NF616 and HCM12A are not quantified. However, HCM12A is expected to have a significantly higher density of interstitial and substitutional solute atoms in the alloy matrix because:

1. HCM12A has higher Cu and Cr compared to NF616 (+1% Cu and +2% Cr). Both solutes were reported to decrease defect mobility in Fe [25, 32]. T. Hamaoka et al. reported a comparative study in which mobility of defect clusters in binary alloys of Fe with various levels of solute atoms were investigated using a high voltage electron microscope. They showed that even 50 appm of Cu significantly decreased the jump distance and frequency of defect clusters in Fe at 298 K. The effect of Cr on defect mobility is discussed later in this section.

2. More importantly, the relatively short tempering time of HCM12A (45 min in HCM12A and 90 minutes in NF616) is expected to result in a significantly higher concentration of solute atoms in the alloy matrix compared to NF616. After the normalization treatment, the solute atoms are homogenously distributed in the alloy matrix and the subsequent tempering treatment allows solute atoms to diffuse and form precipitates. Precipitates in NF616 and HCM12A generally form at grain and lath boundaries; for that reason they have negligible interaction with the irradiation-induced defects in the alloy matrix. Clearly, shorter tempering time will allow less time for diffusion and a relatively high concentration of solute atoms will remain in the alloy matrix.
Consequently, the constant size of defects in HCM12A at 673 K can be attributed to the enhanced trapping of defects by the relatively high concentration of substitutional and interstitial solute atoms in the matrix of HCM12A.

The mechanism by which the alignment of defect structures in NF616 occur is not known, however the mutual elastic interactions between clusters with \(<100>\) Burgers vectors may lead to the formation of these superstructures, possibly to minimize the internal strain energy. The formation of relatively larger and more precisely aligned defect superstructures in Fe compared to Fe-Cr alloys can be attributed to increase in the defect mobility in the absence of solute atoms. Jenkins et al. reported the influence of Cr content on the structure of extended defects. The defects in Fe-8%Cr were smaller and higher in density compared to ones observed in pure Fe. This was attributed to Cr atoms which reduce loop mobility. This was also confirmed by in situ observations of defect motion during irradiation of Fe and Fe-8%Cr \[24\]. However, the mechanism by which this occurs is unclear. Terentiev et al. reported a reduction in mobility of interstitial defect clusters in binary Fe–Cr alloys in relation to pure Fe which is caused by the long-range, attractive interaction between Cr atoms and crowdions in Fe-Cr alloys \[52\]. NF616 has a similar base composition to the Fe-Cr alloys that Jenkins et al. studied, however, it is anticipated that the defect clusters in NF616 to be trapped more efficiently by the additional substitutional and interstitial solute atoms.

The microstructure of NF616 evolved remarkably differently at 773 K. Although defects of sizes 2-5 nm appeared spontaneously under the ion beam, in agreement with lower temperature irradiations: their frequency was low, and they disappeared slowly. However, defect formation at 773 K did not represent a dominant effect. The frequency of defect formation was significantly low which suggest that most defect clusters were not making it to TEM-visible sizes during the irradiation of NF616 at 773 K. There is a steady state of defect production under irradiation, during which point defects and their clusters are constantly
created. Low efficiency of defect production at 773 K can be attributed to the annihilation of defect clusters by recombination at this temperature.

In pure Fe, vacancies, interstitials and their clusters become thermally mobile at relatively low temperatures. This can activate recombination in pure Fe at relatively low temperatures. However, in complex F-M steels like NF616 and HCM12A, the irradiation-induced defects are efficiently trapped and recombination can possibly be activated at elevated temperatures, at which thermal energies can overcome the binding energy of defects with solute atoms.

It is possible that at 773 K, the recombination and absorption is dominant and the TEM-visible defects observed in our experiments represent a fluctuation in this behavior. This is supported by the instability of the 2-5 nm defect clusters observed during in situ irradiation of NF616 at 773 K. In the infrequent event of a 2-5 nm defect formation at 773 K, the newly formed defects started to lose contrast and all defects disappeared under irradiation. The gradual fading of defects was also observed under thermal conditions. The dramatic and gradual decrease in contrast can be attributed to the shrinkage of defects due to the recombination and absorption with the thermally mobile sub-visible defects under irradiation. The fact that 2-5 nm defects were immobile in their lifetime (~28s) suggests that they are still, to an extent, trapped by the solute atoms and only the sub-visible defects are thermally mobile at 773 K.
Chapter 4

Modeling of primary defect formation and accumulation

The theoretical model developed to explain the initial stages of irradiation-induced microstructural evolution is discussed in this chapter. The key question is how to relate the processes of damage creation by ion-matter interaction and succeeding interactions between defects to the microstructure evolution observed using TEM. The objective is to develop a simplified rate-theory model that provides a rough estimate of the primary defect formation and accumulation under heavy ion irradiation in a complex F-M steel, NF616 explaining its principal features listed again in Section 5.2. The difficulty in modeling comes from the following facts:

(i) The gap in length and time scales between what is happening at the atomic scale in the first picoseconds of ion impact and the linked microstructural changes observed on a larger scale over minutes.

(iii) The limitations in the experimental tools do not allow gathering information on the initial stages of irradiation-induced damage development. It is not possible to image or characterize defects smaller than 1-2 nm with electron microscopy techniques.

(ii) The complexity of the initial microstructure makes it difficult to estimate the effect of initial microstructure on irradiation-induced microstructure evolution. The concentration of interstitial and substitutional solute atoms in the alloy matrix strongly affects the mobility of defects; however the exact concentration of solute atoms and the combined effect of these solute atoms on defect mobilities are not known.
4.1 Summary of previous studies on primary damage formation in Fe

During heavy ion irradiations of Fe and Fe-Cr alloys, nanometer sized defects were reported to appear after a threshold dose was reached [14]. Similarly, Robertson et al. reported no visible damage in different purities of alpha-iron following an ambient irradiation to low doses with fission neutrons in a reactor [53]. Theoretical studies, such as molecular dynamics (MD) simulations provide valuable information on sub-visible (<1 nm) cascade events which occur in the first few picoseconds of the cascade impact. MD studies showed that a distribution of point defects and sub-visible clusters form in high energy displacement cascades initiated by heavy ions and neutrons [14]. Interestingly, the intra-cascade clustering fraction of interstitials in Fe is significantly higher than that of vacancies and nanometer sized interstitial clusters are predicted to be highly mobile along <111> [14]. This is confirmed by in situ TEM studies of defect clusters in pure Fe [30].

Because visible damage appears only after a threshold dose, multiple cascade impacts are thought to be necessary for visible clusters to form in bcc Fe and its alloys under neutron and ion irradiation [14, 25]. Cascade-overlap mechanism is based on the experimental observation that TEM-visible defects in Fe were only observed at doses which spatial overlap of multiple cascades is reached. Although multiple cascade impact models based on cascade-overlap mechanism are proposed by many investigators [25, 27], the process of defect formation in these cascade overlaps was not mechanistically explained. Although in cascade-overlap mechanism, the spatial super positioning of cascade damage produces TEM-visible defects, the mechanism by which this occurs is unclear [25, 27].

It is possible, however, that cascade overlap with the preexisting microstructure or with pre-formed defect clusters explains the threshold dose. There are only a few MD studies about the cascade-overlap in Fe which investigated the influence of existing damage from previous cascades on defect formation [14, 54, 55]. These simulations were conducted by initiating displacement cascades near existing defects and the final defect configuration was
compared to the initial one to study the cascade-overlap phenomena. Stoller and Guiriec studied the effect of a cascade impact on various defect cluster configurations commonly observed in the debris of high-energy cascades in pure Fe [14]. The first configuration was comprised of 30 vacancies and interstitials, as well as one di- and one 7-interstitial cluster. The second configuration included a 6-vacancy void and a 9-vacancy loop, with four di-, one tri-, and one 8-interstitial clusters. The third configuration comprised only a single 30-vacancy void. Eight simulations were run by initiating different PKAs in the close proximity of the initial defect configurations mentioned above. The same set of PKAs was used for all three defect configurations and compared with the results obtained for the perfect (initially defect-free) lattice [14]. Figure 4-1 shows a comparison of the results obtained in the perfect crystal and in the crystal with three different defect configurations. On average, a substantial decrease in the number of defects was observed for the two configurations that are characteristic of high energy cascades. A small increase in the number of defects was observed when the cell contained only a small void comprised of 30 vacancies, although the authors note that this increase may not be statistically significant. These results are in accordance with the previous studies by Gao et al. on the simulation of cascade-overlap in Fe, which also reported reductions in defect density when a cascade was initiated in close vicinity of the debris of defects created by the previous cascade impacts [14, 54].

Nathan et al. reported the effect of cascade overlapping on pre-formed interstitial clusters trapped by helium atoms in iron [55]. MD simulations captured de-trapping of TEM-visible (91-member) dislocation loops by high energy PKAs, and changes in cluster size and Burgers vector in some cases [55].
4.2 Model of Defect Accumulation According to Experimental Observations

Given the experimental observations summarized in Chapter 3, we propose a qualitative model of defect accumulation that attempts to rationalize the observations.

1. Because the (i) defect size does not vary with temperature between 20 and 573 K, (ii) defect motion and appearance/disappearance is only observed when the beam is hitting the sample and (iii) no interaction of the damage is seen with the pre-existing material microstructure, it is concluded that in this temperature range visible defect formation and accumulation is driven by cascade impact.

2. Because (i) there is a threshold dose below dose below which no defect accumulation occurs, and (ii) molecular dynamics simulations show that, the size of defect clusters formed directly in the cascade are below the visibility limit, it is concluded that multiple cascade impacts, occurring on regions where a pre-existing defect cluster concentration already exists are necessary for visible defect formation.
3. Because (i) the visible defect jumps (observed in the TEM while the ion beam is on) occur in a direction consistent with glide along the dislocation loop glide cylinder, (ii) the damage accumulation is quite different in pure Fe and Fe-Cr (larger defects) and (iii) molecular dynamics simulations suggest that defect trapping solutes occurs in the material, it is concluded that defect coalescence occurs by cascade induced de-trapping of solute trapped defect clusters leading to allowed glide in their glide cylinder by which they can for larger defects.

4. The visible defect clusters are presumed to be interstitial in nature, in accordance with previous studies in which the defects were large enough for their nature to be determined.

5. The defect cluster density saturates (at different levels) after a dose of ~6 dpa, which is likely caused by the increased concentration of vacancies in the matrix causing the cascade induced glide to no longer be effective at making the defect clusters grow.

6. At high temperature, (673-773 K), thermal effects start to be important so that previously immobile vacancy clusters now cause the visible interstitial defect clusters that are able to form to become unstable and gradually disappear by absorption of vacancy clusters.

According to this model, interstitial clusters are created directly in cascades, and are trapped by impurities in the material. As other cascades hit, and the concentration of much such clusters increases, some of the existing clusters are de-trapped, allowing them to move in the glide cylinder of the defect ((111) direction). During this glide they may interact with and coalesce with other clusters, creating larger clusters. Because such glide is not temperature dependent, the behavior at 20 K is similar to that at room temperature and higher. When many of these coalescence events occur, the defects become big enough to be visible in TEM. In parallel, the separation of interstitials into clusters causes the vacancy concentration in the
lattice to increase, up to a point where the glide cylinders become so saturated with vacancies that glide events no longer cause the clusters to grow. At that point, the observable defect density saturates and the average defect size remains constant with dose.

To properly model the defect accumulation mechanism proposed above, it would be necessary to model the individual defect cluster sizes, from two to 30 or 40-defect clusters, their interaction and size distribution evolution, taking into account both vacancies and interstitial clusters, their different rates of creation in cascades, potentially different mobilities and reaction rates, and trapping by solute impurities. Such modeling is clearly beyond the scope of this work, and an approach based on cluster dynamics would be necessary to fully model the full size distributions, from which the visible defect cluster concentration could be derived.

We attempt in the following section to perform a rough estimate of visible defect accumulation based on a simplified version of the model above with the intention of checking the overall numbers.

4.2.1 Simplified model of defect accumulation

Three main important assumptions lie behind the model proposed to describe primary defect formation in NF616 under ion-irradiation.

**Assumption 1:** The defect clusters observed with the TEM are assumed to be of interstitial nature as stated above. It was not possible to determine the nature of the nanometer sized defects observed in our irradiation experiments, however previous studies about the irradiation-induced defects in Fe showed that defects that were large enough to characterize were of interstitial nature.

**Assumption 2:** Only the largest (20-member) intra-cascade clusters were included in calculations for simplicity. Coalescence of the 20-member clusters provides the shortest path to form TEM-visible clusters according to the model proposed.
**Assumption 3:** Ion beam-induced defect cluster motion is considered in the model. The effect of temperature on microstructural evolution is minimal below 573 K; therefore thermal defect motion is not taken into account in the model. This includes thermally-driven defect recombination and defect loss to sinks.

4.2.2 *Evaluation of the minimum number of interstitials in a visible cluster*

In this section the minimum number of interstitials necessary to form a TEM-visible cluster is estimated. Previous MD studies showed the formation of highly mobile prismatic dislocation loops from the clustering of platelets of interstitials [3], as discussed in Chapter 1. The least number of interstitials in a prismatic loop is given as [46]:

\[
n = \frac{\pi d^2 b}{4V_a}
\]

where \(d\) is the diameter of defect cluster, \(V_a\) is the atomic volume and \(b\) is the magnitude of the Burgers vector of \(\frac{1}{2}<111>\). \(n\) is calculated as \(\sim 80\) using \(V_a = 0.008 \text{ nm}^3\) (\(r_a\) (atomic radius)=0.126 nm), \(d = 2 \text{ nm}\) and \(b = 0.203 \text{ nm}\).

4.2.3 *The primary damage*

Energetic ions travelling through the solid create energetic recoils referred as the primary knock-on atoms (PKA), as detailed in Chapters 1 and 2. A fraction of these PKAs have enough energy to trigger a displacement cascade which results in the formation of interstitial and vacancy clusters of various sizes. Therefore, the PKA spectrum in the sample is essential to estimate the distribution of intra-cascade defect clusters formed in the cascade.
The recoil spectrum of 1 MeV Kr ions in NF616 was generated using the SRIM code [42]. The input for the SRIM includes chemical composition, displacement energies for the elements, energy and angle of the ion beam which are given in Chapter 2 (Table 2-4).

Figure 4-2 shows a SRIM simulation of a 1 MeV Kr ion travelling through a solid with the composition of NF616. Details of the SRIM calculations are given in Chapter 2. The path of the Kr ion corresponds to the red dots and the displacements generated by the ion to green dots. Inset in Figure 4-2 is a close-up view of the ion track and of a sub-cascade initiated by a recoil.

The SRIM code allows to save the number and energy of the PKAs generated by each ion. SRIM runs were performed for $10^4$ ions to obtain good statistics and average results were used in the calculations. On average, ~56.2 PKAs were generated per ion along its path in NF616. A program was written which sorts through the SRIM output and collects the PKA energies to create the recoil spectra. The energy distribution of PKAs obtained by the SRIM simulation of NF616 irradiated with 1 MeV Kr ions is shown in Table 4-1.

Figure 4-2 SRIM simulation of a Kr ion travelling through the 100 nm-thick NF616 sample. Ion track and displacements created by the ion are highlighted by red and green dots, respectively. Inset shows close-up view of the sub-cascade structure.
The data listed in Table 4-1 shows that ~24% of all the PKAs have kinetic energies higher than 1 keV. Table 4-2 lists the fractions of point defects that survive in interstitial and vacancy defect clusters, and the cascade survival efficiency as a function of PKA energy used in more detailed cluster dynamics simulations performed by Xu et al. [46]. Note that interstitial clusters are assigned a “negative” sign and vacancy clusters a “positive” sign.

The survival efficiency is introduced by Xu et al. to account for the total number of interstitials or vacancies that survive both in-cascade recombination during the rapid recovery stage captured in MD simulations, and the initial cascade aging when the remaining mobile interstitial and interstitial cluster defects diffuse through and away from the vacancy-rich core of the cascade following the rapid recovery [46]. The cascade survival efficiency was calculated by considering the cascade healing/in-cascade recombination of

---

Table 4-1 The energy distribution of PKAs for NF616 irradiated with 1 MeV Kr ions as calculated by the SRIM code.

<table>
<thead>
<tr>
<th>PKA Energy (keV)</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-1</td>
<td>76.0</td>
</tr>
<tr>
<td>1-10</td>
<td>18.7</td>
</tr>
<tr>
<td>10-20</td>
<td>2.38</td>
</tr>
<tr>
<td>20-30</td>
<td>0.97</td>
</tr>
<tr>
<td>30-40</td>
<td>0.55</td>
</tr>
<tr>
<td>40-50</td>
<td>0.37</td>
</tr>
<tr>
<td>50-60</td>
<td>0.25</td>
</tr>
<tr>
<td>70-80</td>
<td>0.15</td>
</tr>
<tr>
<td>80-90</td>
<td>0.11</td>
</tr>
<tr>
<td>90-100</td>
<td>0.10</td>
</tr>
<tr>
<td>100-200</td>
<td>0.48</td>
</tr>
<tr>
<td>200-300</td>
<td>0.17</td>
</tr>
<tr>
<td>300-400</td>
<td>0.087</td>
</tr>
<tr>
<td>400-500</td>
<td>0.054</td>
</tr>
<tr>
<td>500-600</td>
<td>0.034</td>
</tr>
<tr>
<td>600-700</td>
<td>0.024</td>
</tr>
<tr>
<td>700-800</td>
<td>0.015</td>
</tr>
<tr>
<td>800-900</td>
<td>0.0057</td>
</tr>
<tr>
<td>900-1000</td>
<td>0.0005</td>
</tr>
</tbody>
</table>
defects in the MD stage. Kinetic Monte Carlo simulations were employed by Xu et al. to take into account the additional recombination during the initial interstitial diffusion stage [46].

Those MD calculations show that intra-cascade interstitial clusters are significantly larger than vacancy clusters, as shown in Table 4-2. The data listed in Table 4-2 is used to calculate the average number of interstitial clusters produced in NF616 by 1 MeV Kr ions. Table 4-2 shows the partition of surviving Frenkel pairs into interstitial and vacancy clusters, $N_C(T)$, calculated using the following formula:

$$N_C(T) = N_{FP}(T) \times f \times C$$  

where, $f$ is cascade survival efficiency, $C$ is the ratio of defect clusters to the NRT number of Frenkel pairs (the values of $C$ are listed in Table 4-2) and $N_{FP}(T)$ is the total number of Frenkel pairs produced by a PKA with kinetic energy $T$ according to the NRT model and it is given by

$$N_{FP}(T) = \frac{0.8T}{2E_d}$$  

Table 4-3 gives the average number of interstitial clusters of a given size that survive upon the impact of a PKA calculated using the values given in Table 4-2 and Equation 4-2. Here negative and positive numbers indicate interstitial and vacancy clusters, respectively. For example, an average of 1.224 20-member interstitial cluster is produced for every 20-100 keV PKA. It is evident from Table 4-3 that a reasonable number of interstitial clusters (>16i) are created by PKAs having energies greater than 20 keV.
Table 4-2 Fractions of cascade-surviving point defects contained in small interstitial (1 to 20-member) and vacancy (1 to 9-member) clusters and survival efficiency of point defects, for four different cascade energy intervals (data from [57]). The energy distribution of PKAs was calculated using SRIM.

<table>
<thead>
<tr>
<th>PKA energy (keV)</th>
<th>≤2</th>
<th>2&lt;10</th>
<th>10&lt;20</th>
<th>≥20</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of PKAs</td>
<td>83.68</td>
<td>10.42</td>
<td>2.36</td>
<td>3.54</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cluster Size/Cascade energy</th>
<th>≤2</th>
<th>2&lt;10</th>
<th>10&lt;20</th>
<th>≥20</th>
</tr>
</thead>
<tbody>
<tr>
<td>-20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.017</td>
</tr>
<tr>
<td>-16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.027</td>
</tr>
<tr>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0.011</td>
<td>0.025</td>
</tr>
<tr>
<td>-9</td>
<td>0</td>
<td>0</td>
<td>0.041</td>
<td>0.038</td>
</tr>
<tr>
<td>-8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.051</td>
</tr>
<tr>
<td>-7</td>
<td>0</td>
<td>0.035</td>
<td>0.097</td>
<td>0.074</td>
</tr>
<tr>
<td>-6</td>
<td>0</td>
<td>0.085</td>
<td>0.11</td>
<td>0.076</td>
</tr>
<tr>
<td>-5</td>
<td>0</td>
<td>0.15</td>
<td>0.12</td>
<td>0.085</td>
</tr>
<tr>
<td>-4</td>
<td>0.069</td>
<td>0.14</td>
<td>0.11</td>
<td>0.1</td>
</tr>
<tr>
<td>-3</td>
<td>0.1</td>
<td>0.13</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>-2</td>
<td>0.37</td>
<td>0.18</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>-1</td>
<td>0.45</td>
<td>0.28</td>
<td>0.27</td>
<td>0.22</td>
</tr>
<tr>
<td>1</td>
<td>0.91</td>
<td>0.67</td>
<td>0.46</td>
<td>0.31</td>
</tr>
<tr>
<td>2</td>
<td>0.095</td>
<td>0.33</td>
<td>0.24</td>
<td>0.21</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
<td>0.16</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.11</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.095</td>
</tr>
</tbody>
</table>

Cascade survival efficiency (f) | 0.4 | 0.25 | 0.13 | 0.12 |
Table 4-3 Average number of interstitial clusters produced in cascades with the given PKA energies (data from [57]). The energy distribution of PKAs was calculated using SRIM.

<table>
<thead>
<tr>
<th>Cascade energy (keV)</th>
<th>≤2</th>
<th>2&lt;10</th>
<th>10&lt;20</th>
<th>20≤100</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of PKAs</td>
<td>83.7</td>
<td>10.4</td>
<td>2.36</td>
<td>2.68</td>
</tr>
<tr>
<td>Cluster Size/Average PKA energy (keV)</td>
<td>1</td>
<td>6</td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>-20</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.22</td>
</tr>
<tr>
<td>-16</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.94</td>
</tr>
<tr>
<td>-12</td>
<td>0</td>
<td>0</td>
<td>0.221</td>
<td>1.8</td>
</tr>
<tr>
<td>-9</td>
<td>0</td>
<td>0</td>
<td>0.824</td>
<td>2.74</td>
</tr>
<tr>
<td>-8</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.67</td>
</tr>
<tr>
<td>-7</td>
<td>0</td>
<td>0.53</td>
<td>1.95</td>
<td>5.32</td>
</tr>
<tr>
<td>-6</td>
<td>0</td>
<td>1.28</td>
<td>2.21</td>
<td>5.47</td>
</tr>
<tr>
<td>-5</td>
<td>0</td>
<td>2.24</td>
<td>2.31</td>
<td>6.12</td>
</tr>
<tr>
<td>-4</td>
<td>0.276</td>
<td>2.09</td>
<td>2.21</td>
<td>7.34</td>
</tr>
<tr>
<td>-3</td>
<td>0.416</td>
<td>2.01</td>
<td>2.21</td>
<td>9.14</td>
</tr>
<tr>
<td>-2</td>
<td>1.5</td>
<td>2.67</td>
<td>2.77</td>
<td>11.3</td>
</tr>
<tr>
<td>-1</td>
<td>1.81</td>
<td>4.14</td>
<td>5.39</td>
<td>15.9</td>
</tr>
</tbody>
</table>

4.3 Calculation of rate of formation of visible defect clusters

From the previous section, there is a continuous production of 20-member interstitial clusters under irradiation. The generation rate of intra-cascade 20-member interstitial clusters (\.nm^3.s^1\), \(G_{20i}\), can be expressed as a function of the ion flux (\(\Phi\)), the average number of PKAs produced per ion (\(N_{PKA}\)), fraction of PKA’s that have enough energy to form intra-cascade clusters (\(P\)), the average number of clusters created per PKA (\(N_C\)), and the thickness of the foil (\(h\)).

\[
G_{20i} = \frac{\Phi N_{PKA} P N_C}{h}
\]  

4-4

Table 4-4 shows the rate of 20-member interstitial (20i) production, \(G_{20i}\), calculated according to Equation 4-4 using the parameters listed.
According to the model, 20i clusters, once formed, are immediately trapped by solute atoms; however the ion beam can detrap them with a certain probability, which allows them to exhibit 1-D movement in their glide cylinder till they are trapped again. This allows 20i clusters to merge with other interstitial clusters while travelling between traps. By this process 40, 60 and 80-member clusters are produced by coalescence of clusters that are de-trapped by the ion beam, as shown schematically in Figure 4-3. As an example, the formation rate of 40i clusters from 20i clusters can be expressed as:

\[
\frac{dC_{40i}}{dt} = (\pi R^2 \bar{x}) \phi \frac{1}{\bar{h}} FN_{PKA} V_C C_{20i} = 4-5
\]

where \( R \) is the cluster radius of the, \( \bar{x} \) is the average glide distance of detrapped clusters when hit by cascade, \( F \) is the fraction of PKA’s with enough energy to cause de-trapping and \( V_C \) is the cascade volume.

The de-trapping frequency of 20i defect clusters (s^{-1}) can be given by

\[
\nu = (\pi R^2 \bar{x}) \phi \frac{1}{\bar{h}} FN_{PKA} V_C C_{20i} = k C_{20i} = 4-6
\]

where \( k \) is a constant which explains the likelihood that an existing cluster will be detrapped by an incoming cascade event. By rearranging the variables in Equation 4-6, \( k \) can be written as:

### Table 4-4 Rate of formation of 20i clusters and the parameters used in calculation.

<table>
<thead>
<tr>
<th>Rate of 20i formation (#.nm^{-3}.s^{-1})</th>
<th>Ion flux (ions.nm^{-2}.s^{-1})</th>
<th>Number of PKAs per ion</th>
<th>Fraction of (20-100 keV) PKAs</th>
<th>Number of 20i produced by a 60 keV PKA (20-100 keV)</th>
<th>Foil thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( G_{20i} )</td>
<td>( \phi )</td>
<td>( N_{PKA} )</td>
<td>( P )</td>
<td>( N_C )</td>
<td>( h )</td>
</tr>
<tr>
<td>0.000092</td>
<td>0.005</td>
<td>56.2</td>
<td>0.0268</td>
<td>1.22</td>
<td>100</td>
</tr>
</tbody>
</table>
The rate constant, $k$, and the values of the parameters used in calculations are listed in Table 4-5. These parameters are determined as follows:

**$F$ (fraction of PKA’s with enough energy to cause de-trapping):** Capps et al. showed that PKAs with energies greater than 5 keV detrapped 92-member interstitial clusters from helium atoms ~20% of the time [55]. This is used to estimate $F$ in our calculations. The fraction of PKAs with energies greater than 5 keV is calculated as 9.44% by using SRIM, and 20% of this value gives $F$.

**$R$ (radius of the 20i cluster):** The radius of the 20i interstitial cluster is calculated by using equation [46]:

$$R = \left( \frac{nV_a}{\pi b} \right)^{1/2}$$

by inserting the values ($V_a = 0.008 \text{ nm}^3$, $d = 2 \text{ nm}$, $b = 0.203 \text{ nm}$) we obtain $R = 0.5 \text{ nm}$

**$\bar{x}$ (average jump distance of defects under irradiation):** In our model, $\bar{x}$ is defined as the average distance between solute traps and it is expected to have the same value for sub-visible and small TEM-visible (2-5 nm) clusters since they see same solute distribution. Therefore, the average jump distance measured (5 nm) for NF616 (Section 3.1.3) is used as $\bar{x}$.

**$V_c$ (cascade volume):** To our knowledge, the cascade volume data for the wide PKA energy spectrum considered in our calculations is not reported. However, MD simulations of cascades in Fe conducted by Stoller et al. estimated an average size of ~5 nm for 5 keV cascades [14]. In our calculations, average diameter of cascade is assumed to be ~9 nm for the
range of PKAs that are assumed to cause detrapping (5-100 keV), and $V_C$ is calculated by assuming a spherical shape for the cascades, and is equal to 3093 nm$^3$. 

Table 4-5 Calculation of rate constant ($k$) and the parameters used in calculation.

<table>
<thead>
<tr>
<th>Fraction of PKAs that cause detrapping</th>
<th>Cluster radius (nm)</th>
<th>Cascade volume (nm$^3$)</th>
<th>Average jump distance (nm)</th>
<th>Rate constant (s$^{-1}$nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F$</td>
<td>$R$</td>
<td>$V_C$</td>
<td>$x$</td>
<td>$k$</td>
</tr>
<tr>
<td>0.019</td>
<td>0.5</td>
<td>3093</td>
<td>5</td>
<td>0.64</td>
</tr>
</tbody>
</table>

As mentioned in Section 4.2.1, the minimum number of atoms for visible defects is calculated as ~80 atoms. Figure 4-4 shows the paths considered in this simplified model in calculating the rate of formation of 80i clusters from sub-visible 20i, 40i and 60i clusters.

![Figure 4-3 Schematic illustration of an interstitial prismatic loop moving in its glide cylinder while interacting with the defects till it is trapped by the solute atom. Blue region is the attractive interaction volume between the interstitial cluster and the solute atom.](image-url)
According to the model, the set of equations given below account for the coalescence events between clusters shown in Figure 4-4 and given as:

\[
\frac{dC_{20i}}{dt} = G_{20i} - kC_{20i}C_{20i} - kC_{20i}C_{40i} - kC_{20i}C_{60i} \\
\frac{dC_{40i}}{dt} = kC_{20i}C_{40i} - kC_{40i}C_{20i} - kC_{40i}C_{40i} \\
\frac{dC_{60i}}{dt} = kC_{40i}C_{60i} - kC_{60i}C_{20i} \\
\frac{dC_{80i}}{dt} = kC_{60i}C_{80i} + kC_{80i}C_{40i}
\]  \(4-9\)

The set of Equations (4-9) can be solved numerically using the parameters given in Table 4-5 to determine the concentration of defect clusters as a function of irradiation time and dose.

### 4.4 Results

The density of 20i, 40i, 60i and 80i were calculated using Equation 4-9 are given as a function of irradiation dose in Figures 4-5 and 4-6. The parameters used to calculate \(k\) and \(G_{20i}\) are given in Tables 4-4 and 4-5.
It was possible to use experimental data from the low-dose in situ irradiation of NF616, as given in Chapter 3 to benchmark the results. In situ irradiation of NF616 at room temperature yielded a defect density of $\sim 9 \times 10^{-7}$ defects nm$^{-3}$ (assumed 100 nm foil thickness) at 0.1 dpa. However, the invisibility criteria, $\mathbf{g} \cdot \mathbf{b} = 0$, states that only a fraction of the total loops formed can be imaged for a given reflection vector, $\mathbf{g}$. While using a 110-type $\mathbf{g}$ vector, 1/2 of $\frac{1}{2}<111>$ and 2/3 of $<100>$ loops are visible. In addition previous studies showed a balanced population of loops of both types in Fe-Cr alloys [25]. Therefore a factor of $\sim 1.7$ is used to account for loops that are invisible due to the $\mathbf{g} \cdot \mathbf{b} = 0$, assuming equal fractions of $\frac{1}{2}<111>$ and $<100>$-type loops, which means that the actual density is $9.1 \times 10^{-7}$ defects nm$^{-3}$.

Furthermore, there was no visible defect formation below 0.01 dpa. Figure 4-5 shows the calculated values of defect density ($C_{20i}$, $C_{40i}$, $C_{60i}$, and $C_{80i}$) as a function of irradiation dose. The accumulation of the sub-visible clusters ($C_{20i}$, $C_{40i}$, $C_{60i}$ and $C_{80i}$) is controlled by the reactions given in Figure 4.4. Note that $C_{20i}$-$C_{60i}$ would all be TEM-invisible.

Figure 4.6 shows the density of TEM-visible ($C_{80i}$) defect clusters as a function of dose. This accounts for the threshold dose required for the onset of defect accumulation in NF616 at 298 K. According to the calculated density of 80i clusters, there is no visible defect formation below $\sim 0.07$ dpa, in agreement with the experimental results. These rough calculations show that by using plausible parameters, it is possible to obtain a good approximation of the visible defect density so that the defect formation mechanism envisaged for this work is reasonable, and can explain the observations. The slope of the defect density curve was higher than would be expected, since the vacancy mobility was neglected.

As mentioned in Chapter 3, saturation of defect clusters was observed at high doses at all temperatures. However, in the current rough estimate the concentration of 80i clusters will continue to increase with irradiation time since no defect elimination term is included in Equation 4-9. It is expected that, with increasing irradiation dose, the vacancy cluster concentration will steadily increase such that interstitial clusters will increasingly gather...
vacancies as they glide between solute traps. This will cause saturation in defect density and limit the interstitial cluster size.

In this scenario, a steady state could be established in which a stable concentration of interstitial clusters of fixed size is formed which will coexist with a high density of vacancies which will preclude further growth.

At high doses, defect superstructures appear (finger like defect agglomeration see Figure 3-32) which likely form as a result of elastic interactions between clusters leading to formation of large cluster “rafts” or “fingers”, as observed. Such behavior has not been modeled in any rate theory or cluster dynamics work we are aware of.
Figure 4-5 The density of 20i, 40i and 60i as a function of irradiation time in NF616 irradiated with 1 MeV Kr ions.
Figure 4.6 The density of TEM-visible defects ($\delta_0$) as a function of irradiation time in NF616 irradiated with 1 MeV Kr ions.

```
Defect density
(\delta_0\text{ defects nm}^{-3})
```

```
0 1x10^6 1.5x10^6
5x10^7
0 0.05 0.1
Dose (dpa)
```

No TEM-visible defects
Chapter 5

Conclusions and future work

5.1 Summary and conclusions

A systematic study was conducted of the microstructure evolution under irradiation of ferritic-martensitic steels, which are primary candidates for fuel cladding and internal applications in the Sodium Fast Reactor, as well as first wall and blanket materials in future fusion concepts because of their favorable properties. Since the microstructure evolution in those materials under irradiation is one of the key issues for the selection of these materials in the demanding environments, developing a fundamental understanding of the irradiation-induced microstructure in these alloys is crucial in designing new alloys with optimal properties.

The goal of this project was to investigate the evolution of the microstructure of the advanced commercial F-M steels, NF616 and HCM12A, under heavy ion irradiation and in a broad temperature range (20-773 K) to doses of up to ~10 dpa. In the range of temperatures and doses observed, the fact that these irradiations were performed in situ and the detailed microstructure observations allowed the determination of a plausible mechanism for defect accumulation in these alloys.

An in situ heavy ion irradiation technique was used to study these alloys by creating irradiation damage in the alloys, while it is being observed in a transmission electron microscope. In situ irradiations provide information on the kinetics of irradiation-induced defect microstructure evolution and its impact on alloy stability in real time with precise control of irradiation dose and temperature.

The main experimental results from this project are the following:

Threshold dose for defect accumulation and initial radiation damage
Defects started to form after a threshold dose was reached between 20 and 773 K in NF616 and HCM12A. Once the threshold for defect accumulation was reached, defects appeared as black dots (2-5 nm in diameter) in bright-field transmission electron microscopy images. These defects are likely clusters or loops with Burgers vectors of $\frac{1}{2}<111>$ or $<100>$, formed as a result of multiple cascade impacts (in 34 ms or less) at all temperatures.

The threshold dose for defect accumulation shifted to higher doses with temperature. Between 20 and 573K, defects appeared around 0.1 dpa, whereas defects appeared around 2.5 dpa at 673 K in NF616 and HCM12A alloys. The threshold dose shifted to even higher doses (3-4 dpa) in NF616 irradiated at 773 K and the rate of defect formation per unit area was lowest of all irradiations.

**Defect formation and elimination**

The appearance and disappearance of defects in NF616 and HCM12A were seen under the ion beam. The defects appeared and disappeared continuously and suddenly, flickering on and off when the ion beam was on. During the irradiation of NF616 at 773 K, 2-5 nm defects formed suddenly similar to the lower temperature irradiations but they were unstable and gradually shrunk and disappeared over a relatively long time. This defect disappearance was also observed when the ion beam was turned off, indicating a thermally driven effect.

**Defect motion**

A significant fraction of defect clusters displayed sudden one-dimensional jumps over several nanometers in between 20 and 573 K. This defect motion was driven by the ion beam, as defect clusters remain thermally immobile after they were formed between 20 and 573K. For the jumps studied, the defect motion was consistently in an apparent $<211>$ direction which projects over the likely Burgers vector direction (111). Interestingly, ion beam-induced jumps were not observed during 673 and 773 K irradiations of NF616 and HCM12A. This
suggests that the TEM-visible defects that form at these temperatures to have Burgers vector \(<100>\), which are predicted to be less mobile than defects with Burgers vector $\frac{1}{2}<111>$.

During the irradiation of NF616 at 673 K, defects coalesced and aligned forming relatively large finger-shaped defects. It is important to note that merging of defects was gradual and could be clearly differentiated from the sudden jumps observed at lower temperatures. In contrast, irradiation-induced defects in HCM12A were stationary and did not participate in coalescence events at 673 K.

**Defect accumulation**

Between 20 and 673 K, the density of defect clusters increased with dose, saturating around 6 dpa. The saturation was dynamic, that is, although the density was constant, defect clusters continuously to appeared and disappeared. Quantitative analysis performed on TEM images of NF616 provided information on the trends in defect size and density with increasing dose and temperature in a wide range. The saturation defect density decreased with increasing irradiation temperature, the reduction in the density being much more noticeable at 673 K. The defect density dropped to zero at 773 K, since there was no net defect accumulation at this temperature.

The average diameter and size distribution of the defect clusters did not change with dose or with temperature for a given irradiation up to 573 K in NF616 and up to 673 K for HCM12A. During the irradiation of NF616 at 673 K, defects were approximately 3-4 times larger than those observed at lower temperature irradiations. The defect cluster density did not vary with foil thickness and there was no denuded zone near the foil edge, demonstrating that the foil surface did not have a significant effect on the defect accumulation process.

**Stability of the pre-existing microstructure**

The stability of the microstructure (grain/lath/sub-gain boundaries, dislocation networks, precipitates) of NF616 and HCM12A was monitored throughout the irradiation to ~10 dpa between 20 and 773 K. The precipitates (carbides, nitrides and Laves phases) did not
undergo amorphisation or dissolution. The pre-existing dislocation network was stable and did not exhibit climb, change morphology or increase in length. Prior austenite/lath/sub-grain boundaries were stable and no modifications in the grain boundaries were observed. These lath boundaries play a crucial role in establishing the desired mechanical properties of NF616 and HCM12A.

Although the emphasis was on studying defect cluster formation and accumulation in this project, other possible forms of radiation damage were systematically investigated. The under focus/over focus contrast technique showed no void formation in NF616 and HCM12A at any temperature. The diffraction pattern was checked systematically for extra spots and there was no precipitation observed in NF616 and HCM12A during irradiation.

**Mechanism of microstructure evolution under irradiation**

The above observations are consistent with the following mechanism of cascade-driven microstructure evolution under irradiation:

The debris of the high energy displacement cascades in NF616 and HCM12A contain interstitial clusters in the sub-visible range and interstitial clusters with Burgers vector of $\frac{1}{2}<111>$ can grow by absorption of smaller clusters through one-dimensional motion under the ion beam. The defect motion is intermittent because solute atoms in the allow matrix can trap them until they are de-trapped by cascade impact. These defect clusters interact with the defects in their glide cylinder until they are trapped again which allows them to merge with other interstitial clusters along the way, recombine with vacancies or get annihilated at the sinks such as grain boundaries, foil surface and pre-existing dislocations. When interstitial clusters with Burgers vector of $\frac{1}{2}<111>$ go through a number of coalescence events defects are created that are observable in TEM ($\sim$2 nm). The clusters with Burgers vector of $<100>$ form through the direct interaction of mobile and sub-visible $\frac{1}{2}<111>$ clusters of similar size through a reaction which can be activated by the thermal part of the cascade. The defect clusters with $<100>$ Burgers vectors have low mobility and they reach TEM-visible size by
absorption of small clusters with $\frac{1}{2}$$<_{111}$ Burgers vectors. The shift of the onset of defect accumulation to higher doses at elevated temperatures (673 and 773 K) can be attributed to the greater quenching of the cascade damage at low temperatures. At high temperatures ($\geq$673 K), the increase in the mobility of vacancy clusters can enhance recombination, which may result in a decrease in the clustering of cascade damage with increasing temperature.

In the temperature regime 20-573 K, as the irradiation proceeds the density of visible defect clusters increases and eventually saturates at ~6 dpa for irradiations. At that point the rate of defect cluster formation becomes equal to the rate of defect cluster elimination.

As the interstitial cluster density increases the vacancy concentration also increases until the glide jumps no longer result in cluster growth. This can explain the saturation of defect density and the continuous appearance/disappearance of defect clusters after saturation.

The relatively large defect size and the low defect density of NF616 at 673 K can be ascribed to the merging of defects and enhanced elimination of defects at the surface due to the increased mobility of defects. This suggests weaker trapping of defects at 673 K compared to the lower temperature irradiations; however the defects have little range of motion since no visible interaction of these relatively mobile defects with grain boundaries (no denuded zones) or with the pre-existing dislocation network (no climb) was observed.

The mechanism by which the alignment of finger shaped defects in NF616 occurs is not known, however the mutual elastic interactions between clusters with $<_{100}$ Burgers vectors may lead to the formation of these superstructures, possibly to minimize the internal strain energy. The constant size of defects in HCM12A at 673 K can be attributed to the enhanced trapping of defects by the relatively high concentration of substitutional and interstitial solute atoms in the matrix of HCM12A.

The absence of defect accumulation during the irradiation of NF616 at 773 K can be explained by the ability of vacancies to move and slowly destroy the interstitial clusters formed in multiple cascade impacts. The defects that were infrequently observed during in
situ irradiation experiments represent a discrepancy from this behavior and eventually, all of these defects gradually shrink due to the recombination with the mobile sub-visible defects under irradiation. The fact that 2-5 nm defects were immobile suggests that they are still, to an extent, trapped by the solute atoms and only the sub-visible defects are thermally mobile at 773 K.

**Modeling of primary defect formation and accumulation**

We have studied the formation of initial defect formation in NF616 using a simplified rate theory model which describes formation of visible interstitial clusters from sub-visible intra-cascade clusters through multiple coalescence events driven by ion beam-induced defect motion detailed earlier in this section.

The SRIM code was used to calculate the energy spectrum of primary knock-on atoms in NF616 under 1 MeV Kr irradiation. These values were used to estimate the type, size and frequency of intra-cascade clusters determined by molecular dynamics and kinetic Monte Carlo simulations. The density of sub-visible (20i, 40i and 60i) and visible (80i) clusters were calculated as a function of dose, by solving a set of coupled equations. According to this formulation, the rate of formation of visible clusters is expressed as a function of experimental and theoretical parameters.

The results are in good agreement with experimental defect density of NF616 measured at 0.1 dpa. In addition the results account for the onset of defect accumulation and build-up of sub-visible defects before visible defects were observed.

**5.2 Recommendations for future work**

The author of this thesis would recommend more extensive TEM analysis of the defect clusters that form in NF616 and HCM12A under irradiation, especially the relatively large ones that form in NF616 at 673 K.
Furthermore, atom probe tomography can be employed in studying the differences in solute atom concentrations of the NF616 and HCM12A. It would be beneficial to study the spatial correlation of defect clusters with solute atom complexes in the alloy matrix.

Additionally, it would be interesting to perform in situ electron irradiations on NF616 and HCM12A using a high voltage electron microscope to study the formation of defect clusters from Frenkel pairs. Furthermore, electron irradiation of a heavy ion-irradiated sample would provide additional information on the role of point defects in microstructure evolution at different temperature regimes.

Including the recombination events to the simple rate theory model would improve modeling of the saturation effects observed at high doses. In addition, the entire distribution of intra-cascade defect clusters can be included in the calculations to better predict the cascade-overlap effects, albeit with a more complex model and at a higher computational cost.

Finally, in order to ensure these alloys are applicable for structural materials in the next generation fission and fusion energy systems, the microstructural evolution of these alloys at higher doses (100-200 dpa) and high temperatures (773-873 K) needs to be evaluated.
REFERENCES

34. ASTM, "A335 / A335M-11 "Standard Specification for Seamless Ferritic Alloy-Steel Pipe for High-Temperature Service"".
41. W.S. Rasband, "ImageJ", 1997-2013, U. S. National Institutes of Health: Bethesda, Maryland, USA.
42. J.F. Ziegler, "SRIM-2011".


Vita

Cem Topbasi

Education and Research

**Ph.D. in Materials Science and Engineering.** The Pennsylvania State University, PA, USA (2014).

**Thesis:** Investigation of the fundamental mechanisms of irradiation-induced microstructure evolution of steels for next generation nuclear energy systems using in situ heavy-ion irradiation technique (GPA: 3.9/4.0).

**M.S. in Metallurgical and Materials Engineering,** Middle East Technical University, Ankara, Turkey (2008).

**Thesis:** Investigation of the effect of alloy composition and aging on the structural and magnetic properties of Ni-Mn-Ga and Ni-Mn-Al alloys for magnetic shape memory and magnetic refrigeration applications (GPA: 3.8/4.0).


Professional Experience

**Research Assistant** (Aug 2008-Aug 2014): Materials Science and Engineering Department, The Pennsylvania State University, PA, USA


**Project 2** (Oct 2010-Aug 2014): "Microstructure and Property Evolution in Advanced Cladding and Duct Materials Under Long-Term and Elevated Temperature Irradiation: Modeling and Simulation" (Sponsor: Department of Energy - Nuclear Energy University Program)


Highlights of Qualifications

- Specialized in irradiation effects in nuclear reactor materials, microstructural characterization of irradiation-induced microstructure by electron microscopy techniques, and ion-solid interactions.
- Experience in alloy production, characterization and modification techniques such as transmission electron microscopy, in situ heavy ion irradiation, X-ray diffraction, scanning electron microscopy, magnetic property measurements, metallography.