MICROSTRUCTURE EVOLUTION OF METALLIC NANOCRYSTALLINE
THIN-FILMS UNDER ION-BEAM IRRADIATION

A Thesis in
Nuclear Engineering

by
Djamel Kaoumi

© 2007 Djamel Kaoumi

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2007
The thesis of Djamel Kaoumi was reviewed and approved* by the following:

Arthur T. Motta  
Professor of Nuclear Engineering  
Thesis Advisor  
Chair of Committee

Jack Brenizer  
Professor of Nuclear Engineering,  
Chair of the Nuclear Engineering Program

Kenan Unlu  
Professor of Nuclear Engineering

Elizabeth Dickey  
Associate Professor of Materials Science and Engineering

Robert C. Birtcher  
Materials Science Division at Argonne National Laboratory  
Special Member

*Signatures are on file in the Graduate School
ABSTRACT

The microstructural evolution of nanocrystalline metallic thin-films under ion irradiation, especially grain growth and second-phase precipitation, was studied with detailed in situ experiments, and a theoretical model was developed to explain the results of grain-growth. Free-standing Zr, Pt, Cu and Au, Cu-Fe, and Zr-Fe nanocrystalline thin films prepared by sputter deposition were irradiated in-situ at the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory with Ar and Kr ions to fluences in excess of $10^{16}$ ion/cm$^2$ at temperatures ranging from 20 to 773 K.

The microstructural evolution of the thin-films was followed in situ by systematically recording bright field images and diffraction patterns at successive ion-irradiation doses. Grain growth was observed as a result of irradiation in all samples at all irradiation temperatures. The results suggest the existence of three regimes with increasing irradiating temperature: a low temperature regime (below about 0.15 to 0.22 $T_m$) where grain-growth does not depend on the irradiation temperature, a thermally assisted regime where both the grain-growth rate and the final grain size increase with increasing irradiation temperature, and a thermal regime where thermal effects dominate ion beam effects. Similarly to thermal grain growth, the ion-irradiation induced grain growth curves could be best fitted with curves of the type: $D^n - D_0^n = K\Phi$ with $n$~3 in the low temperature regime. The effect of solute addition on grain-growth was investigated using Zr(Fe) and Cu(Fe) supersaturated solid-solutions. In the case of Zr-Fe, $Zr_2Fe$ precipitates formed during irradiation (with the dose-to-precipitation of $Zr_2Fe$ decreasing with increasing irradiation temperature), whereas Cu-Fe remained as a solid-solution. The grain-growth rate and final size decreased in both alloys with respect to the pure metallic films as a result of second-phase particle pinning (Zener drag) (Zr-Fe), and solute drag (Cu-Fe). The grain-growth rate was found to depend on material and on irradiation conditions. In particular, neither grain-growth nor precipitation occurred under 1 MeV electron irradiation. Combined with rate-theory calculations, this shows that long range diffusion does not play a role in the process.
A model of grain-growth under ion irradiation in the temperature-independent regime was developed, based on direct impact of irradiation-induced thermal spikes on grain-boundaries. Grain-boundary migration occurs by atomic jumps within the thermal spike biased by the grain-boundary curvature driving force. The model incorporates cascade structure features such as subcascade formation, and the probability of subcascades occurring at grain-boundaries. This results in a power law expression relating the average grain-size with the ion dose, where the exponent is 3 in agreement with the experimental data. In the thermally assisted regime, the increased grain-growth is explained within the framework of the same model, by the increased thermal spike size with higher substrate temperature. At the highest temperatures, other effects such as subcascade overlap and point defect migration to sinks may also enhance the process.
TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... viii

LIST OF TABLES ............................................................................................................. xv

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

DEDICATION ................................................................................................................. xviii

Chapter 1  Literature Review and Motivations ............................................................. 1

1.1 Introduction ........................................................................................................... 1

1.2 Background ......................................................................................................... 2

1.2.1 Basics of Ion Radiation Damage ............................................................. 4

Damage production ................................................................................................. 4

Thermal spike phase .............................................................................................. 8

1.2.2 Phase Transformations under Irradiation .............................................. 11

Mechanism of phase transformation under irradiation ................................ 12

The bigger picture: Driven Systems ..................................................................... 16

1.2.3 Review of Grain Growth Mechanisms: ............................................... 17

General considerations .......................................................................................... 17

Driving forces involved in grain-boundary motion ........................................... 19

Pinning forces involved in boundary motion: .................................................. 21

Thermal grain-growth models ............................................................................. 23

Hillert’s model for curvature-driven grain-growth: “the drift model” .............. 26

The diffusion-like model ...................................................................................... 29

Combination model of curvature-driven and stochastic models ......... 31

Grain growth in nanocrystalline materials ....................................................... 33

Ion-irradiation induced grain growth .................................................................. 37

1.3 Motivations ......................................................................................................... 41

Chapter 2  Description of the experiment ................................................................. 45

2.1 Materials ............................................................................................................ 45

2.2 Thin-film processing by the sputter-deposition method: ......................... 46

2.3 Characterization of the microstructure of the as-deposited specimen using

TEM .......................................................................................................................... 47

2.3.1 Elemental thin-films ............................................................................... 48

2.3.2 Supersaturated solid solutions of Zr-Fe and Cu-Fe ............................ 51

2.4 Irradiation experiments .................................................................................. 59

2.4.1 Determination of ion ranges and number of atoms displaced using

SRIM2003 code .................................................................................................. 59
5.3.3 Assumption 2........................................................................................................... 148
5.3.4 Derivation of the grain-growth rate equation...................................................... 150
  Determination of $P_{GB}$ ......................................................................................... 152
  Determination of the number of displacements ($\eta$) induced in a
  thermal-spike of energy $Q$....................................................................................... 153
5.3.5 Determination of the grain-boundary mobility in the ballistic
  regime..................................................................................................................... 157
5.3.6 The grain growth equation.................................................................................... 158
5.3.7 Theory versus experiment ................................................................................... 160
5.4 Thermally assisted regime ..................................................................................... 169
  5.4.1 Temperature dependence of grain-growth under ion-irradiation ................. 170
  5.4.2 Ion-irradiation-induced grain-growth and radiation-enhanced
      diffusion ............................................................................................................... 172
  5.4.3 Effects of $T_{irr}$ on the primary stage of damage formation .................. 174

Chapter 6 Conclusions and Suggestions for Future Work....................................... 179

Bibliography ................................................................................................................ 183

Appendix A SRIM2003 irradiation simulations....................................................... 191

Appendix B C++ program used to sort through the SRIM2003 outputs to
  generate the PKA energy distribution presented in Figure 5.5......................... 196

Appendix C Number of displacements created in a thermal spike....................... 199

Appendix D Incorporation of the recoil energy distribution in the thermal spike
  model ..................................................................................................................... 204
LIST OF FIGURES

Figure 1.1: Schema of the different possible ballistic interactions of an energetic ion with a solid showing sputtering events at the surface, single-ion/single-atom recoil events, and the development of a collision cascade that involves a large number of low energy displaced atoms. ................................................................. 7

Figure 1.2: Liquid-like region in 10 keV cascades in silicon (upper left), germanium (upper right), aluminum (bottom left), and gold (bottom right). The snapshots were chosen at times when the number of atoms in large continuous liquid regions was at a maximum. The atom size illustrates the kinetic energy of each atom, with the hottest atoms being larger. In the gold cascade shown, two replacement collision sequences emanate out from the center of the cascade, producing a trail of hot atoms in their wake .......... 10

Figure 1.3: Schematic depiction of thermal grooves .................................................. 22

Figure 1.4: Hillert’s stationary distribution function for three-dimensional grain growth, plotted as a function of $R/R_c$ as well as the stationary distribution of Mulheran and Harding’s stochastic growth model in 3D and a lognormal distribution typical of experiment are included for comparison.............................31

Figure 2.1: Sputtering thin-film deposition device at the Materials Research Laboratory at the Pennsylvania State University.................................................. 47

Figure 2.2: Bright field micrographs of as-deposited Au, Pt, and Cu films revealing the nanocrystalline structure of the polycrystalline films and their diffraction patterns. All the diffraction rings can be indexed with the phases indicated in the figure and shown in Table 2.2..................................................... 50

Figure 2.3: The Zr-Fe equilibrium phase diagram.................................................... 52

Figure 2.4: Solid solubility of iron in zirconium ........................................................ 52

Figure 2.5: Cu-Fe equilibrium phase-diagram compiled by Okamoto..................... 53

Figure 2.6: Bright fields and associated diffraction patterns of Cu-3%Fe and Zr-4.4%Fe films as deposited. The films are nanocrystalline with diffraction patterns characteristic of the pure metal: the rings of the Cu-Fe films were all indexed as fcc Cu rings and the rings of the Zr-Fe films were all indexed as hcp α-Zr rings. ............................................................................................... 54

Figure 2.7: a) Schematic model of the structure of nanostructured Cu-Bi and W-Ga alloys deduced from EXAFS and X-ray diffraction measurements. The
open circles represent the Cu or W atoms, respectively, forming the nanometer-sized crystals. The black circles are the Bi or Ga atoms, respectively, incorporated in the boundaries at sites of enhanced local free volume. b) Schematic model of nanocrystalline Ag-Fe alloys according to Mossbauer spectroscopy data. The alloys consist of a mixture of nanometer-sized Ag and Fe crystals (represented by open and full circles, respectively). In the interfacial regions between Ag and Fe crystals, solid solutions Ag-Fe crystallites are formed although both components are immiscible both in the liquid state and in the solid state.57

Figure 2.8: Schematic model of the structure of nanocrystalline Cu-Fe system (Fe atoms in black).58

Figure 2.9: Damage-production cross-sections for the different irradiations of interest in this study: the number of vacancies, replacement collisions, and displacements per ion per angstrom is plotted across the thickness of the film.61

Figure 2.10: IVEM at Argonne National Laboratory.64

Figure 2.11: a): IVEM configuration. b): Sample geometry with respect to the ion beam and the grid, showing irradiated sample area (dark area) and unirradiated area (light area).66

Figure 2.12: Geometry for the evaluation of ion beam heating. \( \Delta T = T_{\text{center}} - T_{\text{Grid}} \) is evaluated. a) is the case where the film is in total contact with the grid; b) shows the case where the film is not always in contact with the grid.67

Figure 3.1: On the left, TEM bright-field image of the as-deposited Zr-1.2%Fe thin films. On the right, the corresponding diffraction pattern (DP): all rings were indexed as \( \alpha \)-zirconium.71

Figure 3.2: Thermal effect on the supersaturated (Zr-3%Fe) film. On the left: DP at room temperature (initial state). On the center: Diffraction pattern at 623 K: the arrows indicate rings associated with the new phase formed during irradiation and identified as \( \text{Zr}_2\text{Fe} \). On the right, the diffraction pattern was taken at 823 K: arrowed inner rings indicating oxide formation. Note: Diffraction patterns are from different regions which explains the different textures.74

Figure 3.3: Zr-1.2%Fe sample irradiated at 300°C with 600 keV Kr-ions (fluence of \( 10^{16} \text{ ions/cm}^2 \)).76

Figure 3.4: 500 keV Kr ion irradiation of Zr-2%Fe sample at 50K. The arrows point at new rings indicating the formation of an unidentified new phase. The
amorphous ring around the Zr101 ring suggests that at 50K the mobility of the Fe atoms is not enough to make some of the amorphous nuclei formed in cascades grow into crystalline precipitates.

Figure 3.5: Integration of the diffracted-ring intensities using ImageJ program. (a) shows the regions (rings) selected for integration by ImageJ software. (b) shows a 3-D plot of intensity versus angular position for the diffraction pattern shown in (a).

Figure 3.6: Ratio of intensity of 112 peak from the Zr2Fe precipitate to the 004 peak from the Zr matrix versus the ion fluence obtained for Zr-1.2%Fe irradiated with 600 keV Kr ions at room temperature.

Figure 3.7: Dose-to-reaction vs. irradiating temperature for Zr-1.2%Fe thin film irradiated with 600 keV Kr ions.

Figure 3.8: Microstructure of the Zr-2%Fe thin film irradiated at room temperature with 1 MeV electrons (post mortem analysis with the Philips 430 microscope).

Figure 3.9: Microstructure of the Zr-2%Fe thin film (sample S577) after irradiation at 723 K (90 dpa): a) bright field picture of the irradiated region (obtained from STEM (430 Philips microscope)); b) EDS spectrum of the irradiated region (corresponding to picture a); c) diffraction pattern of the non irradiated region; d) diffraction pattern of the irradiated region.

Figure 3.10: EDS of three regions in the Zr-1.2%Fe thin film irradiated with 1 MeV electron to a dose of 90 dpa at 723K.

Figure 3.11: Bright field image and diffraction pattern of the as-fabricated Cu-Fe thin-film (top) and the diffraction patterns of the thin-films irradiated to a final fluence of 10^{16} ions/cm^2, at 298 K (bottom left), and 473 K (bottom right), respectively.

Figure 4.1: Sequence of bright-field images taken at different ion doses showing grain growth induced by ion-irradiation (from left to right: as deposited, 5x10^{14} ions/cm^2, 2x10^{15} ions/cm^2). From top to bottom: pure Au and Pt thin-films both irradiated with 500 keV Ar ions and Cu thin film irradiated with 500 keV Kr ions at room temperature.

Figure 4.2: Pure Zr thin-film irradiated with Kr^+ (500 keV) ion at 20K. Sequence of bright-field images taken at different ion doses showing grain growth induced by ion-irradiation.
Figure 4.3: Irradiated/non-irradiated interface region in the Pt thin-film irradiated with 1 MeV Kr ions to $3 \times 10^{15}$ ions/cm$^2$ (in the irradiated area) at room temperature.

Figure 4.4: Bright-field micrograph of the interface between the irradiated (left) and unirradiated (right) regions in a Zr-1.2%Fe film irradiated with 600 keV Kr ions at an ion fluence of $10^{16}$ ions/cm$^2$ at 573 K.

Figure 4.5: Au film irradiated with 500 keV Ar ions at room temperature to a fluence of $10^{16}$ ions/cm$^2$. Top: bright field picture of the irradiated/non-irradiated interface; bottom: diffraction patterns associated with the irradiated (left) and non-irradiated (right) areas respectively.

Figure 4.6: Sequence of bright field images showing the evolution of the irradiated and the non-irradiated areas of an Au film irradiated with 500 keV Ar ions at 473 K and taken at different ion doses: (a) as deposited, (b) $8 \times 10^{14}$ ions/cm$^2$ (47 min annealing time), (c) $5 \times 10^{15}$ ions/cm$^2$ (117 min annealing time), (d) $10^{16}$ ions/cm$^2$ (180 min annealing time). Although the shadowed (non-irradiated) area reveals thermal grain growth in the Au film at 473 K, there is still a significant difference in grain size between the irradiated area and the non-irradiated area.

Figure 4.7: Evolution of the grain size distribution with ion fluence for Zr-4.4%Fe irradiated with Kr$^+$ ions at 20K.

Figure 4.8: Average grain size in Au film irradiated in situ at room temperature with 500 keV Ar ions plotted versus dose in dpa. The final dose corresponds to a dose of $10^{16}$ ions/cm$^2$.

Figure 4.9: Average grain size in Zr-Fe films irradiated in situ at 573K with 600 keV Ar and 600 keV Kr ions versus the dose in dpa.

Figure 4.10: SRIM2003 simulation of ion irradiation in 800Å thick Zr foils (5 ions): longitudinal and lateral views of the path of ions (red dots) and the displacements caused (green dots). On the left is the case of 500 keV Ar ion irradiation and on the right, that of 500 keV Kr. Regions of point defects are bigger and more dense in the case of Kr irradiation than Ar irradiation which means that the resulting thermal spike regions will be larger in the case of Kr than in the case of Ar.

Figure 4.11: Average grain size in Pt films irradiated in situ at room temperature with 500 keV Ar and 1MeV Kr ions plotted versus the dose in ion fluence (top). When plotted versus dpa, the curves collapse into one same curve (bottom).
Figure 4.12: SRIM2003 simulation of ion irradiation in 800Å thick Pt foils (5 ions): longitudinal and lateral views of the path of ions (red dots) and the displacements caused (green dots). On the left is the case of 500 keV Ar ion irradiation and on the right, that of 1 MeV Kr. Regions of point defects do not seem much bigger in the case of 1 MeV Kr irradiation than 500 keV Ar irradiation which means that the resulting thermal-spike regions will be of similar sizes for both 1 MeV Kr ions and 500 keV Ar ions. ................................115

Figure 4.13: Average grain size in Zr-1.2%Fe thin foils irradiated in situ with 500 keV Kr ions plotted versus the dose in dpa for different temperatures. This plot highlights the effect of irradiation temperature on ion beam induced grain growth in the Zr-Fe thin films. ...................................................................117

Figure 4.14: Effect of irradiation temperature on ion beam induced grain growth in Pt thin films irradiated with 1 MeV Kr ions. Average grain size is plotted versus the dose in dpa for different irradiating temperatures. .............................................118

Figure 4.15: Effect of irradiation temperature on ion beam induced grain growth in Au thin films irradiated with 500 keV Ar ions. Average grain size is plotted versus the dose in dpa for different irradiating temperatures. The curves were fitted to Eq. 4.5 and the fitting parameters are reported in Table 4.1, Table 4.2, and Table 4.5 .................................................................119

Figure 4.16: Effect of irradiation temperature on ion beam induced grain growth in Cu thin films irradiated with 500 keV Kr ions. Average grain size is plotted versus the dose in dpa for different irradiating temperatures ..............120

Figure 4.17: Au film irradiated with 500 keV ions at 473 K, at a final dose of \(10^{16} \text{ions/cm}^2\) showing the formation of faceted bubbles decorating the grain boundaries.................................................................123

Figure 4.18: Average grain size is plotted versus the dose in dpa. The plot shows the effect of intrinsic materials properties on ion beam induced grain growth in Pt thin films compared with Au. Both materials have similar collisional properties but different material properties. The Pt film was irradiated with 500 keV Ar ions at room temperature which falls in the “temperature-independent” regime for Pt. The Au foil was irradiated with 500keV Ar ions at 50K which also falls in the temperature-independent regime. .........................126

Figure 4.19: Bright fields and associated diffraction patterns of Cu-3%Fe and Zr-4.4%Fe films as deposited. The films are nanocrystalline with diffraction patterns characteristic of the pure metal: the rings of the Cu-Fe films were all indexed as fcc Cu rings and the rings of the Zr-Fe films were all indexed as hcp α-Zr rings ........................................................................................................129
Figure 4.20: Average grain size in Zr and Zr-4.4%Fe films irradiated in situ at 20K with 500 keV Kr ions plotted versus the dose in dpa ........................................... 130

Figure 4.21: Average grain size in Cu and Cu-3%Fe films irradiated in situ at room temperature with 500 keV Kr ions plotted versus the dose in dpa. The plot highlights the effect of alloying element on ion-beam induced grain growth................................................................. 131

Figure 5.1: Grain configuration: the free-energy gradient across the grain-boundary is due to the curvature driving force......................................................... 137

Figure 5.2: E parameter plotted on logarithmic scale as a function irradiation temperature for Au irradiated with 500 keV Ar ions, Pt irradiated with 1 MeV Kr ions, Zr irradiated with 500 keV Kr ions and Cu irradiated with 500 keV Kr ions. .................................................................................................................. 147

Figure 5.3: Bright-Field image of a Zr-Fe thin-film irradiated with 1MeV electron-irradiation to a dose of 80 dpa ................................................................. 149

Figure 5.4: Schematic representation of the cascade structure induced by an ion transversing a polycrystalline thin-film................................................... 150

Figure 5.5: Recoil energy-spectrum calculated using the PKA-energy data generated by SRIM2003 for simulations running 10000 ions for: 80 nm Au foil irradiated with 500 keV Ar ions, 90 nm Cu foil irradiated with 500 keV Kr ions, 80 nm Pt foil irradiated with 1 MeV Kr ions, 80 nm Pt foil irradiated with 500 keV Ar ions, 80 nm Zr foil irradiated with 500 keV Kr ions, and 80 nm Zr foil irradiated with 500 keV Ar ions.................................................. 161

Figure 5.6: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Pt irradiated with Ar 500 keV ions at 298 K. ................................................................................................................... 167

Figure 5.7: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Pt irradiated with 1 MeV Kr ions at 50 K and 298 K.............................................................................................................. 167

Figure 5.8: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Zr irradiated with 500 keV Kr ions at 20 K. ................................................................................................................... 168

Figure 5.9: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Cu irradiated with 500 keV Kr ions at 50 K. ................................................................................................................... 168
Figure 5.10: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Au irradiated with 500 keV Ar ions at 50 K. .....................................................................................................................169

Figure 5.11: Schematics of the temperature dependence of grain growth under ion irradiation ..............................................................................................................171

Figure 5.12: Mean diameter of the “molten zone” \( d_{\text{melt}} \) as a function of initial lattice temperature in a 10 keV cascade induced in Ni\(_3\)Al. .................................................................175
LIST OF TABLES

Table 2.1: Characteristics of as-deposited samples. .................................................49

Table 2.2: Summary of the irradiation conditions: melting points, temperatures of irradiation, ion type and energy. The collisional properties (displacement rate and deposited damage-energy) $F_D$ were obtained from the SRIM2003[97] Monte-Carlo code using a displacement energy of 25 eV. For Cu-3%Fe irradiated with 500 keV ions and Zr-Fe irradiated with 500 keV Kr ions the same collisional values as Cu and Zr were used.................................................69

Table 4.1: Least-squares error curve fit parameters determined for ion induced grain-growth data at cryogenic temperatures for the different films. The measured grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 50 dpa.................................................................108

Table 4.2: Least squares error curve fit parameters determined for ion induced grain-growth data at room temperature for the different films. The measured grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 50 dpa (except Zr-Fe for which the fit was done in the dose range from 0 to 75 dpa). .................................................................................................108

Table 4.3: Irradiation parameters for Zr-Fe films irradiated with both 600 keV Ar ions and 600 keV Kr ions at 573K........................................................................109

Table 4.4: Irradiation parameters for Pt films irradiated with both 500 keV Ar ions and 1MeV Kr ions at room temperature. ......................................................112

Table 4.5: Least squares error curve fit parameters determined for ion induced grain-growth data at room temperature for the different films. The measured grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 50 dpa (except Zr-Fe for which the fit was done in the dose range from 0 to 100 dpa). .................................................................................................121

Table 4.6: Apparent activation energies in the temperature-dependent regime .........122

Table 4.7: Material properties of Pt and Au and their collisional characteristics obtained from SRIM2003 code for simulations of irradiations of 80 nm thick films irradiated with 500 keV Ar ions with an incident angle of 15 degrees (from Appendix 1). .........................................................................................................................125

Table 4.8: Least squares error curve fit parameters determined for ion induced grain-growth data at room temperature for the different films. The measured
grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 100 dpa.

Table 5.1: Strength expressions for defect sinks [119].................................................. 143

Table 5.2: Parameters values for the determination of $E$................................................. 146

Table 5.3: Values of material properties involved in the thermal spike model of grain-growth under ion irradiation for Zr, Cu, Pt, and Au [133].......................... 165

Table 5.4: Irradiation parameters used to calculate $K$ ...................................................... 165

Table 5.5: Value of the parameter scaling the activation energy for atomic jumps within cascades to the cohesive energy of the material.............................................. 166

Table 5.6: Size of cascade in the thermally assisted regime............................................. 177
ACKNOWLEDGEMENTS

First, I would like to thank my advisor Arthur Motta for his valuable guidance and support throughout my PhD degree, not only on the professional level, but also humanly. This made my experience as a graduate student a very nice one.

Thanks to Bob Birtcher for the productive collaboration at the IVEM at Argonne National Laboratory.

Thanks to the committee members K. Unlu, J. Brenizer, and E. Dickey for supporting my work.

Thanks to the Materials Research Institute at Penn State, especially B. Drawl and L. Pillione for assistance with thin-film deposition.

Thanks to T. Van der Berghe, J. Perinet and I. Monnet for assistance during the electron irradiations performed at the CEA Saclay.

Thanks also to A. Liu, E. Ryan, P. Baldo, A. McCormick, L. Funk at Argonne National Laboratory for their assistance during the ion irradiation experiments.

Thanks to H. S. Kim for assistance in C++ programming.

Thanks Z. K. Liu, M. Jenkins, R. Averback, R. Schaeublin, for useful conversations on the model.

Of course, thanks to the Department of Energy for financial supporting. This study was funded by DOE Nuclear Engineering Education Research program under contract number DOE-NEER (DE-FG07-01ID14115), and by DOE-NERI (DE-FG07-04ID14613).

Enfin, un grand merci à ma mère Ourdia qui m’a bien soutenu tout au long de mes études, ainsi qu’à ma famille (Nouara, Farida, Slimane et mes neveux) et mes amis des USA et de France (surtout Christophe) qui m’ont aussi soutenu durant mon PhD et m’ont permis d’en faire une excellente expérience.
A ma mère Ourdia
Chapter 1

Literature Review and Motivations

1.1 Introduction

The stability of materials under irradiation is a fascinating question which has been the subject of scientific interest for decades, motivated both by its natural importance in terms of fundamental scientific research and its relevance to several technological problems such as the integrity of structural materials of the core components of nuclear reactors, the long term integrity of nuclear waste confinement materials and alloy preparation by ion implantation or ion-beam mixing.

Because most material properties depend strongly on the microstructure (average grain size, grain size distribution, alloying elements, second phase precipitates), it is necessary to understand the basic mechanisms of evolution of the material microstructure under irradiation in order to understand, predict and ultimately control the behavior of materials under irradiation. Two of the basic processes of microstructure evolution under irradiation are grain growth and second phase precipitation/dissolution. They are at the center of this thesis. One of the difficulties of studying these processes is the lack of kinetics information since usually samples are examined \textit{ex situ} i.e. after irradiation has been performed, so that only snapshots of the process are available. Indeed, most studies performed on ion-induced transformations including ion-irradiation induced grain growth were based on results observed after irradiation, i.e. an irradiation dose is applied to the material from which a Transmission Electron Microscopy (TEM) sample is subsequently prepared. Given the dynamic nature of the phenomena, direct \textit{in situ} observation is useful for understanding better the mechanisms, kinetics and driving force of the processes involved. Consequently it is advantageous to work with thin films at the IVEM-Tandem
facility. This facility consists of a transmission electron microscope interfaced with two ion accelerators so that the sample can be irradiated as it is observed, making it the ideal experimental setup for in situ ion beam studies involving ion implantation and/or ion damage [1, 2].

The purpose of the remainder of the chapter is to present the background necessary for understanding the phenomena observed in our study. The chapter also aims to sharpen the purpose and motivations of this study and point out more precisely the questions raised in the literature and that the study will try to answer. First some general background on ion-irradiation interaction with matter is provided as a platform from which one can approach this study. Some definitions and concepts necessary to better understand the experimental analysis are presented, including the concept of “thermal-spike” resulting from energetic particle impact. Then a literature review of irradiation-induced phase transformations is given, as well as a review of grain-growth in conventional polycrystalline materials under thermal annealing. This is followed by a review of grain-growth specific to nanocrystalline materials since all our specimens are nanocrystalline in nature and it has been reported that nanocrystalline materials may behave differently from their coarser-grained counterparts. This section will show that some experimental observations might be related to the specific nanocrystalline nature of the specimens. Finally a review of ion-irradiation-induced grain-growth is given which introduces the thermal-spike model which seems to be the most credible model of ion-irradiation-induced grain-growth. It will also point out some specific questions associated to the model that our study will try to answer.

1.2 Background

The use of charged-particles in general for the experimental study of radiation effects in materials is often required for different reasons. First of all, the displacement rates obtained under charged-particle irradiation are orders of magnitudes higher than those obtained under neutron irradiation; therefore a given level of dpa is achieved much
faster with charged particle irradiations than with neutron irradiation. In addition, a
greater degree of control is available under charged-particle irradiation compared with
the use of neutron sources. Charged-particles can be accelerated to the wanted energy,
focused into a beam and deflected to a well-defined direction and position. Also, the
impact of experimental parameters such as temperature, flux, and particle type and
energy can be more easily controlled and studied in charged-particle experiments.
Finally, charged-particle irradiated samples usually come out being non-radioactive
which eases their handling. However an important difference between neutron irradiation
and ion irradiation is due to their shorter ranges; in other words, only the near surface
layer will be damaged in the case of ion irradiation of bulk materials.

For ion-bombardment to be a useful simulation of neutron irradiation, the nature
of the radiation damage produced must be the same in both cases. One way to ensure this
is to make sure that the energy spectra (i.e. recoil spectra) of the primary-knock-on atoms
(PKAs) produced by the two types of irradiations are similar. Indeed, all damage
processes pass through the intermediate state of PKA production, and therefore if the
primary recoil spectra are sufficiently similar, the nature of the resulting damage will be
the same. For instance, Logan et al. [3] showed that bombardment of niobium by 16.4
MeV protons can produce recoils with energy spectrum very similar to that resulting
from 14 MeV neutron irradiation. However, a drawback is that they produce less than
three times more damage per projectile than 14 MeV neutrons. But since they are very
penetrating, their main use is likely to be the production of rather low damage levels in
thick samples (0.1 mm). Marwick showed, through calculations, that the primary recoil
spectrum in niobium under 33 MeV self-ion bombardment is similar to that of 14 MeV
neutron irradiation [4, 5], which suggests that a close simulation of neutron radiation
damage by ion bombardment is possible. The displacement rate per projectile being more
than 3.7x10^5 times higher in the case of ion irradiation, allowing very high neutron fluxes
(10^{18} cm^{-2}s^{-1}) to be simulated.

Other displacement mechanisms are available for neutron irradiation, from
induced nuclear reactions. By this mechanism, a neutron absorbed by a nucleus causes
radioactive decay, typically emitting an energetic gamma or alpha particle. By
conservation of momentum, the decaying atom recoils in the opposite direction, often with an energy sufficient to cause further displacements. The emitted particle can also cause damage.

In the following section, the basics of ion-irradiation interactions with matter are now presented in details in this section.

### 1.2.1 Basics of Ion Radiation Damage

#### Damage production

As an energetic ion penetrates a solid it slows down by transferring energy to electrons and to nuclei of the solid. During the interaction with the nuclei, target atoms can be displaced from their lattice position resulting in ballistic displacements. The interaction of an ion with the target atoms is governed by both the interaction potential and the kinematics of the elastic collision. The atoms which interact directly with the ion itself are called the primary-knock-on atoms (PKA). If the energy transferred to the PKA is high enough it can be displaced from its equilibrium lattice position creating a vacant lattice site and a self-interstitial atom (SIA). This vacancy-interstitial pair is called a Frenkel pair (FP). Normally the struck atom is not the one that eventually ends as a SIA; instead, the struck atom starts a replacement collision sequence (RCS) along one of the close packed crystallographic directions. The replacement collision sequence causes each atom to displace its neighbor in a “domino” effect, with the creation of a vacancy in the first position and an interstitial at the end of the sequence (hence the creation of the Frenckel pair). This process results in the transport of atoms through repeated single collision events between the incident ions and target atoms. It is at the basis of ballistic mixing technique also known as recoil implantation or recoil mixing.

In addition, when the PKA has enough energy multiple displacement process can occur where an initially displaced target atom (PKA) continues the knock-on-atom
processes producing secondary displaced atoms which in turn may displace other atoms. Overall this process of multiple collisions results in a local region with a high density of displacements called a displacement cascade. In the small region of the cascade so many atoms participate in the dissipation of the energy of the PKA that the very notion of crystalline lattice becomes difficult to define. As one can imagine, the incident ion can induce several cascades before the end of its path. Even secondary recoils can in turn generate relatively isolated “secondary” cascades if they are energetic enough.

This first stage of the displacement cascade is purely collisional in nature; it is sometimes called the ballistic phase or the collisional phase of the displacement cascade. It is well described by a series of one-to-one body elastic collisions of the ion or the PKAs with the lattice atoms. By applying the physics of Binary Collision theory the number of displaced atoms can be computed based on the Kinchen Pease formula [6] or Norgett-Robinson-Torrens (NRT). This “collisional phase” is short, (about 0.1 to 0.2 ps) - which is less than a typical lattice vibration. It ends when the incoming irradiating particle and the displaced atoms no longer have enough energy to cause further displacements.

The number of displacements caused by a PKA of energy $E_{\text{PKA}}$ is given by the NRT formula [7]:

$$\nu(\text{NRT}) = \frac{0.4E_{\text{PKA}}}{E_d}$$  \hspace{1cm} \text{Eq. 1.1}$$

where $E_d$ is the displacement energy threshold. For metals the average $E_d$ is on the order of 20-40 eV. However it is known that $E_d$ is higher in intermetallic compounds and ceramics, where sublattices and chemical ordering exist. The NRT formula 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.

In the calculations leading to the NRT formula the PKA energy is divided among all atoms in the cascade, counting as permanent atomic displacements all energy transfers above $E_d$. In reality, because of the close proximity in which these defects are created,
they interact with each other, creating defect clusters in the cascade core and/or restoring the undamaged lattice by recombinations of interstitials and vacancies reducing the total damage. This causes the final number of free interstitials and vacancies to be smaller than the total number of atoms displaced in the cascade[6]. From an energetic point of view, the cascade can be explained by the fact that when the kinetic energy of a displaced atom is low, the probability of it undergoing further low-energy scattering events will be high. Such scattering events will therefore result in many collision and displacement events occurring in near proximity to each other. Unlike the highly directed recoil implantation process where one target atom receives a large kinetic energy in a single collision event, atoms in a collision cascade undergo multiple low-energy displacement and displacement events. Indeed, calculations of the mean energy of displaced atoms show that at the end of the collisional phase most recoils are produced near the minimum energy necessary to displace atoms, $E_d$. Due to the low-energy stochastic nature of these displacement events, the initial momentum of the incident particle is soon lost, and the overall movement of the atoms in a collision cascade becomes isotropic. This isotropic motion gives rise to an atomic redistribution that can be modeled as a random walk of step size defined by the mean range of an atom with energy near $E_d$.

The knowledge of intra-cascade phenomena has greatly increased in the last 20 years [8]. The interstitials and vacancies in the cascade can either react with similar defects or with opposite defects, or remain isolated. The defect structure created and their mobility at the irradiation temperature of interest are critical to the microstructure changes occurring under irradiation. The final damaged state evolves as a result of intra-cascade clustering and recombination, and consists of a distribution of interstitial and vacancy clusters of different sizes. The spatial distribution of these defects is not homogeneous. 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 physical separation between interstitials and vacancies enhances defect clustering, relative to recombination.

The ballistic interactions of an energetic ion with a solid are indicated schematically in Figure 1.1 which shows sputtering events at the surface, single-
ion/single-atom recoil events, and the development of a collision cascade that involves a large number of low energy displaced atoms. The cascade is shown in the early displacement stage of development, where the displaced atoms occupy interstitial positions surrounding a core of vacant lattice sites.

Figure 1.1: Schema of the different possible ballistic interactions of an energetic ion with a solid showing sputtering events at the surface, single-ion/single-atom recoil events, and the development of a collision cascade that involves a large number of low energy displaced atoms, from [9].

For diffusion-dependent processes it is convenient to define the diffusivity of a species under irradiation. The effective diffusivity, $D_{\text{cas}}$ for a collision-cascade-induced random-walk process is expressed in the diffusion equation as:

$$D_{\text{cas}} = \frac{\eta <r^2>}{6}$$

where $\eta$ is the number of cascade-induced displacements per atom, dpa, $<r^2>$ is the mean squared range of the displaced target atoms, and $t$ is the cascade lifetime. The
effective diffusion coefficient scales with the dose and the damage energy but it does not contain any temperature-dependent terms. The effective diffusion coefficient described in the above equation is independent of temperature and therefore can only be compared with experiments in which mixing is also observed to be independent of temperature.

**Thermal spike phase**

When the displaced atoms have slowed down so that their energies are smaller than the displacement energy threshold $E_d$, they can no longer create displacements, which puts an end to the “collisional phase”. They share the remaining of their energy with the neighboring atoms through lattice vibrations (“phonons”). In other words they transfer their energy to the lattice as heat causing a local temperature spike to occur. In high density cascades, the average energy per atom in the cascade may be higher than 1eV/atom, and if the atom motion is treated as thermal motion with a mean energy of $k_BT$, the corresponding temperature can be thousands of degrees, exceeding the melting temperature of the material. For a high enough energy density, the whole cascade will become liquid-like as shown by molecular dynamics simulations of displacement cascades [10, 11]. The spike formation lasts about 0.1 ps.

A spike relaxation phase follows which lasts for a few ps (~10 ps). It only takes about 3 ps for the temperature to fall below the lattice melting point as the cascade is surrounded by a very large thermal reservoir which quickly “quenches” the cascade by absorbing the energy. At this point the spike undergoes a transition from heated to undercooled liquid. The spike core solidification follows. It is meaningful to talk about a thermal spike only if its lifetime $\tau_s$ is long compared to the period of lattice vibration. The chronology of events during the slowing down of an energetic PKA, and the development of its associated displacement cascade are presented in Table 1.1 adapted from [12, 13] taken from [8]. Figure 1.2 shows the results of a computer simulation of a displacement cascade resulting in thermal spikes. The many-body nature of the interactions during the thermal spike does not allow for simple analytical determination of defect production as
in the collisional phase. The number of displacements has to be calculated another way [14].

The importance of thermal spikes in ion beam mixing phenomena has been discussed over the years. At low temperatures it has been concluded that ion-beam mixing is dominated by diffusion during the thermal spike, in which case, the expression of the diffusivity of a species in a thermal-spike is believed to follow the laws of diffusion in liquids [9].

Table 1.1: Chronology of events during the slowing down of an energetic PKA, and its associated displacement cascade (from [12]).

<table>
<thead>
<tr>
<th>Duration (ps)</th>
<th>Event</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-6}$</td>
<td>Transfer of energy from energetic particle</td>
<td>Primary knock on atoms (PKA)</td>
</tr>
<tr>
<td>$10^{-6}$ 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>
</tr>
<tr>
<td>0.2-3.0</td>
<td>Thermal spike cooldown</td>
<td>Stable Interstitials (SIA) Interstitial clusters Atomic mixing</td>
</tr>
<tr>
<td>3-10</td>
<td>Cascade cooling to bulk solid temperature</td>
<td>Depleted zone in cascade core</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>
</tr>
</tbody>
</table>

As far as the terminology, in the literature, the expression “thermal spike” is used both to refer to the local region where the temperature rise occurs or to the temperature peak phenomenon itself.
Figure 1.2: Liquid-like region in 10 keV cascades in silicon (upper left), germanium (upper right), aluminum (bottom left), and gold (bottom right). The snapshots were chosen at times when the number of atoms in large continuous liquid regions was at a maximum. The atom size illustrates the kinetic energy of each atom, with the hottest atoms being larger. In the gold cascade shown, two replacement collision sequences emanate out from the center of the cascade, producing a trail of hot atoms in their wake (from [10]).

The importance of thermal spikes in ion and neutron radiation damage related phenomena is now well established within the scientific community [14-18]. It is
believed that the large difference between the PKA energies which result in thermal spikes and usual thermal atomic energies is at the root of many of the observed effects of irradiation, and which appear to contradict thermodynamic stability. In fact, the very high energies observed in these cascades are the reason why the material under irradiation may reach crystal structures and defect configurations which are normally inaccessible under thermal driving forces, such as the formation of non-equilibrium phases. The following section presents a review of phase transformations under irradiation.

1.2.2 Phase Transformations under Irradiation

Material properties can change significantly under irradiation as a result of irradiation-induced changes of the microstructure. Some of these microstructure changes are associated with irradiation-induced or irradiation-enhanced phase transformations. Under irradiation the constant production of point defects caused by the impact of energetic particles can cause defect accumulation, ballistic chemical mixing, radiation-enhanced atomic diffusion, point-defect fluxes towards point-defect sinks or towards local recombination centers, and overall changes in chemical composition due to implantation. Various combinations of the above effects are at the origin of phase stability alterations. Defect accumulation and chemical mixing increase the internal energy of the alloy and may induce amorphization [19] or destabilization of compounds such as second phase particles i.e. dissolution of ordered precipitates (intentionally used in the alloy for strengthening). Also, coupling of point defect fluxes with solute fluxes may induce solute segregation or precipitation of solute material with the matrix elements or with other solutes of the solid solution. Second phase precipitation can occur as an “enhanced/accelerated” phenomenon or as an “induced” phenomenon. Irradiation-accelerated transformation refers to the case where irradiation accelerates a solid-state phase transformation which would normally occur outside irradiation according to the phase diagram [20]. This is the case of a quenched supersaturated solid solution: the solid solution is over the solvus curve and another phase should be observed (but is not) and
radiation can accelerate this second-phase precipitation. On the other hand, *irradiation-induced phase transformation* refers to the case where irradiation can maintain the system in a (quasi)steady-state which differs from the thermodynamical equilibrium state outside irradiation. This is the case of irradiation-induced precipitation in *undersaturated* solid solutions [21]: solid solutions which are stable outside irradiation may separate in two distinct phases under appropriate irradiation conditions. Thus, ballistic chemical mixing and irradiation-enhanced diffusion compete to stabilize intermediate states of order or phases which are *metastable* outside irradiation[22].

**Mechanism of phase transformation under irradiation**

There are several mechanisms by which microstructure changes may occur during irradiation. Diffusion coefficients may increase by several orders of magnitude because of the high point defect concentrations created by irradiation. This accelerates diffusion-controlled processes such as growth of second phases. On the other hand, the observation of irradiation-induced phase changes, such as amorphization, precipitate dissolution and order-disorder transitions, has been interpreted in terms of a competition between irradiation-induced disorder and annealing, with irradiation-enhanced diffusion bringing the system back to low energy configurations.

In order to explain the phase transformations that have been observed under irradiation, it is considered that the possible atomistic configurations under irradiation are explored by two mechanisms acting in parallel, the thermally activated diffusion of point-defects on the one hand (radiation enhanced diffusion) and ballistic mixing (i.e. forced jumps due to the replacement collisions or cascade core mixing) on the other hand.

A critical question is to determine whether the structures which develop under irradiation originate from ballistic processes (displacement and replacement sequences, point-defect fluxes and point-defect mutual recombination) or processes originating from classical thermodynamics (minimization of the free energy of the crystal in the presence of the actual point-defect supersaturation) [23]. Martin and co-workers proposed in the
mid seventies that an alloy under irradiation should be looked at as an open dissipative system, and therefore it should be described with an appropriate tool different from classical thermodynamics as far as its stability and its kinetics are concerned [20, 22]. According to this group, the stability criteria for an alloy under external influences, such as ball milling or energetic irradiation, cannot be treated by equilibrium thermodynamics in a straightforward way. Indeed, a system will reach the configuration of minimum Gibbs free energy in cases where the trajectory followed in its phase space is under constant pressure, temperature and composition. Outside irradiation, during a standard thermal annealing treatment, the processes are controlled by thermally activated point-defect migration on the lattice, which promotes atomic exchanges. Under irradiation, in parallel with thermal migration, solute-defect flux coupling or atoms ejected by nuclear collision generate new paths within the phase space explored by the material during irradiation. Non-equilibrium configurations may thus be stabilized by irradiation giving rise to “metastable” phases under irradiation [22].

Some radiation-produced structures are better understood in terms of the thermodynamic approach [20]: for instance, the stability of void lattices is usually accounted for mainly by the interaction energy between voids (although kinetic processes do also contribute to this stability). Similarly, void nucleation or incoherent second phase nucleation under irradiation are described by nucleation models, the driving force of which is the lowering of the free energy of the crystal supersaturated with point-defects. In these models, the non-conservative nature of point defects, which is at the root of the ballistic processes, merely introduces a correction to the expression of the driving force.

The basic underlying assumption in the thermodynamic approach is rather simple: the structure of a crystal under irradiation is in thermodynamical equilibrium with the actual point-defect supersaturation sustained by irradiation. In such an approach, point-defect fluxes and point-defect mutual recombination have no other effect than maintaining the point-defect supersaturation at a (quasi) steady state value.

An example of phase transformation governed primarily by ballistic phenomena rather than simply by thermodynamical energy minimization principle is precipitate re-solution which is explained by dynamical solute atom injection into the matrix. This way,
existing precipitates may be dissolved if intersected by collision cascades which ‘sputter’ atoms from the precipitate surfaces progressively.

Another example where phase stability is not governed by a minimization principle is irradiation-induced precipitation in undersaturated solid-solutions. In many cases, irradiation-induced precipitation is observed to be heterogeneous [24]. The precipitates are found around extended lattice effects, free surfaces, grain boundaries etc. This type of irradiation-induced precipitation has been regarded as a result of the coupling between defect and solute-atom fluxes occurring under irradiation, and more precisely of the accumulation of solute atoms drifted towards the point defect sinks by the point defect fluxes sustained by irradiation. Second phase formation is assumed to occur when the local concentration is larger than the solute solubility outside irradiation. If this were the only mechanism to operate, then irradiation-induced precipitation would always occur heterogeneously.

However, homogeneous irradiation-induced precipitation was also reported in Al-Zn, Al-Ag, W-Re and Cu-Be alloys as well as in AISI 316 steels, for instance. This homogeneous irradiation-induced precipitation observed in undersaturated solutions was attributed to solute accumulation in point defect sinks or point-defect recombination centers. More precisely, it has been proposed by Cauvin and Martin [25, 26] that precipitates can act as recombination centers for point defects [27]. They showed that when both vacancies and interstitials exist, the precipitate-matrix interface becomes a favorable site for recombination of both types of defect leading to a local decrease of solute solubility so that precipitate nucleation and growth can be enhanced by vacancy-interstitial recombination. In their model, they consider a solid solution which contains point defects, vacancies, interstitials, and precipitates (i.e. solute aggregates) embedded in the matrix. The nucleus is visualized as a solute cluster containing solute atoms surrounded by trapped defects. In fact, a large set of parameters is needed to give a detailed description of the clusters: number of solute atoms, number of vacancies, number of interstitials, shape relative location of the species inside the cluster, etc. If one is to predict the evolution of the overall microstructure of the solid solution during irradiation, all the above parameters should be retained: depending on the shape of a cluster quite
different microstructural evolutions might result (e.g. voids instead of vacancy loops etc). In their study, Martin et al. propose that the surface of the precipitates offers trapping sites for point defects. The solute atoms are assumed to diffuse to the precipitates by a vacancy and/or by an interstitial mechanism. Then solute deposition at the cluster is favored by the vacancy-interstitial recombination reaction. Thus this model accounts for the effect of excess vacancies and interstitials on the nucleation of coherent particles which trap point defects at their interface with the matrix. The degree to which irradiation will destabilize the precipitate will be determined by the balance between many irradiation-induced processes, such as irradiation-enhanced diffusion, irradiation-induced segregation, and displacement events.

This type of precipitate growth under irradiation is different from the coarsening of precipitates during thermal ageing of alloys which is well understood. The driving force for thermal coarsening arises from the fact that the solubility of the components of the precipitate phase in the matrix phase depends on the size of the precipitate particles. This effect provides the basis for the classical theory of diffusion-controlled coarsening by Lifshitz and Slyozov and Wagner. In their theoretical study of the kinetics of thermally induced precipitation from supersaturated solid solutions, Lifshitz and Slyozov [28] modeled the case in which grains of a new phase grow as the result of diffusion processes. They depict the phenomenon of precipitation as a two-stage process where first, grains of the second phase nucleate due to concentration fluctuations, and then they either get dissolved or grow by coalescence (incorporation of small grains by the bigger ones) after they reach an appreciable size. They offer a mathematical treatment of the growth by coalescence from thermal annealing. In this approach, anisotropy is ignored and grains are assumed to be spherical. Grains larger than a critical radius grow at the expense of the smaller ones. The critical value of the radius $R_c$ is formulated. At large times $t$, $R_c$ tends asymptotically to depend on time as $t^{1/3}$, the degree of saturation drops as $t^{-1/3}$ and the number of grains as $t^{-1}$. Experimentally the predicted linear increase with time of the cube of the mean precipitate radius has been confirmed in a number of cases.
The bigger picture: Driven Systems

The study of irradiation-induced phase transformation is part of a more general field which is that of “driven systems”. They are defined as materials that are continuously maintained away from thermodynamical equilibrium by an external driving force (e.g. irradiation). For equilibrium conditions, thermodynamics and statistical mechanics can predict the steady state of any system; however driven systems are by nature far from equilibrium, and therefore classical thermodynamics fail to describe the evolution of the system. In fact, under the external driving force (irradiation) the material may reach a (quasi)steady-state configuration whose properties are generally different from the thermodynamical equilibrium properties. Equilibrium thermodynamics are not sufficient to predict phase stability or microstructural evolutions since there is competition between the ballistic, (i.e. random), mixing forced by irradiation, and the thermally activated decomposition or ordering promoted by thermodynamic forces [29]. The parameters that control the evolution of a given “driven” material are temperature and chemical composition but also other parameters related to the external force (irradiation) such as its "intensity" measured by the rate of production of displacement cascades. Geometric parameters may also be part of the control parameters such as the size of the displacement cascades produced, and the range of the forced atomic relocation in these cascades.

As far as the irradiation temperature parameter, Bellon distinguishes three regimes with respect to it [30]. The first regime corresponds to low temperature irradiation cases where thermally activated diffusion is essentially frozen. In this low-temperature regime, chemically ordered phases can be rendered disordered, and precipitates may be dissolved; more complex evolutions involving amorphization and decomposition are also observed during heavy-ion irradiation; phase stability and microstructural evolutions are completely dictated by the nature of the disorder introduced by irradiation, so that a detailed knowledge of the perturbation event, the displacement cascade for heavy-ion irradiation, is sufficient to predict the long-term evolution of the material.
The second regime corresponds to *high-temperature irradiation* where, owing to fast thermally activated diffusion, the compositional and chemical disorder created by each cascade is quickly annealed. The local disorder created by one displacement cascade is annealed over a time scale much shorter than the one separating the production of two overlapping cascades. In this regime, materials typically evolve towards states similar to the ones expected from global or local thermodynamic equilibrium. However, because irradiation creates point defects, atomic diffusion is enhanced and these evolutions are accelerated so that in the end irradiation effects simply amount to an acceleration of kinetics toward thermodynamic equilibrium.

The third regime corresponds to *intermediate irradiation temperatures* where the kinetics of defect production by irradiation is similar to the kinetics of relaxation through thermally activated diffusion. This balanced competition, although present over a smaller temperature interval, can lead to new and complex microstructural evolutions, such as *patterning reactions* [31].

### 1.2.3 Review of Grain Growth Mechanisms:

**General considerations**

Grain-growth is the process by which the average grain size of a polycrystalline material increases while the number of grains decreases respecting volume conservation. It is usually considered that in the process, large grains increase in size while small grains shrink. *Normal grain-growth* is characterized by the following attributes [32]:

1. A narrow range of grain sizes and shapes (uniform appearance)
2. Scaling: a simple change in scale is sufficient to make the distribution of shapes and sizes of two points separated in time coincide with each other. In other words, the distribution of grain-sizes when suitably scaled (by the average grain radius $\bar{R}$) remains statistically invariant (after a possible initial transient) i.e. after sufficient time,
the grain-size distribution remains similar while the average grain size increases. The invariant steady state distribution is found to be more or less independent of the initial size distribution.

3. Both grain sizes and topological parameters such as the number of sides per grain in a planar intersection or number of faces in 3-D can be fitted with a lognormal distribution i.e. the logarithm of the grain diameter and the number of faces can all be approximated by a Gaussian, “normal” distribution, hence the expression “normal grain growth” to call this type of grain growth.

4. Last but not least, during normal grain growth the average grain radius $\bar{R}$ has experimentally been reported to increase according to the power law:

$$\bar{R}^n(t) - \bar{R}^n_0 = Kt \text{ with } n \geq 2$$

Eq. 1.3

Normal grain growth in a pure material results from the interaction between the topological requirements of space-filling polyhedra and geometrical requirements for surface tension equilibrium. In principle, the conditions required for minimal interfacial energy relate the grain shape parameters (topology) with the grain size parameters, and the structural parameters (mean radius of curvature at each point on the grain boundaries. Once a complete distribution of this curvature is prescribed over each grain at every instant in time, the time evolution of the system can in principle be described by use of the principle of minimization of energy.

Indeed, grain growth is generally understood as a result of the universal thermodynamic principle that a system is most stable when it is in its lowest free-energy state. Because grain boundaries contain interfacial energy, polycrystals are at best thermodynamically metastable, with greater thermodynamical stability being achieved when the polycristal has been converted to a monocrystal. Since the network of grain boundaries in a polycrystalline material is a source of excess energy relative to the single-crystalline state, there is a thermodynamic driving force for reducing the total grain-boundary area or, equivalently, increasing in the average crystallite (grain) size. Therefore, the driving force typically associated with grain growth is the reduction of the system energy by reducing the total grain boundary surface area. Hence, by reducing the
curvature of a grain (i.e. increasing its radius) the total grain boundary area is decreased, and so will the interfacial grain-boundary energy.

The mechanism governing grain growth is usually assumed to be grain-boundary migration, which depends on the grain boundary curvature. As a result of such migration the grain boundary curvature is reduced and so is the total grain boundary area per unit volume. Since the volume of the system is constant this results in the increase of the mean grain size and the decrease of the number of grains in the system. Each separate grain will vary in size with time, the larger ones growing at the expense of the small ones. Grain growth can also be affected by other factors such as concentration gradients i.e. chemical-potential gradients. In other words, to understand grain growth in a polycrystal during thermal annealing or under irradiation it is necessary to understand the process of grain-boundary motion under these conditions. It is therefore necessary to express the driving forces and pinning forces involved during the migration of grain-boundaries. Grain growth can also occur by a mechanism of coalescence of adjacent grains [33, 34], in which case the grain growth kinetics can be more complex than the kinetics resulting from the boundary migration mechanism.

**Driving forces involved in grain-boundary motion**

The main driving force for boundary motion (hence for grain growth) is caused by the *curvature of the grain boundary* $F_c$. Because of its curvature a grain boundary is subject to tension, which creates a pressure directed towards the center of the grain boundary curvature. The assumption that the velocity of the grain boundary $v$ is proportional to this pressure difference across the boundary is commonly accepted and leads to [35-38]:

$$v = M F_c$$  \hspace{1cm} \text{Eq. 1.4}$$

where $M$ is called the *mobility* of the grain boundary, and $F_c$ is the driving force for the grain-boundary motion expressed as:
\[ F_e = C_{GB} \gamma \]  
\text{Eq. 1.5}

where \( C_{GB} \) is the curvature of the grain boundary and \( \gamma \) the grain boundary energy. The curvature of the grain boundary can be expressed as a function of the principal radii of the curvature \( r_1 \) and \( r_2 \):

\[ C_{GB} = \frac{1}{r_1} + \frac{1}{r_2} \]  
\text{Eq. 1.6}

If \( r_1 \) and \( r_2 \) are assumed to be equal, Eq. 1.5 becomes:

\[ \Delta F_e = \frac{2\gamma}{r} = \frac{4\gamma}{D} \]  
\text{Eq. 1.7}

where \( D \) is the grain diameter. There are other driving forces for boundary motion within a polycrystal. The \textit{strain energy driving force} \( \Delta F_d \) is one of them. This is actually the driving force due to the difference in dislocation density on each side of the grain boundary; and it acts to move the boundary towards the grain with the greater dislocation density. This is expressed as:

\[ \Delta F_d = \Delta \rho_d \zeta b^2 \]  
\text{Eq. 1.8}

where \( \Delta \rho_d \) is the difference in dislocation density, \( \zeta \) is the shear modulus, and \( b \) is the Burgers vector of the dislocation. \( \Delta F_d \) is referred as the strain-energy driving force because the right-hand term of the equation can be interpreted as the difference in strain energy of the neighboring grains. The system will once again evolve towards its state of lowest energy.

When studying 2-D grain-growth (basically in the case of thin-films having grain-boundaries larger than the film thickness) one should take into account the \textit{surface energy driving force} \( \Delta F_s \). Indeed the free surfaces can be seen as grain boundaries, and the difference in energies of the free surfaces of neighboring grains can be a driving force for
the grain boundary to move towards the grain with larger surface energy $\gamma_s$, leading to the growth of the grain with the smaller surface energy $\gamma_s$. $\Delta F_s$ can be expressed as:

$$\Delta F_s = \frac{2 \Delta \gamma}{\delta}$$  \hspace{1cm} \text{Eq. 1.9}

where $\Delta \gamma$ is the difference in surface energies of the neighboring grains and $\delta$ the thickness of the sample [39].

**Pinning forces involved in boundary motion:**

The forces which pin grain-boundaries and therefore slow down or inhibit grain growth need to be addressed. In the case of alloy systems and more generally impure systems, solute segregation can be a drag force acting to prevent or slow down grain growth. Indeed solute segregation can impede grain boundary migration due to the fact that the solute diffusion rate can be different from the migration rate of a pure grain boundary. The intensity of this dragging force depends on the solute concentration, the interaction of the solute atoms with the boundary, the grain-boundary atomic structure, and the solute diffusivity near the grain boundary [35].

When dispersed second-phase particles are present at the grain boundaries, they can be obstacles to their migration. They can somehow make “holes” in it. The movement of the grain-boundary away from the particle leads to the healing of the holes. This process results in the creation of free boundary surface around the particle, which translates into an increase in free energy:

$$\Delta F_z = \frac{3}{2} \frac{\gamma f}{r}$$  \hspace{1cm} \text{Eq. 1.10}

where $r$ is the radius of the particle, $f$ the volume fraction of the second-phase particles, $\gamma$ the grain-boundary surface energy per unit area, assuming spherical particles randomly and uniformly distributed. Zener [40, 41] was the first one to study this process.
and try and model it hence this pinning force due to dispersed second phase particles is often called the “Zener drag effect”.

In the case of thin-films in which the grain diameter is larger than the film thickness (2-D structure), the grain boundaries move through the sample thickness, laterally. As a result, *thermal grooves* may form at a grain boundary on both free surfaces as shown in Figure 1.3. This can pin the grain boundary for, should it break away from the thermal groove, its area would increase. The drag force is expressed as:

$$\Delta F_g = \frac{\gamma}{3\delta}$$  \hspace{1cm} \text{Eq. 1.11}

where $\delta$ is the film thickness. However in our case, since the initial grain size is about 10 to 15 nm and the film thickness about 80 nm, it is clear that we start with a 3-D microstructure, which means that the driving and dragging forces listed for the case of 2-D microstructures should not apply, at least at the beginning of the experiments. They might play a role towards the end of the experiments only if the grains get bigger than the film thickness.

---

Figure 1.3: Schematic depiction of thermal grooves [35]
Thermal grain-growth models

Although grain growth in polycrystalline materials has been the object of several studies in the past five decades [32, 42-48], the processes involved are still not completely understood. The theory has not evolved much since the model proposed by Turnbull and Burke [47] and the equations derived by Hillert describing isothermal grain growth [46]. Particularly a departure from the commonly accepted parabolic law describing the grain size dependence on time is often observed experimentally but explanation for such a departure is still lacking. In fact, two main features of normal grain growth which seem to be universal (i.e. independent of the type of material) remain unexplained: (i) the power law evolution of the average grain size and (ii) the establishment of a stationary scaled grain-size distribution.

In 1952 Burke and Turnbull proposed that grain-boundary migration is driven by the local curvature of the grain-boundaries and showed that, in this case, the value of the growth exponent $n$ in the power law given in Eq. 1.3 is 2. The other important feature is the establishment of a stationary scaled grain-size distribution i.e. with increasing annealing time, the grain-size distribution $f(R,t)$ is time-invariant when plotted as a function of the normalized grain-radius $\frac{R}{R}$. In 1965 Hillert[46] showed that such scaling behavior is consistent with the predictions of a mean-field model for grain growth driven by grain boundary curvature. Because many features of grain growth are shared by the Ostwald ripening phenomenon, Hillert used the same mathematical analysis used by Lifshitz and Shyozov, and Wagner (LSW) [28] for the study of Ostwald ripening (i.e. second-phase particle coarsening in a supersatured solid solution) in order to obtain the grain size distributions. He used a continuity equation describing the variation with time of the grain size distribution.

During the 1950s and 1960s, more sophisticated analytic models were developed to include the effect of solute drag and second-phase particles on grain-growth [49]. In parallel, experimental investigations of isothermal grain-growth kinetics were extended to a variety of materials measured over a wide range of temperatures. These experimental
studies revealed that the assertion of a single value for the growth exponent—as predicted by the analytic models—was no longer valid. In the experiments, \( n \) was found to take values ranging from 2 to 4. Additionally, the shape of the stationary size distribution was repeatedly better fitted with a lognormal function [32, 50] which is incompatible with the predicted distribution of Hillert’s model for curvature-driven grain-growth.

In 1974, Louat suggested an alternative mechanism for grain growth based on a stochastic diffusion process of unspecified nature in grain-size – time space [51]. Louat’s model predicted a growth exponent of 2 and a stationary scaled grain-size distribution described by a Rayleigh function. This was an appealing result from the standpoint of agreement with experiment, because the Rayleigh and lognormal distributions are quite similar at the standard deviations typical of experimentally observed grain-size distributions [50, 52].

However, Louat’s stochastic growth model was later found to violate volume conservation [53]. In 1992, Mulheran and Harding [54, 55] proposed a correction for this flaw in the form of a physical ‘diffusion’ mechanism for grain growth—the occurrence of stochastic jumps of atoms across grain boundaries—instead of curvature-driven grain-boundary migration. Such a model satisfies volume conservation, but it manifests a growth exponent of 4, rather than 2, and a stationary size distribution that is roughly Gaussian in shape.

Since the range of experimentally measured values for \( n \) is usually found between the corresponding values for purely curvature-driven and purely stochastic grain growth, respectively, it was considered possible that these two mechanisms are simultaneously active during grain growth in real materials. Since 1980, a number of researchers attempted to formulate a self-consistent grain-growth model combining curvature-driven and stochastic mechanisms including Hunderi and Ryum [56, 57], Pande and Dantsker [50, 58-60] and Mulheran and Harding [54, 55]. In most models except for the one developed by Mulheran and Harding, the stochastic term was usually introduced in order to account for the statistical variation in the local environment surrounding each grain, rather than to include the effect of random atomic jumps on the grain-growth kinetics. Moreover, the ‘combination’ models developed prior to the work of Mulheran and
Harding suffered from the shortcoming that volume conservation could be ensured only by postulating a fixed ratio between the rates of the underlying deterministic and stochastic growth mechanisms. This unphysical constraint was finally avoided by combining Mulheran and Harding’s stochastic model with Hillert’s model for curvature-driven growth, because both of these models satisfy volume conservation independently.

Performing a dimensional analysis of the continuity equation governing the evolution of the grain size distribution in such a combination model, Wu [61] found that the instantaneous value of the growth exponent $n$ is a function of the average grain size, changing continuously from 4 when $R$ is small to 2 when $R$ is large. If growth in real materials were governed by this continuity equation, then the measured value of $n$ could depend on the particular grain-size interval traversed during the measurement. The experimentally determined spectrum of values for $n$ would then be a natural consequence of grain-size-dependent competition between the stochastic and curvature-driven growth mechanisms.

Helfen tried to answer a few questions relevant to the validation of such combination models [48] such as (i) whether the discrepancies observed between theory and experiment regarding the value of the growth exponent and the shape of the stationary size distribution arise from a superposition of two different grain-growth mechanisms or not, (ii) the manner in which the system evolves from primarily stochastic growth at small grain sizes to curvature-driven growth at large sizes i.e. if the transition is confined to a narrow range of grain sizes or extends over one or more orders of magnitude in $R$, and (iii) the grain size at which the transition between the two regimes typically occurs.

The results of the study are very interesting and will be reported in this review as it seems that the idea of a “combination model” is more and more accepted but first, the two approaches will be presented separately: Hillert’s model for curvature-driven grain-growth also referred to as “the drift model” in the literature and the model of stochastic grain-growth also referred to as the “diffusion-like model”.
Hillert’s model for curvature-driven grain-growth: “the drift model”

In this model of curvature-driven grain growth, Hillert expresses the velocity of the grain-boundary as a function of the grain radius $R$ as follows:

$$\frac{dR}{dt} = \alpha M_\gamma \left( \frac{1}{R_c} - \frac{1}{R} \right)$$  \hspace{1cm} \text{Eq. 1.12}

where $\alpha$ is $\frac{\pi}{6}$ in the case of 2-D grain-growth and 1 in 3-D grain-growth, $M$ is the (temperature-dependent) mobility of the grain-boundary; the quantity $R_c(t)$ is the so-called critical grain size, the value of which at any given time $t$ is specified by volume conservation ($\int R^3 f(R,t) dR = \text{constant}$) and is such that grains larger than $R_c(t)$ grow and grains smaller than $R_c(t)$ shrink. The mobility and the grain boundary energy are assumed to be independent of $R$ and $t$.

Eq. 1.12 is the basic equation that Hillert used in his derivations. It is the result of a one-grain model of grain growth, i.e. one considers the behavior of only one grain growing in a mean-field created by smearing all the other grains together with their grain boundary energy uniformly out through the system. The rate of growth of a grain of size $R$ is the rate of growth of such a grain in its average homogenized surroundings, which is once again similar to the LSW treatment of Ostwald ripening. In that model, a second phase particle grows in a supersaturation that is the average supersaturation due to all the precipitates in the system (mean field theory) and a grain will grow due to the average out energy of all the grain boundaries in the homogenized ensemble.

The evolution of the grain-radius distribution $f(R,t)$ is governed by the continuity equation:

$$\frac{\partial f}{\partial t} = -\frac{\partial j}{\partial R}$$  \hspace{1cm} \text{Eq. 1.13}

where $j(R,t)$ is the current in grain-size-time space. In the case of Hillert’s model for curvature-driven growth the continuity equation becomes:
\[ \frac{\partial f}{\partial t} = -\frac{\partial (fv)}{\partial R} \]  

Eq. 1.14

where \( v \) is the average-grain boundary velocity under the driving force and using Eq. 1.12, Eq. 1.14 becomes:

\[ \frac{\partial f(R, t)}{\partial t} = -\alpha M \gamma \frac{\partial}{\partial R} \left[ \left( \frac{1}{R_c} - \frac{1}{R} \right) f(R, t) \right] \]  

Eq. 1.15

Based on experimental observations, the distribution of grain sizes must be quasi-stationary. Solving the continuity equation with the boundary limit \( f(R = 0, t) = 0 \) gives the quasi-stationary distribution and the velocity of the critical grain with radius \( R_c \), Hillert [27] found that the stationary scaled grain-size distribution \( P_H \), given a critical size \( R_c(t) \) defined as:

\[ P_H(u) = (2e)^m \frac{mu}{(2-u)^{2+m}} \exp \left( \frac{2m}{u-2} \right) \text{ for } 0 \leq u < 2 \]  

Eq. 1.16

where \( u \) is the normalized grain size defined as \( u = \frac{R}{R_c} \). \( R_c \) is equal to the average grain size \( \bar{R} \) for \( m=2 \) (for 2D grain growth) and \( \frac{9}{8} \bar{R} \) for \( m=3 \) (for 3D grain growth). For this solution, the average grain radius \( \bar{R} \) was found to increase parabolically with time \( t \) according to

\[ \bar{R}^2(t) - \bar{R}_0^2 = Kt \]  

Eq. 1.17

Where \( K \) is proportional to the grain-boundary mobility. The distribution \( P_H(u) \) is rather inconsistent with a lognormal function typical of growth-induced grain-size distributions measured in polycrystalline metals and ceramics. Especially the rather shallow increase in \( P_H \) at \( R<R_c \) and the steep fall off above \( R_c \) are and the Hillert distribution’s small population of grains larger than \( \sim 1.5R_c \) and maximum allowed grain size of \( 2R_c \). It is shown in Figure 1.4.
Discussion of Hillert’s model: the basis of the model is Eq. 1.12. However there is no good physical foundation for this relationship which was postulated by Hillert. Hillert explicitly states that this drift velocity is chosen because it is the simplest one with the required behavior that small grains shrink while large grains grow. Eq 1 is practical in the sense that after evaluating the magnitude of $\alpha$ the mathematical treatment of grain growth according to the drift model is identical with coarsening of second-phase particles when the rate controlling step is the particle-matrix inter-phase reaction also known as Ostwald ripening phenomenon. In fact Eq. 1.12 works for the treatment of Ostwald ripening in case of infinite dilution but because grain growth does not occur in an average environment, there is no counterpart to the infinite dilution case of Ostwald ripening in grain growth: grains share common boundaries in a topologically connected ensemble. The equivalent would be Ostwald ripening for large volume fractions but there is no commonly accepted theory for such a case. Hence Pande argues that the use of LSW approach cannot be justified for grain growth. Pande argues that the main problem with the deterministic equation is that it ignores the topological environment of the grains, i.e. it assumes that the coarsening rate of a grain is independent of its surroundings and is determined only by its size. Eq. 1.12 results from arguments that grain boundary migration is driven by the curvature of the boundary curvature. However this approach ignores the topological environment of grains, i.e. how the grain-boundaries are joined together into a space-filling ensemble with requirements to the number of grains that can meet. Moreover the grain size distribution calculated with Hillert’s model has found poor agreement with experimental studies. Indeed, there is a large discrepancy between the grain size distribution it predicts and the experimentally observed one. This shows that this Eq. 1.12 may not be a good approximation of the drift velocity. The Hillert distribution is much more peaked than the distribution found experimentally, which means that driving force suggested by Hillert levels off too rapidly with increasing $(R/R_c)$.

In fact, Hillert’s approach was to assume an expression for $v$ and then solve for $f(R,t)$ in the continuity equation given in Eq. 1.14 and his analysis resulted in an expression for the variation with time of the mean grain radius (power law). Another
approach would be to take the distribution of grain sizes \( f \) as the input in the analysis since \( f(R,t) \) can be determined experimentally, and then derive an expression for \( v(R,t) \) and the average grain growth rate. An approach like this was tried by Feltham and then by Hunderi and Ryum but resulted in a very complex expression for the velocity of the grain-boundary.

The diffusion-like model

Louat’s stochastic model for thermal grain growth: Louat [51, 52] notes that in contrast to Ostwald ripening, and as consequence of grain contiguity “grain collisions” occur in which faces are gained or lost and that the process of addition and subtraction of faces during grain growth is seen to have a random component. He thus assumed random walk for grain-boundaries in real space resulting in a diffusion-like motion in grain size space and thus ignored grain curvature effects. Louat argued that \( D \) is independent of \( f, R, \) and \( t \), which led to the continuity equation:

\[
\frac{\partial f(R,t)}{\partial t} = D \frac{\partial^2 f(R,t)}{\partial R^2}
\]

Eq. 1.18

Using the boundary conditions \( f(0,t)=0 \) and \( f(\infty,t)=0 \), and the condition of conservation of volume, a solution is proposed of the form:

\[
f(R,t) = A R \exp \left( -\frac{R^2}{k} \right)
\]

Eq. 1.19

where \( A \) is a normalization constant which varies with time and \( k \) is another time independent parameter. Hunderi and Ryum [57] argued that the physical basis of this diffusion model is even weaker than of the drift model. Louat and later Pande have certainly emphasized the stochastic nature of the grain growth process but the it is not completely clear. The stochastic nature of the process is due to the fact that the grains of a particular size \( R \) have different surroundings so that some of these grains will grow while
others of the same size will shrink at a given time. How this effect of variable surroundings should be treated in an analytical model is not clear.

Mulheran and Harding’s model for stochastic grain growth: Mulheran and Harding [54, 55] proposed an interpretation of Louat’s stochastic model for grain growth based on the physically plausible assumption that atoms located at grain boundaries may jump from one grain to another in a stochastic manner. Mulheran and Harding obtained the following continuity equation:

$$\frac{\partial f(R, t)}{\partial t} = \frac{\partial}{\partial R} \left[ \frac{D_0}{R^{m+1}} \frac{\partial}{\partial R} f(R, t) \right]$$  \hspace{1cm} \text{Eq. 1.20}

where $D_0$ is a positive constant and $m=2$ for 2-D grain-growth and $m=3$ for 3D grain-growth. After applying volume conservation considerations, Mulheran and Harding found the following stationary scaled grain-size distribution:

$$P_{MH}(u) = Ku^m \exp\left( -\frac{K}{m+1} u^{m+1} \right) \text{ with } K = (m+1) \left( \frac{\Gamma[2m/(m+1)]}{\Gamma[(2m-1)/(m+1)]} \right)^{1/m}$$  \hspace{1cm} \text{Eq. 1.21}

where $\Gamma$ is the gamma function and $u$ is defined as $R/R_c$. $R_c$ is found to be equal to $\bar{R}$ for 2-D grain-growth, and $R_c \approx 1.08 \bar{R}$ for 3-D case. As in the Hillert model, the average grain radius increases according to a power law, but, unlike the Hillert case, the exponent depends on the dimensionality of space:

$$R^{m+1}(t) - R_0^{m+1} = \beta D_0 t$$  \hspace{1cm} \text{Eq. 1.22}

where $\beta \approx 6.41$ for two-dimensional growth ($m=2$) and $\beta \approx 10.80$ for three-dimensional growth ($m=3$).

Figure 1.4 shows the stationary distribution of Mulheran and Harding’s stochastic growth model in 3D plotted as a function of $R/R_c$ compared to Hillert’s stationary distribution function for three-dimensional grain growth, and a lognormal distribution typical of experiment. For $R<R_c$, Mulheran and Harding’s stationary distribution increases with a slope similar to that of experimental distributions, but at larger grain
sizes $P_{\text{MH}}$ falls off much too rapidly, resulting in an unphysically small population of grains larger than $\sim 1.5R_c$.

Figure 1.4: Hillert’s stationary distribution function for three-dimensional grain growth, plotted as a function of $R/R_c$ as well as the stationary distribution of Mulheran and Harding’s stochastic growth model in 3D and a lognormal distribution typical of experiment are included for comparison; from [48]

**Combination model of curvature-driven and stochastic models:**

Hunderi and Ryum [57] and more recently Pande [60] have argued that in real materials stochastic growth may occur simultaneously with curvature-driven boundary migration, i.e. both the “drift” and the diffusion mechanism play a role in the grain growth process [56]. Hunderi and Ryum agree with Pande that a stochastic element is inherent in the grain growth process but argued that the physical basis for this effect is not a stochastic motion of grain boundaries in real space but a stochastic motion in grain size space, and the reason for that stochastic behavior is because all grains of a given size R have different environments. But they find the basis of that model unrealistic.
Grain-growth is formally looked at as the motion of individual grains in grain-size-time space. In the grain-growth model combining curvature-driven and stochastic mechanisms, the flux $j$ of grains in this space is caused by a diffusion like process and by a driving force:

$$j(R,t) = -D \frac{\partial f(R,t)}{\partial R} + f(R,t)v(R,t)$$

Eq. 1.23

where $f(R,t)$ is the grain-size distribution function, $v$ is the drift velocity due to the curvature driving force and $D$ is formally equivalent to a diffusion coefficient [57].

The continuity of the grain flux in the size-time space then becomes:

$$\frac{\partial f}{\partial t} = \frac{\partial (-j)}{\partial R} = \frac{\partial}{\partial R} \left( D \frac{\partial f}{\partial R} \right) + \frac{\partial}{\partial R} (fv)$$

Eq. 1.24

This expresses that a change in the number of grains in a size-class $R$ is caused by a flux from neighbouring size classes. If grain growth is considered as a diffusion-like process in the grain-size time space like Louat does, the “drift term” ($fv$) is set to zero.

Consistent with this approach, Wu proposed that the overall current $j(R,t)$ in grain-size space can be specifically written as the sum of the currents corresponding to the Hillert and Mulheran–Harding models [61]:

$$j(R,t) = j_H(R,t) + j_{MH}(R,t)$$

Eq. 1.25

Helfen & al. derived the resulting continuity equation for grain growth:

$$\frac{\partial f(R,t)}{\partial t} = -M_0 \frac{\partial}{\partial R} \left[ \left( \frac{1}{R_c} - \frac{1}{R} \right) f(R,t) \right] + D_0 \frac{\partial}{\partial R} \left[ R^{1-m} \frac{\partial}{\partial R} f(R,t) \right]$$

Eq. 1.26

The constants $M_0$ and $D_0$ act as weighting coefficients for the relative contributions made by the curvature-driven and stochastic mechanisms, respectively, to the total flux in size-time space. A solution $f(R,t)$ for a particular pair of nonzero constant values ($M_0,D_0$) can be determined for arbitrary values of $M_0$ and $D_0$. The same holds for the time evolution of the critical grain size $R_c$. 
Helfen et al. [48] evaluated this grain-growth model incorporating both curvature-driven and stochastic boundary migration mechanisms for arbitrary relative weighting of the two mechanisms. The numerical solution of the corresponding continuity equation confirmed the results of Wu’s dimensionless analysis i.e. at small average grain size R, the kinetics of grain growth follow a power law with an exponent \( n \) equal to 4, as expected for growth resulting entirely from stochastic jumps of atoms across grain boundaries, whereas at large grain sizes the growth kinetics are governed by the parabolic law (\( n=2 \)) for curvature-driven growth (Hillert’s model). The transition between the two regimes is smooth and occurs over approximately one order of magnitude in grain size. Within the transition region, the instantaneous value of the exponent \( n \) is a function of the grain size, suggesting that any value between 2 and 4 could be observed in a given material, depending on the range of grain sizes traversed during the measurement. In reality, experimental values of \( n \) are indeed bounded by these limits, but the underlying reason is unlikely to be a superposition of the stochastic and curvature-driven growth mechanisms considered in the model, as the transition to fully curvature-driven growth is estimated to be complete by a grain size of about 20 nm.

Helfen et al. argue that even in specimens with an initial grain size well below 20 nm, it would be challenging to obtain experimental evidence for the stochastic mechanism, given the likelihood that the rate-controlling step for curvature-driven boundary migration is itself a function of the grain-size in nanocrystalline materials.

**Grain growth in nanocrystalline materials**

As mentioned before, according to classical models for grain growth, the rate at which the grain size (diameter) \( \bar{D} \) increases is governed by the intrinsic grain-boundary mobility, which depends strongly on temperature, and by such factors as defect concentrations, second-phase precipitates, and the segregation of impurity atoms to the boundary cores. Since all of these parameters are usually assumed independent of \( \bar{D} \), the classical models assume that a single growth mechanism is rate-controlling at all length
scales. Measurements of grain-growth kinetics in conventional polycrystalline samples ($\overline{D} \sim 1 \, \mu m$) have uncovered no exceptions to the latter assumption; however, studies performed in nanocrystalline materials ($\overline{D} \leq 100 \, nm$) have found the growth rate to be much slower than that derived from an extrapolation from the coarse-grained regime.

The prevailing view has attributed this unexpected slowdown to the solute drag resulting from impurities introduced during the preparation of nanocrystalline samples. It, therefore, comes as a surprise that recent theoretical considerations present suggest an enhanced intrinsic stability with respect to coarsening in materials with nanometer-sized grains, even in the absence of significant impurity concentrations.

These theoretical models claim the existence of a critical grain size $\overline{D}_{cr}$—likely in the submicron range—below which the rate-controlling step for grain-boundary migration is not the boundary-curvature-driven diffusion of atoms across and along the boundary cores (as in conventional, coarse-grained materials) but rather the migration and/or rearrangement of other features associated with the grain boundaries, such as the triple junctions (intersections of three or more grain boundaries) or the excess volume localized in the core regions. These other mechanisms have been introduced in attempts to explain the repeated experimental observation that, contrary to expectations, grain growth in nanocrystalline materials, prepared by any method, is very small up to a reasonably high temperature.

This resistance to grain growth has been attributed to factors such as narrow grain size distribution, equiaxed grain morphology, low-energy grain boundary structures, relatively flat grain boundary configurations, and porosity of the consolidated samples.

One important feature of nanostructured materials is the large density of triple junctions. The inhibiting effect of triple junctions on grain growth has been demonstrated in [62-64]. Molecular dynamics simulations also suggest that triple junction drag is important in materials exhibiting small grain sizes, high symmetry grain misorientations, at low temperatures. Under ion irradiation the destruction of triple junctions under the direct impact of ion-induced defect cascades followed by recrystallization is go against this drag effect.
Another possible cause of thermal stability of nanocrystalline materials against grain-growth was highlighted in [65] where the authors investigated the inhibiting effect of vacancy generation on grain growth. It is suggested that vacancies produced as a result of the reduction of the grain-boundary area, i.e. of the elimination of the excess volume, increase the free energy of the system. Therefore, the ‘injection’ of vacancies into the bulk of the material acts as an inhibiting factor leading to a decrease in the grain growth rate. Andrievski reports that this vacancy generation during the grain boundary migration has been observed in the positron-annihilation study of recrystallization of ultrafine powders [66] and confirmed by a molecular dynamics simulation [67]. In the approach proposed, uninhibited grain-growth is considered to occur only during a limited time. It was assumed that after that time, upon reaching the condition when the time derivative of the Gibbs free energy becomes positive, ‘locking’ of grain growth occurs. It was further assumed that grain growth remains arrested during the time it takes for the excess vacancies to be removed by diffusion. Conditions of stability of a polycrystalline material against grain growth were proposed. In the proposed model, grain growth mechanism is pictured as a sequence of “locking-unlocking” events where “locking happens for grain sizes under the critical size

\[ D_c = \left[ \frac{24N_a k_b T Z (\delta \beta)^3 m}{D_{SD}} \right]^{1/3} \]  

Eq. 1.27

where \( \delta \), \( \beta \) and \( m \) are respectively the grain-boundary thickness, its relative excess free volume and its mobility, \( N_a \) is Avogadro’s number, \( Z \) is coordination number, \( D_{SD} \) is the bulk self-diffusion coefficient. For \( D_0 < D_C \) the generated vacancy-supersaturation inhibits grain growth but for \( D_0 > D_C \) grain growth occurs following the parabolic law. In the case of nanocrystalline materials, dislocations are supposed to be unlikely and the vacancy sinks are provided by grain boundaries \( (D_C/2~d) \); in such conditions, the critical grain size becomes

\[ \frac{D_c}{2} = \frac{24N_a k_b T Z (\delta \beta)^3 m}{D_{SD}} \]  

Eq. 1.28
For aluminum, for \( m=2 \times 10^{-14} \text{ m}^4 \text{ J}^{-1} \text{ s}^{-1} \) at 300°C and \( D_{SD}=1.3 \times 10^{-17} \text{ m}^2 \text{ s}^{-1} \), \( Dc/2 \) is of the order of 100nm which is typically the maximum grain size in nanocrystalline materials.

As far as experimental data on grain-growth in nanomaterials, numerous studies of grain-growth kinetics of nanocrystalline materials have revealed a lot of diverse information. Distributions of grain-size were found to be typically log-normal or normal for many nanostructured materials in initial and annealed state. However, abnormal grain growth has been observed in some cases, which could result from non-uniformity of the initial grain size distribution in the as-prepared specimens or/and of non-uniform admixture segregation.

Also, it has been shown that in many cases the grain growth mechanism can not be based on the unique value of exponent \( n \) because the data revealed fit for several values (\( n=2 \) to 4). This again highlights the tendency of nanostructured materials to resist grain-growth commented before, which has been related with many factors such as initial grain size distribution, pores having a Zener-type of drag effect on grain-growth, impurity doping and so on. It has also been reported that the exponent \( n \) may depend not only on the material but also on temperature, varying from 2 to 10 according to the temperature interval [68] suggesting a change of grain growth mechanism with temperature. This idea is also supported by observations that the activation energy \( Q \) for grain growth in nanocrystalline materials depends on the temperature interval in some cases. Indeed, it has been reported that \( Q \) for grain growth at higher temperatures (e.g. at temperatures higher than 773 K for nanocrystalline iron) is close to the activation energy for lattice diffusion \( Q_L \), while at lower temperatures, it is close to \( Q_{GB} \) suggesting that the mechanism of grain growth in nanocrystalline materials at low temperatures is different from that in coarse-grained materials.
**Ion-irradiation induced grain growth**

In the mid-eighties ion-implantation in metals and semi-conductors was at the center of several studies as the semi-conductor industry developed. In parallel, ion-induced grain growth in metals and semi-conductors also gained considerable interest and became the subject of systematic studies. Ion-irradiation was observed to cause grain-growth in thin films at temperatures where thermal effects alone did not induce any grain-growth. It has been observed experimentally that ion-irradiation induces *normal grain growth* in which the average grain size increases uniformly. The uniformity of grain growth combined with the dose dependence of grain size (or time dependence for a constant dose rate) are similar to grain-growth behavior observed in isothermal annealing experiments (power law). This observation suggests that the driving forces are the same in both cases. Attempts to model grain growth as assumed by the thermal grain-growth models under irradiation have been made [69-71], all of which assumed the same driving force of reducing the system free energy by the total reducing grain boundary area. *However it is important to recall that the thermodynamic principle of minimization of free energy applies only to an isolated system (except for interactions with thermal or mass reservoirs) and a system under irradiation is not an isolated system* [20, 29, 30, 72-75].

In 1980, in his study of ion-irradiated Ni thin films, Wang observed a linear trend of grain growth as a function of dose and a linear dependence of the grain-boundary mobility on the deposited damage energy [76, 77]. In 1988, Atwater and co-workers worked with Au, Ge, and Si thin films in a systematic study of ion-induced grain growth [70]. Atwater found a dose dependence of grain size varying from $D^4 \propto \Phi$ to $D^{1.96} \propto \Phi$ yet did not mention saturation effects. *Normal grain-growth* was observed in all their irradiated thin-films even those exhibiting *abnormal grain-growth* under purely thermal annealing conditions (500Å Au films for instance). Atwater reported a “weak” dependence of ion-irradiation-induced grain-growth on temperature. Activation energies were found to be about 0.15 eV for Ge films irradiated in the temperature range of 723 - 973 K and less than 0.1eV for Si films irradiated between 1023 K and 123 K which are
similar to activation energies found in ion-beam mixing experiments. The model proposed failed to account for these activation energies. In the study, an atomistic model was proposed to describe the observed results of ion-bombardment enhanced grain-growth. The model is based on independent processes all consisting of (1) the formation of a vacant site into which an atom can jump and (2) an atomic jump across the boundary into the vacant site. Four different processes are possible:

1. A purely thermal process where both the vacant site formation and the atomic migration are induced thermally. This case was excluded by Atwater et al.
2. A vacant site is formed at the boundary by ion bombardment and migration of the vacant site occurs thermally
3. A vacant site is formed at the boundary thermally and an interstitial atom is moved to the vacant site through a collision.
4. A collision-induced vacant site is formed at the boundary and filled with a collision-induced interstitial atom.

Atwater concluded that in the case of ion-beam grain growth, either process #2 or process #4 was the rate limiting step. This model which is ballistic in nature did not take into account the properties of the target materials. It resulted in the prediction of a linear dependence of mobility on the defect generation rate, i.e. on $F_D$, the deposited damage energy per ion, which failed to describe the experimental results.

This study was done at about the same time as another important study of ion-induced grain growth carried by Liu and co-workers which led to a very different model. In 1987-1990, Liu et. al. worked on pure metal thin-films of Co, Ni, Cu, Pd, Pt and Au and co-evaporated alloy systems of Ni-Co, Ni-Cu, and Pd-Pt [71, 78]. All the materials studied have a fcc crystallographic structure, except for Co which is hcp. Liu’s experimental results followed a power law in a similar way to Atwater’s with an exponent averaging 3. The study would have benefited from in situ information. Liu mentioned a saturation effect on grain size and suggested that the saturation grain size is related to the size of the defect cascade generated by a single ion[71]. However no theoretical derivation was given to support this conjecture. Like Atwater, Liu observed a weak dependence of the process involved in ion-induced grain growth on temperature.
However in one particular study of Cu films at temperatures from -160°C to 200°C [78], Liu identified two temperature regimes of ion-induced grain growth. Below - 60 °C, grain growth was independent of temperature but above this temperature, ion-induced grain growth displayed a weak temperature dependence with an activation energy of 0.14 eV and above 102°C abnormal grain growth was observed in the covered (thus unirradiated) part of the samples.

The observation of significant variations in grain growth rates among systems that exhibit similar collisional damage behavior (namely Pt and Au, and Ni-Cu alloys of different atomic concentrations) showed that a purely collisional model is inadequate for describing ion-induced grain growth. Intrinsic material properties must be taken into account in any attempt to model ion-induced grain growth. Furthermore, it was observed that greater grain growth was induced in those materials with low cohesive energy $\Delta H_{coh}$. This can be explained by assuming the activation energy for grain growth scales with the cohesive energy. The grain boundary mobility was related with the cohesive energy of the material - the cohesive energy of a crystal being defined as the energy that must be added to the crystal to separate its components into neutral free atoms at rest, at infinite separation, with the same electronic configuration. Liu then suggested that ion-irradiation-induced grain-growth may be related to the “thermal spike” effects of ion-irradiation. It was implied that the mobility of grain-boundaries depends on the number of atomic jumps generated in a thermal spike expressed in Vineyard’s analysis of thermal spikes [14, 79]. For thermal spikes of cylindrical geometry, it was proposed that the mobility of grain boundaries varies with $\frac{F^2_d}{\Delta H^2_{coh}}$.

In 1989-1992, Alexander and co-workers further supported the application of the thermal spike model to ion-induced grain growth with their studies of the ion-irradiated binary systems Ni-Al, Pt-Ti, Pt-V, Pt-Ni, Au-Co, some of which are miscible systems and some of which are not [69, 80, 81]. In all the films, normal grain growth was induced by irradiation with the average grain size increasing with ion dose according to

$$\bar{D}^n - \bar{D}_0^n = K\Phi$$

Eq. 1.29
Despite observed grain-growth exponents spanning values from 1.9 to 4.3 (averaging n=3) Alexander associated the deviations from ideal parabolic (n = 2) grain growth kinetics with the drag effect of inhibiting driving forces. Also, saturation effects were not at all taken into consideration nor the possible impact of the cascade size.

The initial structure of the films, multilayered versus co-evaporated, was observed to significantly affect subsequent ion-induced grain growth. In all alloys studied but the Pt-V system, multilayers generally showed greater grain growth than co-evaporated thin films of the same overall chemical composition for systems with $\Delta H_{\text{mix}} < 0$ and inversely for systems with $\Delta H_{\text{mix}} > 0$. These observations further supported the idea that a purely collisional model cannot describe accurately ion-induced grain growth and that properties of the material should be taken into account. This is possible within the framework of the thermal spike model. An enthalpy release associated with the heat-of-mixing, $\Delta H_{\text{mix}}$, was evoked as a possible mechanism through which the initial structure of the films might have affected ion-induced grain growth. This enthalpy release during irradiation would occur in the multilayers but would be absent in the homogenized coevaporated films. The energy release could lead to enhanced atomic motion and hence faster grain growth in the multilayers. It was also suggested that the heat-of-mixing might have affected the kinetics of grain growth via a Darken effect, in which atomic diffusion is enhanced across composition gradients. Such an effect had already been proposed to explain enhanced ion beam mixing efficiencies observed in systems with large negative heats-of-mixing by other authors as reported in [9].

The thermal spike model of ion-irradiation grain growth developed by Alexander incorporated grain-curvature and chemical gradients as the driving forces for atomic migration across boundaries within thermal spikes. Alexander found a dependence of grain-boundary mobility on $\frac{F_D^2}{\Delta H_{\text{coh}}^2}$ in contrast with $\frac{F_D^2}{\Delta H_{\text{coh}}^2}$ proposed by Liu. The model accounted successfully for ion-irradiation-induced grain-growth in coevaporated alloy films where the sole driving force considered is boundary curvature. The exception was the Ni-Al system, for which Alexander argued that this deviation was due to the lower
average atomic number of Ni-Al system which made it experience fewer, less developed thermal spikes thus preventing the application of the thermal spike model for this alloy.

As for the incorporation of the influence of $\Delta H_{\text{mix}}$ into the thermal spike model, it failed to describe observed grain growth data in the multilayer thin-films i.e. it failed to explain the difference observed between multilayer and coevaporated films of the same alloy. The multilayer grain growth rates did not scale with $\Delta H_{\text{mix}}$ between alloy systems and in fact an opposite correlation was observed among the alloys between calculated and experimental values of grain growth rates. Alexander concluded that the effect of chemical concentration gradients and heat-of-mixing were not prevailing factors affecting ion-irradiation-induced grain-growth in multilayers. Other driving forces associated with texture, film stress possibly absent in the coevaporated films but present in the multilayers were evoked to explain the difference in ion-irradiation-induced grain-growth behavior of the two types of films. Diffusion Induced Grain Boundary Migration (DIGM) was also invoked to explain concurrent phase formation and rapid grain growth such as in Ni-Al where grain-growth was enhanced in multilayers vs. coevaporated films.

1.3 Motivations

In this section, the motivations for the study are given; pointed out in italic are the points that were missing or incomplete in previous studies and that our study will include.

Previous thermal spike model of grain-growth under ion-irradiation considered cylindrical thermal spikes along the path of the ion of linear energy density $F_D$, the average energy deposited in nuclear interactions per unit length obtained from TRIM. Thus the model ignored the cascade structure such as subcascade formation (i.e. the idea that energetic recoils may break into subcascades), which is a general feature of energetic PKA [82]. Alexander and Was did acknowledge that their thermal spike model of grain-growth under ion-irradiation was a highly idealized picture of how ion irradiation affects grain growth, especially since it did not take into account the nature of the cascade
structure which is expected to vary considerably among different ion-target combinations and in turn lead to varying grain-growth behavior [83].

-> *This important feature of ion-irradiation induced damage needs to be incorporated in the model. This is a critical point to give the model a realistic basis.*

Although most studies of grain-growth under ion-irradiation have reported an average grain-growth exponent of 3, this was attributed to deviations from the parabolic law which was taken as a reference, as usually is the case in conventional polycrystalline materials. Those deviations, although systematically observed, were interpreted as resulting from impurities or other “classical” drag effects. However, as reported in the literature review above, some studies in the last 15 years have questioned the validity of this parabolic law even in the case of thermal grain-growth.

-> *This study will investigate whether the grain-growth exponent of 3 is not in fact an inherent feature of ion-irradiation-induced grain-growth.*

In 2003, an interesting result was reported by Voegeli et al. who used molecular simulations to study 5 keV cascades in nanocrystalline Ni samples of 5 and 10 initial grain size. They showed that ion-induced grain growth is observed if the thermal spike volume is larger than the grain volume or overlaps the grain-boundary area, in which case the shrinkage or growth of grains is accumulated over several events. If the spike volume does not reach the grain-boundary area we do not observe ion-induced grain growth [84]. This result supports the idea of a cascade size effect on the kinetics of ion-irradiation-induced grain-growth.

-> *This cascade-size effect needs to be further evidenced experimentally and there is need to see how it can possibly be included in a model of ion-irradiation-induced grain-growth. The possible saturation effects on the kinetics also need to be studied in more details.*

It is also worth mentioning that in Alexander’s study, all irradiations were performed at room temperature; hence no investigation of a possible temperature effect was performed.

-> *The influence of temperature on ion-irradiation-induced grain-growth needs to be done in a systematic way for different materials. This will shed some light on the very*
mechanisms of the grain-growth processes. It will be interesting to determine how the
temperature dependence, if any, compares with other ion-irradiation-induced phenomena
such as ion-beam mixing or amorphization etc where the temperature regime in which
the experiment is carried out has proven to strongly influence the mechanisms of the
transformation.

-> Lastly, this study will contribute more insight on the stability of
nanocrystalline materials under irradiation, which, as a novel field, lacks information
and needs more attention (as consistently pointed out in the few extensive global reviews
of the field [66, 85, 86]).

Therefore, in this work, we study the microstructure evolution of nanocrystalline
Zr, Pt, Cu and Au thin films under ion-beam irradiation, in situ in a transmission electron
microscope (TEM). The microstructure evolution of the thin-films is followed in situ by
systematically recording bright field images and diffraction patterns at successive ion-
irradiation doses.

1. The influence of irradiation temperature is investigated by carrying out ion
irradiations at temperatures ranging from 20 to 773 K.
2. The effect of solute addition is investigated using Zr and Cu solid-solutions
supersaturated with Fe irradiated with 500 keV Kr ions, and 1 MeV electrons. The phase
transformations under irradiation, if any, are studied and reported.
4. The influence of the ion type/energy (i.e. recoil spectra) is investigated on Zr-
Fe irradiated with 600 keV Kr ions vs. 600 keV Ar ions and on Pt irradiated with 500
keV Ar ions and 1 MeV Kr ions.
5. Also, the influence of intrinsic material properties such as the melting point,
cohesive energy is investigated by comparing results of materials which exhibit similar
collisional properties, but different material properties; this is the case of Au and Pt, both
irradiated with 500 keV Ar ions.

This study is done in situ so that the kinetics and mechanisms of the observed
phenomena can be better determined, leading to a more precise determination of the
power law exponent and the underlying physical phenomena. More generally, working
under controlled parameters, as we do, allows for evaluating their separate influences on the phenomena studied by keeping all parameters constant but the one of interest. Indeed, the control over the different experimental parameters (i.e. irradiation temperature, ion type, ion dose, ion dose rate (or flux), and composition of the material) makes our system a model system ideal for systematic studies.

A model is developed that will incorporate the nature of cascade structure within the limitations associated with present knowledge of the exact nature of cascade structure, its variation from one material to another, its dependence on ambient temperature, etc. The model explains inherently the main features of grain-growth under ion irradiation.
Chapter 2

Description of the experiment

In this chapter the experimental methods used in this study are described. This includes the processing of specimens which were electron transparent so they could be used in a Transmission Electron Microscopy (TEM) by depositing thin films onto soluble substrates such as salt crystals using a sputtering film deposition device. The characterization of such films and the preliminary calculations needed to estimate the damage are described. The experimental procedures to irradiate these samples \textit{in situ} in the IVEM are also described in this chapter.

2.1 Materials

Elemental thin films of Zr, Cu, Pt and Au, and supersaturated solid solutions of Cu-Fe and Zr-Fe were co-sputter deposited onto NaCl substrates and onto Si wafers. The films deposited on NaCl were intended for TEM whereas the films deposited on Si were meant for Rutherford Backscattering Spectroscopy (RBS) characterization (thickness and composition). The sodium chloride rocksalt NaCl 10 mm cubes used as substrates were obtained from SPI-supplies (Structure Probe, Inc). 300 Mesh and 400 Mesh copper TEM grids were bought from SPI-supplies (Structure Probe, Inc). Double-oyster copper grids 100/100 Mesh were also used for the samples containing Fe to prevent the potential loss of the samples in the TEM column. These were obtained from Electron Microscopy Sciences. The Silicon wafers were provided by the Material Research Laboratory at the Pennsylvania State University where the sputtering thin-film depositions were carried out.
2.2 Thin-film processing by the sputter-deposition method:

The film deposition used a dual gun system at a base pressure of less than $10^{-6}$ Torr at room temperature (at the Materials Research Laboratory (MRL) at the Pennsylvania State University). In an evacuated chamber, an argon partial pressure of approximately 0.05 mbar is established through a gas dosing valve, and a glow discharge is ignited between an anode (specimen) and a cathode (metal target) by means of high voltage. The resulting positively charged argon ions are accelerated toward the cathode and through their impingement knock out (sputter) the metal atoms and clusters off the target. Many collisions occur between the sputtered metal atoms and the gas molecules in the process chamber, resulting in strong scattering of the metal atoms. These are deposited uniformly onto the substrate in the chamber as a homogeneous thin metal film. By monitoring the thickness during the deposition, the resulting films were made electron-transparent for Transmission Electron Microscopy. Figure 2.1 is a picture of a sputtering device used for the processing of the films.
Film thickness and deposition rates were measured with a thickness profilometer. Deposition rates varied depending on the metal but were usually between 0.1 and 1 nm/sec. Elemental composition analysis of the thin films was also performed by X-ray dispersive spectroscopy in an ESEM (FEI Quanta 200 ESEM) equipped with an energy dispersive x-ray (EDS) system.

2.3 Characterization of the microstructure of the as-deposited specimen using TEM:

The as-deposited thin films were measured with the profilometer and found to be 80-90 nm thick which ensured that they were electron transparent. The coated NaCl
substrates were cleaved into small pieces and the specimens were floated on a liquid solution of 80(vol%) de-ionized water – 20(vol%) ethanol onto TEM copper grids, cleaned in de-ionized water, and dried before they were used in the IVEM.

2.3.1 Elemental thin-films

The non-equilibrium processing of the thin films resulted in a nanocrystalline structure. The as-deposited foils were laterally homogeneous and nanocrystalline, with an initial mean grain size between 10 and 15 nm, as shown in Table 2.1. Grain size was determined by measuring the grains on the TEM bright-fields micrographs; the grain size was averaged over the number of grains measured; the initial average grain size was determined for each sample used for each irradiation experiment; hence the error reported is a combination of the error associated with the measurements (typically ±1nm) and the spread of average grain-size values from sample to sample (or area to area of the sample).

Figure 2.2 (left) shows bright-field TEM micrographs of the as-deposited elemental Au, Pt, and Cu films. The films exhibit a more or less equiaxed grain morphology and show many Moiré fringes when examined in TEM, indicating there are several layers of grains, rather than a columnar structure. However no cross-sectional examinations were performed. The diffraction patterns of the as-deposited films were consistent with the expected crystal structures and lattice parameters of the bulk phases of Au, Cu, Pt (Figure 2.2 (right)). Table 2.1 includes the measured lattice parameters of the specimen crystal structures versus the ones from the corresponding powder diffraction files (pdf).

With such grain-sizes these materials fall within the class of nanostructured materials. Nanocrystalline materials have a high density of grain-boundaries i.e. junctions between grains in a polycrystal, the structure of which can be complex. In fact, in materials with nano-sized grains, up to 50% of all atoms are associated with grain boundaries or interfaces, depending on grain-size. In comparison, coarse-grained materials have less than 3% of all atoms associated with grain boundaries or interfaces. It
is important to keep this fact in mind when studying grain growth or second phase formation in our nanocrystalline thin-films since grain-boundaries can play a large role in these transformations.

As a matter of fact, a consequence of the increased volume fraction of grain boundaries is that the atomic structure of nanostructured materials is unlike that seen in glasses or crystals. It is suggested that [86] the misfit between adjacent crystallites give rise to distortions in the atomic short-range surrounding the atoms in the grain-boundaries between differently oriented grains. They result in changes in the atomic structure of the boundary regions such as reduced average atomic density, modified nearest-neighbor coordination, excess volume per atom, etc., which in turn are reflected in changes in the material properties. This is of particular importance when the volume fraction of grain boundaries becomes comparable with the volume fraction of the crystalline regions. i.e. when the crystal diameter becomes comparable with the thickness of the interfaces, which is the case for nanocrystalline materials where crystal sizes are on the order of one or a few nanometers. Therefore these microstructural differences between nanocrystalline materials such as our thin films and their coarse-grained counterparts should be kept in mind when comparing their properties and the evolution of these properties under thermal/irradiation conditions.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystal Structure observed</th>
<th>Measured lattice parameters (nm)</th>
<th>Lattice parameters from pdf (nm)</th>
<th>Foil thickness (nm)</th>
<th>Initial grain-size (nm) (±error in nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>fcc</td>
<td>a=4.09</td>
<td>a=4.08</td>
<td>80</td>
<td>12 (1.2)</td>
</tr>
<tr>
<td>Pt</td>
<td>fcc</td>
<td>a=3.88</td>
<td>a=3.92</td>
<td>80</td>
<td>13 (2.4)</td>
</tr>
<tr>
<td>Cu</td>
<td>fcc</td>
<td>a=3.60</td>
<td>a=3.615</td>
<td>90</td>
<td>13 (1.4)</td>
</tr>
<tr>
<td>Cu-(3 at%)Fe</td>
<td>fcc</td>
<td>a=3.63</td>
<td>a=3.615 for pure Cu</td>
<td>90</td>
<td>15 (1.4)</td>
</tr>
<tr>
<td>Zr-(1.2 at%)Fe</td>
<td>hcp</td>
<td>a=3.28, c=5.23, c/a=1.594</td>
<td>a=3.23, c=5.15, c/a=1.593 for pure Zr</td>
<td>80</td>
<td>14 (1.6)</td>
</tr>
</tbody>
</table>
Figure 2.2: Bright field micrographs of as-deposited Au, Pt, and Cu films revealing the nanocrystalline structure of the polycrystalline films and their diffraction patterns. All the diffraction rings can be indexed with the phases indicated in the figure and shown in Table 2.2.
2.3.2 Supersaturated solid solutions of Zr-Fe and Cu-Fe

The phase diagram for the Zr-Fe system has been assessed by several workers [87-90]. These assessments show significant disagreements with each other including on the eutectoid temperature and the range of stability of the Zr$_2$Fe phase. However all proposed phase diagrams do agree on the region of interest in this study (low temperatures and Fe concentrations less than 5%). The Zr-Fe phase diagram proposed by Arias [87] is presented in Figure 2.3. For temperatures below the eutectoid temperature (795°C) and concentrations less than 24 at% the stable phases are α-Zr and Zr$_3$Fe. In this range, Zr$_2$Fe phase is therefore a non-equilibrium phase. There have also been detailed studies of the solid solubility of Fe in [91, 92] with some disagreements. Borelly et al. [92] have found the maximum solid-solution solubility of Fe in α-Zr to be 180 ppm at the eutectoid temperature and that below that temperature the solubility decreases exponentially with temperature as shown in Figure 2.4. Thus, for the iron content (>1 at%) and temperature range of interest in this study, according to the phase-diagram the equilibrium state is a two-phase system composed of α-Zr and orthorhombic Zr$_3$Fe phases.
Figure 2.3: The Zr-Fe equilibrium phase diagram [87].

Figure 2.4: Solid solubility of iron in zirconium [92]
Figure 2.5 shows the phase diagram for the Cu-Fe binary system as compiled by Okamoto[93]. For temperatures of interest in our study, the system is reported to be immiscible. Indeed, the iron-copper system does not form intermetallic compounds and has negligible mutual solid solubility at temperatures below 973K because of the large positive enthalpy mixing ∆H_{mix} = +13 kJ.mol^{-1} for Fe-Cu system of 50 at% Fe – 50 at% Cu [94].

![Cu-Fe phase diagram](image)

Figure 2.5: Cu-Fe equilibrium phase-diagram compiled by Okamoto [93]

Figure 2.6 shows the bright field and associated diffraction pattern for both the Zr-1.2 at%Fe and Cu-3at%Fe thin-films processed for this study. The same observations made on the grain size and morphology of the elemental thin films described above are also true for the solid solutions of Cu-Fe and Zr-Fe. In the case of the Zr-Fe films the diffraction patterns revealed that the grains were preferentially oriented with the basal planes perpendicular to the foil surface, as shown by the relatively high intensity of the (002) diffracted ring in Figure 2.6 (bottom). This preferential normal orientation of the Zr
grains differs from that observed in previous experiments [95]. As for the Cu-Fe films, the relative intensity of the diffracted rings was as expected for powder patterns of coarse-grained Cu with no preferential orientation. Overall, no in-plane texture was visible on the diffraction patterns for either system.

Figure 2.6: Bright fields and associated diffraction patterns of Cu-3%Fe and Zr-4.4%Fe films as deposited. The films are nanocrystalline with diffraction patterns characteristic of the pure metal: the rings of the Cu-Fe films were all indexed as fcc Cu rings and the rings of the Zr-Fe films were all indexed as hcp α-Zr rings.

In both cases the structure of the matrix (Cu and Zr) is the only pattern seen in the respective diffraction patterns. No second phase was present, although the RBS and EDS analysis confirmed an iron content in the Zr-Fe and Cu-Fe films well beyond the solubility limit of Fe respectively in Zr and Cu as shown in the phase diagrams. The solid-solutions of Cu and Zr are therefore both supersaturated with Fe.
Because Cu and Fe have practically the same atomic size (~1.179x10^{-23} \text{ cm}^3) the solid-solutions of Fe in Cu is substitutional whereas in the case of Zr-Fe, the Fe solute atoms are twice as small as the Zr matrix atoms so that it is likely the Fe atoms occupy interstitial sites. The measured lattice parameter for the Cu-Fe solid solution was close to that measured for the pure Cu thin-films, and with the value of the lattice parameter obtained from the pdf of Cu. This is consistent with the idea that the Cu-Fe solid-solutions processed were of the substitutional type as suggested above. On the other hand the lattice parameters for the hcp Zr-1.2%Fe thin-films are slightly bigger than the pdf values for pure Zr, although the c/a ratio is the same. This suggests that the Fe atoms occupying interstitial sites may exert some stress on the Zr atoms of the matrix, which may result in slightly bigger lattice cell to accommodate the stress.

As mentioned above, since the thermodynamic-equilibrium solubility limit of the material is exceeded, the Zr-Fe and Cu-Fe thin films processed for this study are supersaturated solid solutions. As such, they are thermodynamically in a metastable state. This enhanced solubility may be the result of the method of fabrication of the materials. Indeed, the sputtering-method used to process our thin films inherently involves a rapid temperature quench during the deposition of the sputtered atoms (or small clusters of atoms) onto the substrate which would prevent the freshly built layer of atoms to evolve towards its thermodynamic equilibrium. As a result, the supersaturated solid solutions of Zr-Fe and Cu-Fe could result from the rapidity of the effective quench during the film deposition process and the sluggishness of the thermodynamically expected decomposition at room temperature.

Since the resulting thin-films are nanocrystalline in nature, the enhancement of solute solubility may also be related more specifically to their smaller grain sizes (note, however that the small grain size is related also to the rapidity of the deposition itself). Another contributing factor to the formation of supersaturated solid-solutions is the nanocrystalline nature of the thin-films. In fact, the formation of non-equilibrium phases and supersaturated solid solutions in nanocrystalline materials which do not exist in coarse-grained polycrystals has been previously reported [66]. These metastable structures can appear readily in nanocrystalline films prepared by mechanical alloying
and film/coating technology which is our case. Indeed if two metallic elements of limited solute solubility are prepared in the form of a coarse-grained polycrystal and in the form of a nanocomposite (i.e. a nanometer-sized polycrystalline dispersion of the two metallic elements) an enhanced solute solubility has been noted in the nanocomposite relative to the coarse-grained material in several alloy systems [66, 86, 96]. The inverse (i.e. a reduced solute solubility in the nanocomposite relative to the coarse-grained counterpart) has not been reported so far. The solute solubility seems to increase as the crystal size decreases. This enhanced alloying of elements which are immiscible in the solid and/or the molten state and, more generally, the formation of supersaturated solid solutions has been observed in various systems, such as Fe-Cu, Fe-Ni, Fe-Ti, Fe-Al, W-Cu, Ni-Al and others.

Gleiter et al. have tried to relate the enhancement of solute solubility with the smaller grain sizes of nanocrystalline materials [96], keeping in mind the most important factors which govern the solid solubility in bulk metallic systems are: (i) the difference between the atomic sizes of the component elements, (ii) the formation of stable intermediate compounds, and (iii) the electronic structure. They suggested that the enhanced solubility may actually be an electronic effect. The modification in the electronic structure would result from the space charge which exists in the vicinity of the inter-phase boundaries between the two elements with different Fermi energies. The space charge would modify the electronic structure locally in such a way that the Fermi energies of the two components become equal in equilibrium, which in turn would locally enhance the solute solubility. In metallic systems, the width of the space charge region is about 1 nm or less. Hence if the crystals of a polycrystal are of the order of a few nanometers in size the enhanced solute solubility in the space charge regions is noticed macroscopically. In coarse-grained polycrystalline materials the solute solubility usually hardly differs from single crystals of infinite size because the volume fraction of the space charge regions is small. However in nanocrystalline alloys the volume fraction of the electric space charge regions is much larger since grain-boundaries may occupy 50% or more of the total volume. In fact it was reported that in several nanostructured alloys, it
is the solute solubility in the boundary regions that was noticed to deviate from the solute solubility in the crystal lattice.

In the case of alloying of immiscible elements, two cases are distinguished. In the first one (depicted on the left in Figure 2.7 taken from [86]), solute atoms with little solubility in the lattice of the crystallites segregate to the boundary cores (in which case the free energy of the system is reduced by the segregation of large solute atoms to the boundary core). In the other case (depicted on the right in Figure 2.7 for Ag-Fe), even if the constituents are immiscible in the crystalline and/or molten state solid solutions can form in the grain boundary regions of the nanocrystalline materials. For instance, in the case of Ag and Fe which are immiscible in the liquid as well as in the solid, the Ag–Fe solid solution was shown to be formed in the vicinity of the interphase boundaries between the Fe and Ag crystals. Similar alloying effects in the vicinity of interphase boundaries between immiscible constituents were reported in other alloy systems, e.g. in Cu–Fe–Ni.

![Figure 2.7: a) Schematic model of the structure of nanostructured Cu-Bi and W-Ga alloys deduced from EXAFS and X-ray diffraction measurements. The open circles represent the Cu or W atoms, respectively, forming the nanometer-sized crystals. The black circles are the Bi or Ga atoms, respectively, incorporated in the boundaries at sites of enhanced local free volume. b) Schematic model of nanocrystalline Ag-Fe alloys according to Mössbauer spectroscopy data. The alloys consist of a mixture of nanometer-sized Ag and Fe crystals (represented by open and full circles, respectively). In the interfacial regions between Ag and Fe crystals, solid solutions Ag-Fe crystallites are formed although both components are immiscible both in the liquid state and in the solid state [86].](image-url)
In the light of the above arguments, it is therefore possible that, in the case of our Zr-Fe and Cu-Fe films, a high fraction of the iron atoms are located in the grain boundary regions from the beginning. It is true that a priori a random dispersion of solute inside the grains should not be excluded, however because of the high volume fraction of grain-boundaries in nanocrystalline materials, up to 50% of all atoms (including solute atoms) are associated with a grain-boundary. Moreover because of the small grain sizes it is likely that interstitials (in the case of Zr-Fe solid solutions) may be able to migrate easily to a grain-boundary even at room temperatures, resulting in a structure alike that of Figure 2.7 on the left. Since no iron diffraction ring was detected, the case depicted on the right in Figure 2.7 may not apply. The configuration depicted on the left is indeed more likely. However in the case of a substitutional solid-solution such as the Cu-Fe films, a configuration such as the one shown in Figure 2.8 is more probable since some Fe atoms may be “trapped” within the grains.

Figure 2.8: Schematic model of the structure of nanocrystalline Cu-Fe system (Fe atoms in black); adapted from [86].
2.4 Irradiation experiments

2.4.1 Determination of ion ranges and number of atoms displaced using SRIM2003 code

To properly conduct the experiments it is necessary to evaluate the range of ions and their displacement rate in the materials of interest. The SRIM code was used for this purpose. SRIM (Stopping and Range of Ions in Matter) is a Monte Carlo program which simulates ion transport and damage production in materials. The program SRIM is freely available for download online at www.srim.org.

The program can calculate the stopping and range of ions (up to 2 GeV/amu) into matter using an empirically derived "universal" interatomic potential of ion-atom collisions (assuming a moving atom as an "ion", and all target atoms as "atoms") [97]. This "universal" potential has been validated against experiments and is valid for energies below the threshold where nuclear reactions are possible. The potential is of the form:

\[ V(r) = \frac{Z_1Z_2e^2}{r} \psi\left(\frac{r}{a}\right) \tag{Eq. 2.1} \]

where \( Z_1 \) and \( Z_2 \) are the atomic numbers of the energetic ion and the target atoms, \( e \) is the electric charge, \( \psi \) is the "universal" screening function determined by exact fitting of the calculated interatomic potentials of 521 randomly selected element combinations and is given by:

\[ \psi\left(\frac{r}{a}\right) = \sum_{i=1}^{4} A_i \exp\left[-B_i\left(\frac{r}{a}\right)\right] \tag{Eq. 2.2} \]

where \( r \) is the interatomic distance, and \( a \) is an empirical screening length given by the semi-empirical formula:
where $a_{\text{Bohr}}$ is the Bohr radius. Using this potential, SRIM code gives the partitioning of ion energy loss to electrons and to nuclei. The code keeps track of energy loss, number of displacements, ion range and various other parameters. The program does not consider nuclear reactions (thus it is not valid for very high energy ions), the crystal structure of the material (i.e. the material is considered amorphous but with the specified density of the crystalline form) or the accumulation of damage (i.e. each ion sees virgin material). The program does explicitly account for polyatomic targets, atomic sputtering, and allows for up to three layers of material with up to four elements each.

The code was run for different ion energies. The ion range profiles generated by the code helped choose the ion-beam energy to use so to minimize ion implantation in the films. In other words, the ion energy was chosen so that most ions transverse the thickness of the samples. The various ion-irradiations simulations of interest for the study are tabulated and presented in Appendix A. All irradiation simulations were run in full cascade mode with 5000 ions to have good statistics. The target material, density, thickness of slab, ion type and energy and angle of incidence for which the simulations were run are listed in the tables of the appendix. The results of interest such as the number of ion transmitted, the sputtering yields, the energy loss repartition between electrons and nuclei, and the damage production cross-sections are also reported.
Figure 2.9: Damage-production cross-sections for the different irradiations of interest in this study: the number of vacancies, replacement collisions, and displacements per ion per angstrom is plotted across the thickness of the film.
SRIM was also useful for the evaluation of the ion-irradiation damage in terms of the number of displacements-per-atom (dpa). Figure 2.9 shows the damage production cross-sections for the different cases of interest in this study in terms of the number of displacements per ion per angstrom (K) across the thickness of the film. Because the target slab was thin the damage production is rather homogeneous across the depth as can be seen in Figure 2.9. An average value $\bar{K}$ of the number of displacements per ion per angstrom is then derived from the plots. Values of $\bar{K}$ for all irradiations of interest are reported in Appendix A. Then, the number of displacements per atom in the thin-films is expressed as:

$$\frac{\Phi \bar{K}}{N_{\text{at}}}$$  \hspace{1cm} Eq. 2.4

where $\Phi$ is the fluence (in ions/cm$^2$), $N_{\text{at}}$ the atomic density (expressed in #atoms.Å$^{-1}$.cm$^{-2}$), and $\bar{K}$ is the average number of displacements per ion per angstrom (obtained from the code SRIM2003).

**Note:** It is important to run the code for a large enough number of irradiating particles in order to eliminate the possible statistical errors. The choice of the displacement energy has an impact: for instance, when varying the $E_d$ value from 25 eV to 40 eV, all other parameters being kept the same (including the number of ions for which the code is run), the resulting average number of displacements/ion-Å decreases proportionally by a factor of about 1.9. The choice of $E_d$ is therefore important. For the present study, default $E_d$ values assigned by SRIM2003 were used, basically 25 eV for all the elements of interest in our study. For Zr, this value is in accordance with the experimental study done by Griffiths [98].
2.4.2 The IVEM-TANDEM facility at Argonne National Laboratory

The irradiations were carried out at Argonne National Laboratory in their IVEM facility which is described below.

*Description of the Intermediate Voltage Electron Microscope (IVEM)*

The IVEM-Tandem is a unique facility which consist in a transmission electron microscope interfaced with two ion accelerators for in situ ion beam studies involving ion implantation and/or ion damage [1, 2]. A picture of the facility is shown in Figure 2.10 where the ion beam attachment is shown at the top left.

The ion beam device can deliver low energy (up to 600 keV) ions using a 650 kV accelerator. For higher energy ions the system uses the TANDEM accelerator. Different ion species are possible, from noble gases to hydrogen and metal ions (Fe, Ni, Cu, Au); the ions are supposed to be positively single charged. The ion flux at the specimen location is typically $10^{12}$ ions/cm$^2$·s but can be adjusted. The ion beam diameter at the specimen location is about 1.5mm. The ion beam dosimetry is performed within 2 cm of the specimen using a Faraday cup system.

A variety of specimen holders allows various kinds of *in situ* experiments such as cooling and heating experiments (with or without ion irradiation) from 15-1200K, in situ tensile experiments from 300-600K and electrical biasing experiments from 300-800K.

The electron energy in the TEM can be chosen between 100 kV to 300 kV. The specimen chamber vacuum is less than $4 \times 10^{-7}$ Torr. The spherical aberration coefficient ($C_s$) is 2.8 mm. The minimum spot size at 300 kV is about 8 nm. The image resolution at 300 kV is about 0.25 nm when the ion beam line is connected. When the ion beam line is disconnected, the resolution at 300 kV can attain 0.14 nm. The ability to take micrographs at any moment during the experiment makes it possible to follow the kinetics of the observed processes. It is also possible to use the video camera to keep record of the grain growth evolution when possible.
This experimental setup offers the advantages of an in situ study vs. previous work done on bulk materials. Indeed, as reported in chapter 1, most studies done on ion-induced phase transformations (including ion-irradiation induced grain growth) were based on results observed after irradiation, i.e. an irradiation dose is applied to the material from which a TEM sample is subsequently prepared to study grain growth. Given the dynamic nature of the phenomenon, a direct observation of ion-irradiation induced grain growth is advantageous for a better understanding of the mechanism, the kinetics and driving force of this process, hence the advantage of working with thin films in the IVEM.
This experimental method also allows for control over irradiation parameters (irradiation temperature, dose rate, ion type, ion energy). By changing these parameters, it is possible to evaluate their separate influences on the phenomena studied by keeping all parameters constant but the one of interest. It is possible to independently control and monitor the irradiation temperature, the ion type, the ion dose, the ion dose rate (or ion flux), the composition of the material, and it is possible to stop the experiment at any time to record the diffraction patterns and bright-field micrographs. The control over the different experimental parameters makes this facility ideal to perform systematic studies.

**Geometry of the system**

Figure 2.11 shows schematically the geometry of the system. The angle between the incident electron and the ion beam is 30°. The sample was held with an inclination angle of 15° with respect to the ion beam. Due to the geometry of the system (illustrated in Figure 2.11) some regions of the sample were systematically shadowed by the thickness of the TEM grid, and hence not irradiated by the beam. The microstructure evolution in these regions is thus the result of thermal effects alone, while the irradiated areas reveal the impact of both temperature and irradiation. Thus the non-irradiated regions provide a built-in control to separate the purely thermal effects from those that require irradiation. To further understand thermal effects on grain growth, selected isothermal runs were performed in the absence of irradiation.
**Figure 2.11**: a): IVEM configuration. b): Sample geometry with respect to the ion beam and the grid, showing irradiated sample area (dark area) and unirradiated area (light area).

---

**Ion beam heating evaluation**

The energy deposited by the electron and ion beam can help heat the sample. Therefore, ion beam heating needs to be estimated in order to determine its contribution to the observed transformations. Calculations based on a simple heat-transfer model show that in the given configuration, with the sample holder in contact with the grid, itself in total contact with the sample, the temperature rise in the sample is negligible in terms of thermal activation processes involved in either thermal grain growth or thermally induced precipitation. The calculations for the case of Zr films on copper TEM grid are given below. It is assumed that the film is in contact with the copper grid, which is at the nominal temperature of the specimen holder. The geometry assumed for the calculation is shown in Figure 2.12 (a).
Figure 2.12: Geometry for the evaluation of ion beam heating. $\Delta T = T_{\text{center}} - T_{\text{Grid}}$ is evaluated. a) is the case where the film is in total contact with the grid; b) shows the case where the film is not always in contact with the grid.

It is assumed that the heat generated in the regions of the sample directly in contact with the grid directly goes through the grid to the sample holder which acts as a thermal sink. This assumption is supported by the high thermal conductivity of copper which is 3.85 W/cm-K (about 17 times that of Zr) and the fact that the grid is in close contact with the sample holder which act as a thermal sink. Thus, the only part subject to a temperature difference from the sample holder temperature is the sample region above the center of a grid hole which is not in contact with the copper grid. The heat flux to be considered is the one in the x direction (parallel to the grid). In this case, the temperature rise is given by:

$$\Delta T = T_{\text{center}} - T_{\text{Grid}} = \frac{q''''s^2}{2k_f}$$  \hspace{1cm} \text{Eq. 2.5}

where $s$ is half the grid-spacing, $k_f$ is the thermal conductivity of the metal and $q''''$ is the heat generation per unit volume. Given the experimental conditions, $q''''$ was calculated to be 4000 W/cm$^3$ (using data from SRIM). For our 300 mesh TEM grids, $s=2.5 \times 10^{-3}$ cm; $k_f$ for copper is 3.85 W/cm-K and for Zr 0.23 W/cm-K. For these values, $\Delta T$ in the Zr film is found to be 0.055K, hence it is negligible. However it should be noted that the case where the film is in total contact with the grid is probably ideal; it is
likely that some areas of the film are not in complete thermal contact with the grid, in which case they accumulate a little more heat than the regions in contact with the grid as shown in Figure 2.12 (b), and therefore those regions should experience a little larger ∆T. In any case the observations and micrographs were always taken from an area resembling case a) in Figure 2.12. As noted later, the sample regions shadowed by the grid give us a built-in standard which can be used to assess the purely thermal effects and they are negligible.

**Experimental method and Summary of Irradiations**

Samples were irradiated with 500 keV Ar, Kr ions, 600 keV Kr ions and with 1 MeV Kr ions to a fluence in excess of $10^{16}$ ions/cm$^2$-s, at different temperatures ranging from 20 K to 573 K. Ion fluxes were typically around $2.50 \times 10^{12}$ ions/cm$^2$-s. The evolution of the microstructure was followed by sequentially taking bright-field images and diffraction patterns (DP) of the films while they were being irradiated. This made it possible to follow the kinetics of the irradiation induced phenomena. Table 2.2 summarizes the experiments performed and the associated relevant irradiation-damage parameters obtained from SRIM2003.
Table 2.2: Summary of the irradiation conditions: melting points, temperatures of irradiation, ion type and energy. The collisional properties (displacement rate and deposited damage-energy) $F_D$ were obtained from the SRIM2003[97] Monte-Carlo code using a displacement energy of 25 eV. For Cu-3%Fe irradiated with 500 keV ions and Zr-Fe irradiated with 500 keV Kr ions the same collisional values as Cu and Zr were used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Melting point (K)</th>
<th>Ion type / energy</th>
<th>Average deposited damage energy $F_D$ (eV/ion-Å)</th>
<th>Average displacement cross-section $\overline{K}$ (# disp/ion-Å)</th>
<th>Average displacement rate $K_0$ (dpa/sec)</th>
<th>Irradiation Temperature $T_{irr}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>1337</td>
<td>Ar 500 keV</td>
<td>100</td>
<td>2.83</td>
<td>0.012</td>
<td>50, 298, 473</td>
</tr>
<tr>
<td>Pt</td>
<td>2041</td>
<td>Ar 500 keV</td>
<td>120</td>
<td>3.50</td>
<td>0.013</td>
<td>298</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kr 1 MeV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>1358</td>
<td>Kr 500 keV</td>
<td>323</td>
<td>7.91</td>
<td>0.023</td>
<td>50, 298, 573</td>
</tr>
<tr>
<td>Zr</td>
<td>2128</td>
<td>Kr 500 keV</td>
<td>194</td>
<td>3.67</td>
<td>0.021</td>
<td>20</td>
</tr>
<tr>
<td>Cu-3%Fe</td>
<td>~1358</td>
<td>Kr 500 keV</td>
<td>323</td>
<td>7.91</td>
<td>0.023</td>
<td>298, 473</td>
</tr>
<tr>
<td>Zr-1.2%Fe</td>
<td>~2128</td>
<td>Kr 600 keV</td>
<td>194</td>
<td>3.25</td>
<td>0.019</td>
<td>298, 423, 573</td>
</tr>
<tr>
<td>Zr-4.4%Fe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 3

Phase-Transformation in Zr-Fe and Cu-Fe Solid-Solutions Supersaturated with Fe under Irradiation

The question of irradiation-induced or irradiation-enhanced precipitation, and more generally, phase formation, has received both experimental and theoretical attention [20, 25, 72, 73]. One of the problems with studying irradiation induced phase transformations is that the kinetics are not usually accessible to the experimentalist, and thus the phase transformation mechanisms are difficult to determine. In this study, we use in-situ ion irradiation in an electron microscope to study phase formation in supersaturated metallic solid solutions. The Zr-Fe system is chosen as a model system to study, and ultimately understand, the kinetics of precipitation reactions in metallic alloys under irradiation. The binary Zr-Fe alloy system has been the focus of a number of studies because of its technological importance especially in the nuclear industry where Fe-containing Zr alloys are used as fuel cladding material. The system has also received attention because the Zr-Fe binary alloys are excellent glass formers over a wide range of compositions. Studies of the crystallization of Zr-Fe glasses showed that the immediate products of crystallization are often metastable phases which would not have been predicted from the Zr-Fe phase diagram[99].

3.1 Characterization of the as-deposited Zr-Fe thin-films:

3.1.1 Microstructure of the initial system:

The microstructure of the initial system was described in chapter 2. Figure 2.6 (bottom) is reproduced again here as Figure 3.1, which shows a bright field TEM micrograph and the associated diffraction pattern of a typical Zr-Fe film in the as-deposited state. These films
were ~80 nm thick, laterally homogeneous, and nanocrystalline, with an initial mean grain size between 10 and 15 nm. The diffraction patterns show rings which can be indexed as the hexagonal $\alpha$-Zr phase with no second phase present, although the Rutherford Backscattering (RBS) analysis confirmed an iron content in the Zr-Fe films beyond the solubility limit of Fe in Zr which is on the order of a few ppm at room temperature [92]. In the case of Figure 3.1 the Fe content was 1.2%. The Zr grains were preferentially oriented with the basal planes perpendicular to the foil surface, as verified by the high 002 intensity in the diffraction pattern. The as-deposited films have a more or less equiaxed grain microstructure and they show a lot of Moiré fringes which means there are several layers of grains. However the cross-sectional microstructure could not be analyzed. It is possible that the presence of alloying elements and impurities inhibits the grain growth since the early stages of the film deposition hence preventing a columnar microstructure from developing.

The diffraction patterns of some samples showed some amorphous intensity, likely caused by disordered regions near the grain-boundaries. Some exhibited micro or nano cracks.

Figure 3.1: On the left, TEM bright-field image of the as-deposited Zr-1.2%Fe thin films. On the right, the corresponding diffraction pattern (DP): all rings were indexed as $\alpha$-zirconium.
3.1.2 Metastability of the initial system:

As mentioned before, in the as-deposited state, the Zr-Fe thin films processed for this study showed diffraction patterns characteristic of $\alpha$-Zr with no second-phase diffracted rings. However their Fe content (1.2 at% to 4.4 at%) was much higher than the maximum solid-solution solubility of Fe in $\alpha$-Zr. This solubility was found to be 180 ppm at the eutectoid temperature and decreases exponentially with decreasing temperature below the eutectoid point[92]. Therefore, the as-deposited thin-films are solid-solutions of $\alpha$-Zr supersaturated with Fe. As such, they are thermodynamically in a metastable state resulting from the method of film-deposition itself (the co-sputtering method). According to the phase-diagram proposed by Okamoto [88] and presented in Figure 2.3, for the iron content and temperature range of interest in this study, the equilibrium state is a two-phase system composed of $\alpha$-Zr and orthorhombic Zr$_3$Fe phases. However, because of the rapidity of the effective quench during thin film deposition, second phases do not form and these films are formed as supersaturated solid solutions of Fe in $\alpha$-Zr.

3.2 Phase formation in irradiated or annealed Zr-Fe thin-films:

3.2.1 Phase formation under thermal conditions (thermal ramp runs):

Thermal-ramp runs were performed in the IVEM. The experimental temperature was increased gradually and held for short times (less than 20 min) at each temperature step and the effects were detected and recorded on the corresponding diffraction patterns. The goal of these runs was to determine at which temperature phase precipitation occurred readily without irradiation. As mentioned previously, the diffraction patterns of the as-fabricated films initially showed only the rings associated with hcp Zr indicating that the Fe is in solid solution in the Zr. The thermal ramp runs showed that new rings appeared on the diffraction patterns upon reaching 673 K. Figure 3.2 (center) shows the diffraction pattern taken after 10 min at 693 K including the new rings indicated by
arrows and identified as Zr$_2$Fe. As the temperature was further increased, inner rings identified as oxide rings appeared on the diffraction pattern as shown in Figure 3.2 (right) on the diffraction pattern taken upon reaching 823 K.

### 3.2.2 Phase formation under ion irradiation

**Description of the phenomenon:**

For all irradiation temperatures ion irradiation of the Zr-Fe thin films showed the formation of a new phase, as indicated by the presence of new rings in the diffraction pattern. For irradiation temperatures above room temperature these new rings were identified as the body-centered tetragonal Zr$_2$Fe phase.

During ion irradiation of the Zr-Fe thin films several new rings appeared in the diffraction pattern. These new rings (about 7) were identified as the body centered tetragonal Zr$_2$Fe phase. The rings were indexed as (211), (112), (220), (213), (411), (420), (332). As mentioned above, at temperatures below the eutectoid temperature (795°C) and concentrations less than 24 at%, the equilibrium phase diagram indicates that the stable phases are \(\alpha\)-Zr and Zr$_3$Fe \[88\]. In this range, the Zr$_2$Fe phase is therefore a metastable phase. Although a mixture of Zr$_2$Fe and Zr is not the most stable thermodynamically, Zr$_2$Fe is often observed in melts of compositions where normally the orthorhombic Zr$_3$Fe phase (the most stable phase thermodynamically) is expected to be observed. This is due to the sluggish formation of this last \[100\]. However the formation of Zr$_2$Fe likely still constitutes a net free energy decrease in the system relative to a solid solution of Fe in Zr. The kinetics depend on the temperature.
Figure 3.2: Thermal effect on the supersaturated (Zr-3%Fe) film. On the left: DP at room temperature (initial state). On the center: Diffraction pattern at 623 K: the arrows indicate rings associated with the new phase formed during irradiation and identified as Zr₂Fe. On the right, the diffraction pattern was taken at 823 K: arrowed inner rings indicating oxide formation. Note: Diffraction patterns are from different regions which explains the different textures.
Under thermal annealing, at 623 K and below no “immediate” change in the films was observed during the experiment. The apparent inability of Zr$_3$Fe to nucleate may possibly be attributed to a high interfacial energy between the Zr$_3$Fe phase and the Zr matrix and to the large difference (~15%) in molar volume between Zr$_3$Fe and α-Zr. Figure 3.3 shows both the bright-field and the dark-field micrographs obtained during in-situ 600 keV Kr ion irradiation at 300°C and the corresponding diffraction patterns. The right-hand-side region was shadowed from the beam by a specimen grid and is therefore unirradiated, and the left-hand-side region was irradiated to a fluence of 10$^{16}$ ion/cm$^2$ Kr ions. The diffraction pattern associated with the unirradiated area shows only the lines associated with the hcp phase, while the diffraction pattern from the irradiated region shows the new lines from the irradiation induced precipitates. The dark-field image taken by using one the precipitate (211) reflection (top right) shows the presence of irradiation-induced precipitates in the region exposed to the beam. However it should be mentioned that the dark-field micrographs were obtained as much as possible from the Zr$_2$Fe rings, although they are close to the Zr rings, and thus it may not be possible to completely eliminate the Zr intensity from the dark field.

For irradiation of Zr-Fe films conducted at 50 K it is clear that a new phase is formed, (new lines appear in the diffraction pattern) but the new phase was not indexed; the pattern of rings formed (i.e. their ratio of d-spacings) suggests an fcc phase. Interestingly, some amorphous intensity is visible in parallel with the appearance of the crystalline rings corresponding to the new phase.
Examining the results, it is clear that at irradiation temperatures above room temperature the precipitation process is similar to that observed under purely thermal conditions, i.e., showing homogeneous precipitation of the metastable Zr\(_2\)Fe phase evenly distributed in the Zr matrix. The dose necessary for precipitation decreases with increasing irradiation temperature indicating that the precipitation process is not a purely collisional process, with precipitate nucleation and growth occurring solely within the region where displacement cascades occur. The fact that irradiation enhances a naturally occurring process suggests that the irradiation induced point defect fluxes allow the Fe
atoms in metastable solid solution to arrive at the precipitates nuclei and cause them to grow. At 50 K, although there is second phase formation (Figure 3.4), the new phase was not identified. The appearance of amorphous rings suggests that at low temperature the mobility of the Fe atoms is not enough to make some of the amorphous nuclei formed in cascades grow into crystalline precipitates.

Figure 3.4: 500 keV Kr ion irradiation of Zr-2%Fe sample at 50K. The arrows point at new rings indicating the formation of an unidentified new phase. The amorphous ring around the Zr101 ring suggests that at 50K the mobility of the Fe atoms is not enough to make some of the amorphous nuclei formed in cascades grow into crystalline precipitates.

Study of the precipitation kinetics:

- Quantification of precipitation: “Speed” of reaction

Studying the kinetics of the precipitation requires the ability to quantify the amount of precipitates formed at successive fluences and then take the derivative with respect to the fluence or the corresponding dpa. However, as mentioned previously, it is difficult to map the precipitates with direct TEM imaging such as dark-field imaging because the diffracted beams corresponding to the main ring of $\alpha$-Zr and that of the new phase are too close to one another (i.e. the corresponding d-spacings are very close) and
the smallest objective aperture is still too large to select only the diffracted beam of interest. As a consequence, the dark-field images may very well include some Zr grains which could falsify any attempt to measure the amount of precipitates directly from the dark-field pictures.

Another way to perform the quantification of the reaction is to work with the diffraction patterns themselves. As the precipitates form, their corresponding diffracted rings become more and more intense. By integrating the intensity of these rings over the rings at different fluences, the kinetics can be studied. This method requires an imaging program that can create a map of the intensity of the entire diffraction pattern. It also requires being able to derive an equation for each ring position (which can be approximated by a circle) and integrating the intensity over the corresponding ring. Even in case these requirements are fulfilled, it should be stressed that the accuracy of the results depends on the quality of the scans of the diffraction pattern negatives (all scans should be of same quality), and more importantly on whether the micrograph exposure times were the same when the diffraction patterns were taken. Indeed, to be able to compare the intensity of diffraction patterns taken at different fluences they should be taken in equivalent conditions and with the same exposure time.

Using this method, for a given set of diffracting planes \{hkl\}, the diffracted intensity is proportional to the amount of phase present \(Q\), the square of the the unit cell structure factor \(F_{hkl}\) and the multiplicity of the family of planes \{hkl\} of interest \(M_{hkl}\). Hence, one can write:

\[
\frac{I_{\text{(hkl)precipitate}}}{I_{\text{(h'k'l')αZr}}} \propto \frac{Q_{\text{precipitate}} F_{hkl}^2 M_{hkl}}{Q_{αZr} F_{h'k'l'}^2 M_{h'k'l'}}
\]

Eq. 3.1

where \(Q\) is the amount of each phase, \(F_{hkl}\) and \(M_{hkl}\) are, respectively, the unit cell structure factor and the multiplicity of the diffracted beam for the \{hkl\} planes of interest. Thus:

\[
\frac{Q_{\text{precipitate}}}{Q_{αZr}} \propto \frac{I_{\text{(hkl)precipitate}}}{I_{\text{(h'k'l')αZr}}}
\]

Eq. 3.2
In case of texture being present, a correction factor would have to be added. By integrating the intensity of the diffracted beams over the corresponding rings at different fluences, the ratios were calculated for successive fluences. Hence, the kinetics of the ratio of precipitate amount to the amount main phase can be followed. This requires exposure times to be in the linear region of the response curve of the photographic film: gray scale intensity on the film vs. diffracted electron intensity (i.e. exposure time). The diffraction pattern negatives were scanned with the same size, the same resolution. The integrations were done with the use of the image processing software ImageJ. Figure 3.6 shows the ratio of intensity of 112 peak from the Zr₂Fe precipitate to the 004 peak from the Zr matrix versus the ion fluence obtained for Zr-1.2%Fe irradiated with 600 keV Kr ions at room temperature. This ratio gives a measure of the relative amount of precipitate that is formed versus the ion fluence as suggested by Eq. 3.3.
Figure 3.5: Integration of the diffracted-ring intensities using ImageJ program. (a) shows the regions (rings) selected for integration by ImageJ software. (b) shows a 3-D plot of intensity versus angular position for the diffraction pattern shown in (a).
Figure 3.6: Ratio of intensity of 112 peak from the Zr$_2$Fe precipitate to the 004 peak from the Zr matrix versus the ion fluence obtained for Zr-1.2%Fe irradiated with 600 keV Kr ions at room temperature.

“Dose-to-reaction” vs. irradiation temperature curve:

In any case, the parameters influencing the kinetics can be studied by examining at the point where the reaction starts and see how this point shifts with composition (Fe content in the film), the type of ion used (in our study: Ar or Kr), the temperature at which the irradiation is performed etc. For that, one needs first to define the dose-to-reaction which is defined as the dose at the onset of the reaction. In this study, this point was defined as the time when a “reasonable intensity” of the new rings appear around the ring indexed as $\alpha$-Zr (101) on the initial diffraction pattern with reasonable intensity. The dose to the onset of precipitation was determined by eye, from examination of the negatives. Previous studies have shown this is a reliable way to obtain a reasonable estimate of the amount of reaction[19]. Figure 3.7 shows the dose to onset of precipitation as a function of temperature for Zr-1.2%Fe film irradiated with 600 keV Kr ions at different temperatures. It is clear that the dose to precipitation decreases with
increasing irradiation temperature, reflecting the fact that this is an irradiation-enhanced, rather than irradiation-induced, process. Above 673 K, the precipitation can occur in the absence of irradiation as thermal processes suffice for the second phase precipitates to form.

![Dose-to-reaction vs. irradiating temperature for Zr-1.2%Fe, 600 keV Kr ions](image)

Figure 3.7: Dose-to-reaction vs. irradiating temperature for Zr-1.2%Fe thin film irradiated with 600 keV Kr ions.

### 3.2.3 Effect of the mass of the charged particle: e- irradiation at Saclay

The High Voltage Electron Microscope at the Commissariat a l’Energie Atomique (CEA), (Saclay, France) was used to carry out one-MeV-electron irradiations of Zr-Fe thin films. This was done in order to complement the results obtained with the ion irradiated samples and help answer the question of whether the phase formation depends
on the details of the damage structure or whether the transformation depends simply on the level of displacements per atom (dpa). Answering this question would give further insight on the mechanisms of the precipitation formation.

The resolution of the HVEM was limited in diffraction mode, therefore post-mortem analysis was done using a Philips 430 TEM. After a few irradiations at temperatures ranging from room temperature to 573K, we could see no discernible effect of electron irradiation in enhancing the formation of Zr$_2$Fe precipitation, compared with the results obtained in the study of the effect of ion irradiation on the phase stability of the Zr-Fe thin films done previously. Instead, the results indicated instead that electron irradiation enhanced the formation of some new phase identified as zirconium oxide (Figure 3.8). In contrast, the experiments at high temperature (723 K) showed clearly Zr$_2$Fe intermetallic formation, but this occurred due to thermal effects in the non-irradiated area. In the irradiated area the diffraction pattern was much more complex showing many new rings as can be seen in Figure 3.9. EDS spectra were obtained from 3 different regions (in the irradiated area (region labeled “box 1”), in the non-irradiated area (“box 3”) and in between the two regions (“box 2”). The spectra presented in Figure 3.10 clearly showed oxygen content in the irradiated area in larger proportion than in the non-irradiated area, confirming the idea that electron irradiation favored oxidation, as observed previously [101]. This is an artifact, likely caused by enhanced breakdown of carbohydrates and other molecules present in the vacuum of the TEM, occurring under the electron beam.

In summary, a study of irradiation enhanced precipitation in solid solutions of Zr supersaturated with Fe was performed by exposing free-standing thin-film samples to an ion beam while observing in situ the evolution of the microstructure in a transmission electron microscope. The results presented here indicate that at irradiation temperatures between 273 and 573 K the metastable Zr$_2$Fe phase is formed instead of the thermodynamically more stable Zr$_3$Fe. At 50 K, second phase formation occurs, but the phase formed has not yet been identified. The ion-irradiation dose necessary to cause significant precipitation decreases with increasing irradiation temperature. Above 673K
the reaction occurs readily without irradiation assistance. The absence of phase formation under electron irradiation suggests the idea that dense cascades of defects are necessary for the precipitation to occur.
a) Bright Field of the irradiated region

b) Initial diffraction pattern (before irradiation)

c) Diffraction pattern of the non-irradiated region at the end of the experiment (unchanged compared to the initial diffraction pattern)

d) Diffraction pattern of the irradiated region (80 dpa) (using the 430 Philips microscope). (Arrowed rings indicate sample oxidation in the TEM)

Figure 3.8: Microstructure of the Zr-2%Fe thin film irradiated at room temperature with 1 MeV electrons (*post mortem* analysis with the Philips 430 microscope).
Figure 3.9: Microstructure of the Zr-2%Fe thin film (sample S577) after irradiation at 723 K (90 dpa): a) bright field picture of the irradiated region (obtained from STEM (430 microscope)); b) EDS spectrum of the irradiated region (corresponding to picture a); c) diffraction pattern of the non irradiated region; d) diffraction pattern of the irradiated region (extra inner rings discernible as in the DP from the non irradiated region).
3.3 Kr ion irradiation of Cu-3%Fe:

Solid-solutions of Cu supersaturated with Fe (3 at%) thin-films were also irradiated with 500 keV Kr ions at room temperature and at 473 K. The irradiations at 298 K and 473 K both showed no second-phase precipitation at all. Figure 3.11 shows the bright field image and diffraction pattern of the as-fabricated Cu-Fe thin-film (top) and the diffraction patterns of the thin-films irradiated to a final fluence of $10^{16}$ ions/cm$^2$, at 298 K (bottom left), and 473 K (bottom right), respectively. The diffraction patterns of the irradiated samples showed no extra ring when compared to the initial diffraction pattern. The diffraction patterns of the irradiated samples were spottier, revealing that grain-growth had occurred during irradiation, which was verified in the bright-field images.
Figure 3.11: Bright field image and diffraction pattern of the as-fabricated Cu-Fe thin-film (top) and the diffraction patterns of the thin-films irradiated to a final fluence of $10^{16}$ ions/cm$^2$, at 298 K (bottom left), and 473 K (bottom right), respectively.

Because of the positive heat of mixing of the system, the precipitation of Fe particles was expected during the experiments, which was not observed. A possible explanation is to be found in the nature of the irradiation process. Indeed, as described in chapter 1, ion-irradiation is characterized by the formation of dense defect cascades which are followed by localized thermal spikes as the cascade cools down. During that thermal spike phase, the local temperature can exceed the melting temperature of the material so that the local regions, where the thermal spikes occur, are liquid-like. It is noticed that although the heat of mixing of Cu-Fe system is positive in solid state, it is negative in liquid state (whereas in the case of Zr-Fe the heat of mixing is positive in both
solid and liquid states). Thus, in Cu-Fe, the thermal spike regions may actually enhance the mixing of Cu and Fe and prevent segregation of the Fe species. This could explain why no Fe precipitation is observed in the Cu-Fe thin-films under ion irradiation.

3.4 Summary:

Zr and Cu solid-solutions supersaturated with Fe were irradiated with 500 keV Kr ions at different temperatures. In the case of Zr-Fe, the examination of the diffraction patterns revealed the formation of second-phase particles which were identified as Zr$_2$Fe precipitates at all irradiating temperatures above room temperature. Heat treatment in the absence of irradiation was observed to cause also precipitation of the Zr$_2$Fe intermetallic phase, but only above 673 K. In the bulk, this phase is thermodynamically metastable in the range of temperatures investigated (relative to the orthorhombic Zr$_3$Fe intermetallic phase). The kinetics of the irradiation-enhanced second-phase precipitation was followed by recording the diffraction patterns at regular intervals. The dose to precipitation was found to decrease with increasing irradiation temperature. The systematic study of the phase-transformation induced in the Zr-Fe thin-films by irradiation is reported in chapter 3 where a method for studying the kinetics of the precipitation is described briefly. Also, 1 MeV electron-irradiations of Zr-Fe thin-films were performed in a High Voltage Electron Microscope. The results revealed that no intermetallic precipitation occurred under electron irradiation. This implies that a certain density of defects is needed for the Zr$_2$Fe precipitation. In the case of Cu-Fe irradiated with 500 keV Kr ions, no second-phase formed. The fact that no Fe precipitation occurred in the Cu-Fe thin-films could be a result of the nature of the ion-irradiation induced damage. Indeed, it is considered that within the thermal spikes induced by ion-irradiation the local temperature can exceed the melting temperature so that the local regions are liquid-like. Although the heat of mixing of Cu-Fe system is positive in solid state, it is negative in liquid state (whereas in the case of Zr-Fe the heat of mixing is positive in both solid and liquid states). Thus, in Cu-Fe, the thermal spike regions may actually enhance the mixing of Cu and Fe and prevent segregation of the Fe species.
In both the Zr-Fe and Cu-Fe thin-films, the bright field images revealed that grain-growth was decreased with respect to the pure Zr and Cu thin-films respectively and in the case of Zr-Fe irradiated with 1 MeV electrons, no grain-growth occurred at all. This is described and discussed in more details in the next section which reports the experimental results of the grain-growth study.
Chapter 4

Experimental Results on Ion-Irradiation-Induced Grain-Growth

This chapter presents the results of experiments conducted to investigate the process of grain-growth under ion irradiation. As explained in chapter 2, during the in situ experiments, successive bright-field pictures were taken, from which measurements of grain size were obtained. This allowed a precise determination of the kinetics of grain-growth under irradiation at different temperatures.

In this study, Zr, Pt, Au, Cu were chosen as target materials to independently investigate the role of collisional processes and materials properties on grain-growth under irradiation. Pt and Zr have similar melting temperatures but very different atomic masses (i.e. different recoil spectra); and the same is true for Au and Cu. On the other hand, Pt and Au are adjacent elements in the periodic table of elements and therefore, have similar collisional characteristics (i.e. recoil spectra) under the same irradiation conditions, but the two elements have very different melting points. Hence, comparing results for both elements should highlight the role of melting temperatures of the elements (and correlated properties) on the grain growth process. Also, both Pt and Au are noble metals and are expected to be resistant to chemical reactions which may occur under thermal heating or irradiation; one does not need to worry about possible oxidation. Indeed the diffraction patterns of irradiated Au and Pt films showed no traces of oxidation or impurity reaction.

4.1 In-situ observations of ion-irradiation induced grain growth:

Direct observation of the metallic films under irradiation revealed a dynamic picture of ion-irradiation induced grain growth, i.e. a gradual increase of the average grain size (i.e. average grain diameter). The impact of the energetic ions and the defects
they caused were briefly visible in the microscope during irradiation. During the experiment, diffraction contrast changes caused by individual ion impacts could be discerned. The “inner” structure of the grains “flickered” on and off as the local contrast changed, likely due to the creation of defect structures within the cascades, such as defect clusters and small dislocations loops. Although the defects could not be resolved, due to their high density within the region of ion impact, the change in defect structure is suggested by the change of contrast in different areas of a grain under the impact of the ions.

The phenomenon of ion-irradiation-induced grain-growth is illustrated by Figure 4.1 which shows a sequence of bright field pictures of different elemental films irradiated at room temperature taken at different ion fluences. Pt and Au were irradiated with 500 keV Ar ions and Cu was irradiated with 500 keV Kr ions. The increase of grain size is apparent on the micrographs, with more grain-growth in Au and Cu than in Pt at a given dose. In parallel, the corresponding diffraction patterns became spottier as the fluence increased, also indicating grain size increase. Ion-irradiation induced grain growth was observed to be visually uniform (relatively narrow range of grain size and shape) at all doses examined for all materials. No secondary or abnormal grain growth was noticeable. These qualitative observations were later confirmed by measurement of the grain size distribution as a function of dose.

During the early part of the irradiation a small amount of grain recrystallization occurred that eliminated some amorphous-like structure observable in the as-deposited film, such that some of the diffraction rings became sharper and the grains more visible. This was particularly noticeable for some Zr films for which some of the inner rings in the diffraction pattern seemed to start somewhat amorphous. A dose of $10^{14}$ ions/cm$^2$ was enough to diminish the amorphous diffracted intensity and to sharpen the grain-boundary contrast observed in bright-field.
Figure 4.1: Sequence of bright-field images taken at different ion doses showing grain growth induced by ion-irradiation (from left to right: as deposited, $5 \times 10^{14}$ ions/cm$^2$, $2 \times 10^{15}$ ions/cm$^2$). From top to bottom: pure Au and Pt thin-films both irradiated with 500 keV Ar ions and Cu thin film irradiated with 500 keV Kr ions at room temperature.

Grain growth occurred for all ion energies, and all irradiation temperatures examined, even below 50 K, where thermal diffusion should be very small. Figure 4.2 shows a sequence of bright field pictures of a pure zirconium film irradiated with 500 keV Kr$^+$ ions at 20K taken at different ion fluences.
Grain-growth occurred as a direct result of ion irradiation and not as the simple result of heating of the sample induced by energy deposited by the incident ion beam. Indeed, the experimental observations confirmed the expectations (based on the calculations reported in chapter 2) that beam-heating does not play an important role in ion-irradiation-induced grain-growth.

It is possible to discern the roles of irradiation, beam heating, and temperature by examining the region shadowed by the TEM grid (Figure 2.11). As shown in Figure 4.3, sharp interfaces were observed between irradiated and non-irradiated areas shadowed by the TEM grid. The absence of grain growth in the unirradiated area indicates the lack of influence of beam heating in the grain growth process. This is because if it did play a
major role, the grain growth should also occur in the unirradiated area, since the high thermal conductivity of the metallic film would induce an increase in temperature in the shadowed area as well. Similar conclusions were drawn by Wang in his study of Ni films irradiated with Ag ions[76, 77] and by Atwater [70]. In the latter study [70], it was argued that if beam heating were to influence grain growth, then changing the beam flux should have a noticeable impact on the grain growth, which he did not observe after changing the ion beam flux by a factor of 10. Figure 4.3 shows the irradiated/non-irradiated interface region in the Pt thin-film irradiated with 1 MeV Kr ions at room temperature. It can be seen on the micrograph that no grain-growth has occurred in the non-irradiated area, as confirmed by grain-size measurements reported later in this chapter.

Figure 4.3: Irradiated/non-irradiated interface region in the Pt thin-film irradiated with 1 MeV Kr ions to $3 \times 10^{15}$ ions/cm$^2$ (in the irradiated area) at room temperature.

Even at the higher irradiation temperatures grain growth was not simply a thermal effect, induced only by holding the sample at high temperature inside the microscope. Figure 4.4 shows the limit between the irradiated area and the non-irradiated area (shadowed by the grid) in a Zr-1.2%Fe sample irradiated with 600 keV Kr ions at the irradiating
temperature of 573 K. There is a sharp demarcation line of the two regions: grains are clearly much bigger in the irradiated area. In this case, grain growth did not occur in the non-irradiated area which was held at 573 K for the time of the experiment (about 2.5 h). The absence of grain growth in the shadowed region was expected, since, purely thermal runs were conducted for selected samples at the Materials Research Laboratory (at PSU) using a heating holder in a Philips 420 TEM operated at 120 kV as detailed in section 4.2.

Figure 4.4: Bright-field micrograph of the interface between the irradiated (left) and unirradiated (right) regions in a Zr-1.2%Fe film irradiated with 600 keV Kr ions at an ion fluence of $10^{16}$ ions/cm$^2$ at 573 K.

In most cases grain growth occurred without noticeable change in either the in-plane or overall crystallographic texture of the grains. However, in Au some texture changes were observed during grain-growth. Figure 4.5 shows the interface between irradiated and non-irradiated area of the Au films after irradiation with 500 keV Ar ion/cm$^2$ at room temperature with the corresponding diffraction patterns. The diffraction pattern of the irradiated area of the Au films reveals that with increasing dose the (111), (002) rings progressively disappear while the (022) rings become increasingly spottier indicating grain-growth. This indicates that the grains which have (111) planes parallel to the beam tend to shrink, while the ones with (022) planes parallel to the beam grow.
Curiously, in this case the grains are not equiaxed, showing elongated shapes, with the largest grain axes perpendicular to the beam direction as shown in Figure 4.5. Because there is no rotation of the diffraction pattern relative to the image, the 111 plane normal is perpendicular to beam direction and that is also the direction of elongation of the grains. It is not clear, at this point, whether the grain-growth apparent anisotropy is induced by the beam or by crystallographic orientation. The diffraction pattern from the non-irradiated area is similar to the initial diffraction pattern. However the bright field revealed some (equiaxed) grain growth even though the experiment was conducted at room temperature. Other researchers have shown that grain growth can be observed in Cu[102], Ag, and Pd [103] under long duration near room temperature. As noted later this is likely because room temperature is a higher homologous temperature for Au than for Pt.
Figure 4.5: Au film irradiated with 500keV Ar ions at room temperature to a fluence of $10^{16}$ ions/cm$^2$. Top: bright field picture of the irradiated/non-irradiated interface; bottom: diffraction patterns associated with the irradiated (left) and non-irradiated (right) areas respectively.
4.2 Thermal grain-growth vs. irradiation grain-growth:

As mentioned previously, the sample geometry in the IVEM made it possible to obtain the information about the thermal effects alone, by examining the areas of the samples which were shadowed by the thickness of the grid thus unirradiated. Purely thermal runs were also conducted for selected samples at the Materials Research Laboratory (at PSU) using a Philips 420 TEM operated at 120 kV. The heating sample-holder was of the same model as the one used at Argonne National Laboratory. This section reports the results of these runs.

For Zr thin films held at annealing temperatures up to 873K, grain growth was not observed during the observation time (up to 6 hours). Indeed annealing times of more than 6 hours did not result in noticeable grain growth. The only noticeable phenomenon was the crystallization of some of the samples which were initially somewhat amorphous, during the early stages of irradiation, as mentioned above. Temperatures higher than 973 K were not investigated because of possible damage to the sample. Already at 973 K, thermal stresses induced some tearing or “wrinkles” of some regions and the sample stuck to the washers used in the sample holder.

The absence of grain-growth in the Zr films annealed at such temperatures appears to be at odds with bulk recrystallization temperatures: for example for bulk Zr in the 723-783 K temperature range, recrystallization can occur [104]. However, similar observations on the relative thermal stability of nanocrystalline materials are found in the literature. They show that, contrary to expectations, grain growth in nanocrystalline materials is small compared to that of their bulk counterparts. This is true up to a reasonably high (homologous) temperature, although in some instances, abnormal grain growth has been observed. This resistance to grain growth has been attributed to factors such as equiaxed grain morphology, relatively flat grain boundary configurations, and porosity of the consolidated samples. The effect of pores as Zener drags on the inhibition of grain growth is also evident. In addition, nanocrystalline materials contain large number of triple junctions which can further inhibit grain growth [62]. Molecular dynamics simulation further suggest that the triple junction drag is comparatively more
important for small grain sizes, low temperatures and high grain-symmetry mis-
orientation [105].

Thus it is likely that thermal grain-growth did not occur because of the greater
resistance of nanocrystalline materials to thermal grain-growth. In contrast, under ion-
irradiation, the ion-induced collision cascades (if large enough) can destroy triple
junctions and thus promote grain boundary motion upon rearrangement of the atoms
involved in the cascades. This may account for irradiation induced grain growth at low
temperatures where triple junctions are the most hindering to grain boundary migration.

Pt also showed resistance to thermal grain growth up to 773 K, but for Au and Cu,
thermal grain growth did occur at lower annealing temperatures. Figure 4.6 shows a
sequence of bright-fields of a Au thin-film irradiated with 500 keV Ar ions at 473K. The
unirradiated area showed grain growth with increasing time at 473 K (albeit smaller than
in the irradiated area). In this particular case, the experimental time was about 3 hours.
Figure 4.6: Sequence of bright field images showing the evolution of the irradiated and the non-irradiated areas of an Au film irradiated with 500 keV Ar ions at 473 K and taken at different ion doses: (a) as deposited, (b) $8 \times 10^{14}$ ions/cm$^2$ (47 min annealing time), (c) $5 \times 10^{15}$ ions/cm$^2$ (117 min annealing time), (d) $10^{16}$ ions/cm$^2$ (180 min annealing time). Although the shadowed (non-irradiated) area reveals thermal grain growth in the Au film at 473 K, there is still a significant difference in grain size between the irradiated area and the non-irradiated area.
4.2.1 Grain-growth kinetics

Grain-size measurements

The bright-field TEM micrographs were used to find the average grain size at the different fluences. In a given micrograph, the grain diameter was calculated as the average of the smaller and larger diameter of each grain, and then averaged over as many grains as were discernible on the micrograph (typically between 30 and 80 grains, less at higher fluences when the grains have grown). The micrographs were all taken at the same magnification to reduce errors. Grain-size measurement from grain-surface area determination was not possible for the use of a software would lead to major errors. Indeed, softwares identify grains according to the contrast a grain-boundaries, and grains with Moire fringes or stacking faults, are considered wrongly as many grains. The eye can determine better what is a grain from what is not. The grain size methodology discussed above converts the particle into an equiaxed grain. Since the surface to volume ratio of different shape grains vary, it is necessary to evaluate the effect of grain anisotropy on grain growth.

Effect of “anisotropy” of geometry of the grains assuming an ellipse of major radius \( a \) and minor radius \( b \) (where \( a=2b \)) versus a circle (2-D case) of equivalent area on the probability of cascade occurring at the boundary.

The area of the ellipse is \( \pi ab \), the radius of a disc of equivalent area is

\[
 r = \sqrt{ab} \quad \text{Eq. 4.1}
\]

In the case of ellipsoid grains,

\[
 \rho_{GB} = \frac{\pi \sqrt{2(a^2 + b^2) - (a-b)^2}}{\pi ab} \quad \text{Eq. 4.2}
\]

and the probability term \( P_{GB} \) becomes:
In the case of circular grains of equivalent area, $P_{Gb}$ is:

$$P_{Gb} = \sqrt{\frac{2(a^2 + b^2) - \frac{(a-b)^2}{2}}{ab}} \frac{d_{\text{spike}}}{2}$$  \hspace{1cm} \text{Eq. 4.3}

Assuming $b=2a$, $P_{Gb}$ in the case of an ellipsoid is only 8.9% more than in the case of a circular grain of equivalent area (2-D geometry). Hence the effect of anisotropic grain geometry is not significant.

**Grain-size distributions**

As mentioned previously, ion-irradiation-induced grain-growth in the films was observed to be uniform at all doses examined. No secondary or anomalous grain-growth was observed. As an example, Figure 4.7 shows the evolution of the grain size distribution with ion fluence for Zr-4.4%Fe irradiated with Kr$^+$ ions at 20K. As the ion dose increases, the peak of the distribution shifts to larger average grain sizes. The grain-size distributions were observed to be similar to those observed in thermally-induced normal grain-growth.

**Grain growth curves**

The average grain size in the metallic thin-films (calculated according to the procedure explained above) was then plotted versus ion dose for the different ions and irradiating temperatures. In order to compare the grain growth kinetics between different materials, it is more meaningful to plot the average grain growth rate and other properties as a function of the number of displacements per atom (dpa) rather than as a function of the ion fluence (ions/cm$^2$). As explained in chapter 2, the estimation of the number of dpa
was made using the Monte-Carlo code SRIM2003 which calculates displacement cross-sections for ions interacting with matter [97]. The calculated displacement rates were reported in Table 2.2.

Figure 4.7: Evolution of the grain size distribution with ion fluence for Zr-4.4%Fe irradiated with Kr+ ions at 20K.

The grain growth curves reveal a common trend for all compositions considered and for all irradiating temperatures: grain size increases gradually and monotonically but the rate of grain-size increase decreases steadily with ion dose until the grain-size reaches saturation. One “typical” evolution of the measured grain sizes with fluence is presented in Figure 4.8 which shows the average grain diameter of a Au film irradiated in situ with 500 keV Ar ions plotted as a function of ion dose in dpa.
Figure 4.8: Average grain size in Au film irradiated in situ at room temperature with 500 keV Ar ions plotted versus dose in dpa. The final dose corresponds to a dose of $10^{16}$ ions/cm$^2$. Typical error bars are shown.

Note on grain size measurement errors: Possible sources of errors include: (i) reproducibility, (ii) 2D measurements on TEM micrograph of a process that is occurring in 3D, (iii) measurement itself (binocular resolution, eye resolution), (iv) dose determination (counts, accuracy of the faraday cup etc), (v) Magnification calibration, (vi) statistical error (number of grains available for measurement). At the beginning of the experiment there are more grains to measure, therefore the statistical error is small however there is a little more inaccuracy associated (i, ii, and iii). At the end of the experiment, grains have grown much, measurements are more precise, (ii) and (iii) are less important but there are less grains hence (vi) is more important.
Grain-growth curve fitting

Similarly to the relationship between the average grain size ($D$) and annealing time ($t$) in the case of thermally induced grain growth (Eq. 1.3) [32, 45], the grain-size increase with ion irradiation can be described by the expression:

$$D^n - D_0^n = K\Phi$$  \hspace{1cm} \text{Eq. 4.5}

where $D_0$ is the initial mean grain diameter, $\Phi$ is the ion dose (dpa or ions/cm$^2$), $n$ is a constant and $K$ is proportional to the grain boundary mobility of the material and the driving force. The “grain-size versus ion-dose” curve fittings were performed using the expression given above. DataFit 9.0 software by Oakdale Engineering was used to perform the least-squares fits of the data. It was observed that the fitting parameters ($K$, $n$) took different values depending on the material, the temperature, and the range of doses in which the fits were determined.

As observed on all grain growth curves, the grain growth rate decreases with dose until it becomes negligible at high doses. The thickness of the thin foil is not the limiting factor in our case, since for Au and Cu films the grain size exceeded the thickness of the foil, long before reaching saturation. Furthermore the grain sizes were not affected by the use of thinner foil (500 Å thick film) in one of our experiments. Thus foil-thickness effects are not the reason for grain-size saturation. Under purely thermal conditions, grain-growth “saturation” occurs because of the decrease in grain-boundary curvature as the grain-size increases and topological metastable configurations take place. However, in this study, grain growth saturation may be ascribed only partly to the loss of driving force as the curvature of the grain boundaries becomes smaller. One likely explanation for the “saturation” effect is that the probability of cascades hitting the grain boundaries decreases as the grain size increases. It will be shown in chapter 5 that the primary contribution to ion-irradiation induced grain-boundary migration is the direct occurrence of cascades at the grain-boundaries. As a result, as the grain size increases, cascades are less likely to hit the grain-boundaries and grain-growth decreases. Thus, in the early stages of irradiation, when the grain size is small, the probability of hitting grain
boundaries is high - in fact if the cascade size is bigger than the grain size, the damage region could include entire grains. When the average grain size approaches and finally becomes larger than the diameter of the ion-induced cylindrical damaged region, the probability of hitting a grain boundary decreases. This process will be quantitatively modeled in chapter 5.

Variation in grain-growth exponents: Table 4.2 and Table 4.1 show the least squares error curve fit parameters determined for ion induced grain-growth data obtained from experiments performed in the various single-element films at room temperature and at cryogenic temperature respectively. The measured grain size D and ion dose Φ were fit to Eq. 4.5 in the dose range from 0 to 50 dpa. The grain growth exponents obtained showed little scatter from n=2.68 for 500keV Ar ion-irradiated Au to n=3.30 for 500 keV Kr ion-irradiated Cu foils, showing an average value close to n=3 i.e. cubic kinetics.

This average value of n is similar to values determined by Atwater et al. [70] and Liu et al. [71, 78, 106] for irradiated single-element thin-films. In his study of ion-irradiation-induced grain-growth in alloy thin-films (irradiated with 1.7 MeV Xe ions) Alexander’s growth exponents determined from fits to the grain size data varied from n=1.9 for Pt-Ni multilayers to 4.3 for Au-Co multilayers, again with an average of about 3.0 [69, 80, 81, 83, 107, 108]. In addition to the scatter from measurement error Alexander also attributed the observed variation in growth exponents to the presence of retarding driving forces in the films such as solute drag and free surface (thickness) effects without showing exactly how they would affect the value of n.

It should be pointed out that, although most studies showed an average value for ion-irradiation-induced grain-growth exponent of 3, the idea that this value is inherent to ion-irradiation-induced grain-growth I yet to be explored. Instead, this value was seen as a result of various drag effects slowing down the grain growth relative to the parabolic kinetics predicted by Hillert’s model of thermal grain-growth [107] which was normally assumed. As reported in chapter 1, Hillert’s model has been questioned on many aspects over the years and in any case it would have to be revisited to apply to the case of nanocrystalline materials. In chapter 5, it will be shown that the value of n results naturally from our thermal-spike model of grain-growth under ion-irradiation.
Table 4.1: Least-squares error curve fit parameters determined for ion induced grain-growth data at cryogenic temperatures for the different films. The measured grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 50 dpa.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion type / Energy</th>
<th>Temperature (K)</th>
<th>$D_0$ (nm)</th>
<th>$n$</th>
<th>$K$ ($\text{nm}^n/\text{dpa}$)</th>
<th>Coefficient of determination $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Ar/500keV</td>
<td>50</td>
<td>9.24</td>
<td>2.91</td>
<td>$1.66\times10^3$</td>
<td>91.3%</td>
</tr>
<tr>
<td>Cu</td>
<td>Kr/500keV</td>
<td>50</td>
<td>12.30</td>
<td>3.30</td>
<td>$2.91\times10^3$</td>
<td>99.1%</td>
</tr>
<tr>
<td>Pt</td>
<td>Kr/1MeV</td>
<td>50</td>
<td>12.36</td>
<td>3.12</td>
<td>$7.36\times10^3$</td>
<td>97.5%</td>
</tr>
<tr>
<td>Zr</td>
<td>Kr/500keV</td>
<td>20</td>
<td>14.17</td>
<td>2.74</td>
<td>$0.41\times10^3$</td>
<td>99.7%</td>
</tr>
</tbody>
</table>

Table 4.2: Least squares error curve fit parameters determined for ion induced grain-growth data at room temperature for the different films. The measured grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 50 dpa (except Zr-Fe for which the fit was done in the dose range from 0 to 75 dpa).

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion type / Energy</th>
<th>Temperature</th>
<th>$D_0$ (nm)</th>
<th>$n$</th>
<th>$K$ ($\text{nm}^n/\text{dpa}$)</th>
<th>Coefficient of determination $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Ar/500keV</td>
<td>Room temp.</td>
<td>13.2</td>
<td>2.68</td>
<td>$12.2\times10^3$</td>
<td>97.3%</td>
</tr>
<tr>
<td>Cu</td>
<td>Kr/500keV</td>
<td>Room temp.</td>
<td>13.6</td>
<td>3.17</td>
<td>$4.15\times10^3$</td>
<td>99.6%</td>
</tr>
<tr>
<td>Pt</td>
<td>Kr/1MeV</td>
<td>Room temp.</td>
<td>14.5</td>
<td>3.27</td>
<td>$12.4\times10^3$</td>
<td>99.0%</td>
</tr>
<tr>
<td>Ar/500 keV</td>
<td>Room temp.</td>
<td>12.0</td>
<td>2.97</td>
<td></td>
<td>$4.15\times10^3$</td>
<td>99.0%</td>
</tr>
</tbody>
</table>

4.3 Effect of Ion mass:

Zr-Fe thin-films

In order to determine the influence of the projectile mass, Zr-Fe films were irradiated at 573K with both 600 keV Ar ions and with 600 keV Kr ions. Table 4.3 summarizes the experimental parameters of these irradiations. The displacement cross-
sections and damage energy were obtained from SRIM as described in section 2.4.1. The SRIM results are reported in detail in Appendix 1.

Table 4.3: Irradiation parameters for Zr-Fe films irradiated with both 600 keV Ar ions and 600 keV Kr ions at 573K.

<table>
<thead>
<tr>
<th>Ion type/energy</th>
<th>Atomic mass (a.m.u.)</th>
<th>Damage energy deposited (eV/ion-Å)</th>
<th>Displacement rate from SRIM (#disp/ion-Å)</th>
<th>Displacement rate (dpa/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar 600keV</td>
<td>40</td>
<td>40.9</td>
<td>0.82</td>
<td>0.004</td>
</tr>
<tr>
<td>Kr 600keV</td>
<td>83.8</td>
<td>180</td>
<td>3.25</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Figure 4.9 shows the average grain size in the Zr-Fe films irradiated at 573K with 600 keV Ar ions and 600 keV Kr ions versus ion fluence (ions/cm²). At a given fluence grain growth is more pronounced for Kr ion irradiation than for Ar ion irradiation. The saturation grain size also appears to be larger under Kr irradiation than under Ar ion irradiation. Figure 4.10 shows screen captures showing the recoil spatial distribution for 500 keV Ar ions in Zr (left) and 500 keV Kr ions in Zr (right). Shown in green are the locations where recoils atoms were generated. The three plots show the three planes of observation. These qualitative estimations of cascade size using SRIM showed a clear difference in cascade size between the two ions as seen in the figure. The Kr ions generate larger cascades than the Ar ions do. This is explained by the values of the maximum-energy transfer parameter \( \Lambda = \frac{4M_1M_{\text{ion}}}{(M_1 + M_{\text{ion}})^2} \) (where \( M_1 \) is the atomic mass of the target material). Indeed, in Zr, \( \Lambda \) is close to 0.84 for Kr and 0.56 only for Ar. This causes more energetic recoils in Kr than in Ar.

According to the model presented in chapter 5, if a cascade hits the grain-boundary it will cause it to migrate. Therefore a larger average cascade size means that a larger region at the grain-boundary can contribute to grain-growth and saturation will occur at larger grain sizes.
Figure 4.9: Average grain size in Zr-Fe films irradiated in situ at 573K with 600 keV Ar and 600 keV Kr ions versus the dose in dpa.
Figure 4.10: SRIM2003 simulation of ion irradiation in 800Å thick Zr foils (5 ions): longitudinal and lateral views of the path of ions (red dots) and the displacements caused (green dots). On the left is the case of 500 keV Ar ion irradiation and on the right, that of 500 keV Kr. Regions of point defects are bigger and more dense in the case of Kr irradiation than Ar irradiation which means that the resulting thermal spike regions will be larger in the case of Kr than in the case of Ar.
Pt thin-films

Similar experiments were conducted in Pt films irradiated at room temperature with both 500 keV Ar ions and 1MeV Kr ions (the higher energy was chosen to minimize Kr ion implantation). In this case, however the difference in energy may have erased the mass difference as shown below.

Table 4.4 summarizes the main experimental parameters of the irradiations conducted in Pt films.

<table>
<thead>
<tr>
<th>Ion type/energy</th>
<th>Atomic mass (a.m.u.)</th>
<th>Damage energy deposited (eV/ion-Å)</th>
<th>Displacements/ion-Å</th>
<th>Displacement rate (dpa/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar 500keV</td>
<td>40</td>
<td>120</td>
<td>3.504</td>
<td>0.0128</td>
</tr>
<tr>
<td>Kr 1MeV</td>
<td>83.8</td>
<td>367</td>
<td>9.772</td>
<td>0.0185</td>
</tr>
</tbody>
</table>

Figure 4.11 (top) shows the average grain size measured in a Pt thin-film irradiated at room temperature with 500 keV Ar ions and 1 MeV Kr ions versus ion fluence (ions/cm²). Grain growth is faster and larger for 1-MeV-Kr ion irradiation than for 500-keV-Ar ion irradiation at a given fluence. However, when the data are plotted with respect to dpa, the curves collapse into one as shown in Figure 4.11 (bottom) revealing the same kinetics and “saturation grain size” for either irradiation.

The final grain-size in the saturation regime is expected to be a function of the collision cascade size. So it is possible that both Ar and Kr induced cascades are of similar size. Indeed, at higher ion-energy the nuclear stopping cross-section is smaller relative to the electronic stopping cross-section and less recoils are produced. Even if collision dynamics dictate that recoils of higher energies can be kinematically produced in the case of 1 MeV Kr irradiation, they are more likely to break into subcascades. Overall, this causes rather small (although more frequent) (sub)cascades in the case of
Figure 4.11 Average grain size in Pt films irradiated in situ at room temperature with 500 keV Ar and 1MeV Kr ions plotted versus the dose in ion fluence (top). When plotted versus dpa, the curves collapse into one same curve (bottom).
higher energy ion-irradiation (here 1 MeV Kr ions). This argument seems to be supported by the qualitative estimations of cascade size using the SRIM code presented in Figure 4.12, which show similar cascade sizes during 500 keV Ar and 1MeV Kr irradiations, although they appear to be more numerous in the case of Kr irradiation. This does not mean that the recoil spectra are identical for both irradiation cases - in fact the SRIM simulations show that in the case of Ar irradiation there are more recoils created with very low energies than in the case of Kr. However this suggests that the maximum subcascade sizes are similar in both cases. This results in the same final size, but with a more frequent production of subcascades per ion in the case of Kr ion irradiation, and hence the faster grain-growth in terms of fluence. So when the grain size is plotted versus ion fluence we can see a difference, but against dose in displacements-per-atom there is basically no difference.

In a study of ion-irradiation induced grain growth in Pd films[71], Liu also observed that grain growth in the Pd films irradiated with 560 keV Xe ions was larger than that induced by 185 keV Ar ions and 100 keV Ne ions, leading to the conclusion that the cascade size may have a direct effect on the final grain size. In that study average the final average grain-sizes for Xe, Ar and Ne irradiations in Pd were respectively, about 60, 40 and 25 nm. In that case the SRIM simulation gives an estimate of cascade size that is quite different among the three. This further supports the idea that the final size is related to the average size of a single thermal-spike. This can be taken into account quantitatively by considering the probability of spikes occurring at the grain-boundaries, which should be directly proportional to the size of the spikes (and the density per unit volume of grain-boundaries). This point will be further developed in chapter 5 where the modelization of ion-irradiation-induced grain-growth will be introduced.
Figure 4.12: SRIM2003 simulation of ion irradiation in 800Å thick Pt foils (5 ions): longitudinal and lateral views of the path of ions (red dots) and the displacements caused (green dots). On the left is the case of 500 keV Ar ion irradiation and on the right, that of 1 MeV Kr. Regions of point defects do not seem much bigger in the case of 1 MeV Kr irradiation than 500 keV Ar irradiation which means that the resulting thermal-spike regions will be of similar sizes for both 1 MeV Kr ions and 500 keV Ar ions.
4.4 Influence of irradiation temperature:

Temperature dependence of grain-growth under ion irradiation:

The temperature effect on ion-irradiation induced grain growth has been investigated for Si and for Ge thin films by Atwater et al [70]. They found that the temperature dependence was weak in the rather narrow temperature ranges of their study, which were 1023-1123 K for Si and 723-973 K for Ge. Liu investigated ion-irradiation induced grain growth in Cu thin films with a wider temperature range 113-473 K and found a temperature dependence of grain growth kinetics for temperatures higher than 213 K[78].

In this study, irradiations of Zr-Fe [109] and Pt, Au, Cu, thin films were carried out at temperatures varying from 20 K to 773 K depending on the material. Figure 4.13 shows the average grain size vs. ion dose for irradiations conducted at 20 K, 293 K, 473 K, 573 K in the Zr-Fe thin-films. The data shows little difference in the curves obtained at 20 K and at 293 K, which suggests that ion-beam induced grain growth in the Zr-Fe films are independent of temperature in this temperature range. This suggests that in this temperature range, “ballistic” or collisional effects of ion irradiation dominate the grain growth process. At higher temperatures, both the rate of grain growth and the final saturation grain size increase with higher substrate temperatures. In that temperature range, grain growth is a result of the combined effects of irradiation and the substrate temperature.

The same observation was done in the case of Pt films irradiated with 1 MeV Kr ions at different irradiation temperatures $T_{\text{irr}}$ shown in Figure 4.14 which shows the average grain size vs. ion dose for irradiations conducted at 50 K, 293 K, and 773 K in the Pt thin-films. There is no effect of $T_{\text{irr}}$ on grain-growth below room temperature and the kinetics are enhanced with $T_{\text{irr}}$ at higher temperatures. The existence of a low temperature regime where ion-irradiation induced grain growth does not depend on the irradiation temperature suggests that in this regime, the migration of the grain boundary is controlled by intra-cascade ballistic processes. On the other hand, in the higher
temperature range, the dependence on irradiation temperature suggests the expression of the mobility should include a temperature-dependent term [78].

---

**Figure 4.13:** Average grain size in Zr-1.2\%Fe thin foils irradiated in situ with 500 keV Kr ions plotted versus the dose in dpa for different temperatures. This plot highlights the effect of irradiation temperature on ion beam induced grain growth in the Zr-Fe thin films.
Figure 4.14: Effect of irradiation temperature on ion beam induced grain growth in Pt thin films irradiated with 1 MeV Kr ions. Average grain size is plotted versus the dose in dpa for different irradiating temperatures.

The grain growth curves for Pt and Zr (Figure 4.13 and Figure 4.14) indicate that the transition temperature from temperature-independent regime to temperature-dependent regime for these elements, is above room temperature. This is not the case for the Cu and Au thin-films. Figure 4.15 and Figure 4.16 show the grain-growth curves at various temperatures for Au and Cu respectively. In both cases grain growth is enhanced at room temperature compared with the cryogenic run, which indicates that for Au and Cu the transition temperature between the two regimes is below room temperature. Hence the transition temperature from temperature-independent regime to temperature-dependent regime changes from material to material. However, when scaled with the melting temperature of the material (i.e. in terms of homologous temperatures $\tau = \frac{T}{T_{melt}}$)
it falls within a common range. For the different elements in this study, this transition temperature $\tau_x$ is determined with more or less precision as:

$$0.14 < \tau_{\text{Zr}} < 0.19,$$

$$0.14 < \tau_{\text{Pt}} < 0.23,$$

$$0.03 < \tau_{\text{Cu}} < 0.22,$$

$$0.04 < \tau_{\text{Au}} < 0.22.$$

We note that our results for Cu agree with [78] where it was observed that ion-irradiation-induced grain-growth in Cu foils increased with temperature only above 213 K, which corresponds to a homologous transition temperature $\tau$ of 0.16.

---

**Au, 500keV Ar ions**

![Graph](image)

**Figure 4.15:** Effect of irradiation temperature on ion beam induced grain growth in Au thin films irradiated with 500 keV Ar ions. Average grain size is plotted versus the dose in dpa for different irradiating temperatures. The curves were fitted to Eq. 4.5 and the fitting parameters are reported in Table 4.1, Table 4.2, and Table 4.5.
Figure 4.16: Effect of irradiation temperature on ion beam induced grain growth in Cu thin films irradiated with 500 keV Kr ions. Average grain size is plotted versus the dose in dpa for different irradiating temperatures.

Table 4.5 reports the fitting parameters of the grain-growth curves for Au irradiated with 500 keV Ar ions at 473 K, Cu irradiated with 500 Kr ions at 573 K, Pt irradiated with 1 MeV Kr ions at 773 K. The exponent values are still close to 3.00 for Au and Pt; however for Cu, the exponent is higher. It should be noticed that one of the issues with carrying out the irradiations at temperatures which belong to the temperature-dependent regime was the fact that the irradiation of the samples was started after some thermal grain had already occurred in the sample during the heating stage. This is reflected by higher initial average grain sizes $D_0$ as reported in Table 4.5. That was especially relevant to the case of Cu for which thermal grain growth already occurred at
temperatures lower than 473K so that the average grain size was more than 70 nm before the irradiation started. This means that when the irradiation actually started, the initial grain size distribution was not really the same as for the low temperature runs since grain growth had already occurred while heating up of the sample to the wanted irradiating temperature. And more importantly this also means that the initial driving force was not the same. The larger initial average grain size is synonymous with a lower initial driving force due to grain-boundary curvature because it is inversely proportional to the grain size according to Eq. 1.11. This results in slower kinetics (higher n exponent).

Table 4.5: Least squares error curve fit parameters determined for ion induced grain-growth data at room temperature for the different films. The measured grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 50 dpa (except Zr-Fe for which the fit was done in the dose range from 0 to 100 dpa).

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion type / Energy</th>
<th>Temperature (K)</th>
<th>$D_0$ (nm)</th>
<th>$n$</th>
<th>$K$ (nm$^3$/dpa)</th>
<th>Coefficient of determination $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Ar/500keV</td>
<td>473</td>
<td>25.53</td>
<td>3.00</td>
<td>1.86x10$^5$</td>
<td>91.3%</td>
</tr>
<tr>
<td>Cu</td>
<td>Kr/500keV</td>
<td>573</td>
<td>72.4</td>
<td>3.55</td>
<td>5.82x10$^5$</td>
<td>94.6%</td>
</tr>
<tr>
<td>Pt</td>
<td>Kr/1MeV</td>
<td>773</td>
<td>20.22</td>
<td>3.25</td>
<td>4.10x10$^4$</td>
<td>99.1%</td>
</tr>
</tbody>
</table>

Apparent activation energies from Arrhenius plots

In the temperature-dependent regime, if grain-boundary migration (which is directly proportional to the fitting parameter $K$) is assumed to be controlled by two types of grain-boundary mobilities, a temperature-independent one (derived later in Eq. 5.50) added to a temperature-dependent one $M_{\text{dep}}$, $M$ can be written as:

$$M = M_{\text{indep}} + M_{\text{o}} \exp \left( \frac{E_a}{k_B T} \right)$$  \hspace{1cm} \text{Eq. 4.6}

It was possible to estimate the apparent “activation energies” ($E_a$) from plots of Arrhenius-type even though we were limited by the number of different temperature runs (only 2 different temperatures lying in the temperature-dependent range for each system). The data was fitted with the equation $D^3 - D_o^3 = K\Phi$ and the parameter $K$ was obtained for the different temperatures. The mobility is directly proportional to $K$ therefore there is
no need to compute the actual values of the mobilities, we can work with the K values.
The apparent activation energy of the temperature-dependent component can be obtained by subtracting \( K_{\text{indep}} \) (obtained from the low-temperature irradiation experiments and reported in table Table 4.1) from the overall K value obtained from the fits mentioned above, and plotting \( \ln(K-K_{\text{indep}}) \) versus \( 1/T \). The values of \( E_a \) obtained for Cu, Au, and Zr-Fe, are reported in Table 4.6.

Table 4.6: Apparent activation energies in the temperature-dependent regime

<table>
<thead>
<tr>
<th>Ion/target system</th>
<th>Temperatures (K)</th>
<th>Apparent activation energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kr 500 keV in Cu</td>
<td>273-573</td>
<td>0.1</td>
</tr>
<tr>
<td>Ar 500 keV in Au</td>
<td>273-473</td>
<td>0.15</td>
</tr>
<tr>
<td>Kr 500 keV in Zr-1.2%Fe</td>
<td>423-573</td>
<td>0.24</td>
</tr>
</tbody>
</table>

These values are close to values obtained in other studies. Indeed, in their study of irradiated Ge and Si films irradiated at temperatures of 1023 – 1088 K for Ge and 1023 – 1123 K for Si, Atwater et al. reported apparent activation energies of 0.1 eV for Si and 0.15 eV for Ge from grain-growth rate plots of Arrhenius-type. For comparison, activation energy for thermal grain growth is about 2.5 eV for Ge and 1.3 eV for Si. More generally, for thermal grain growth, activation energies determined with Arrhenius plots are usually half of the activation energies for lattice self-diffusion. In the study of grain-growth under ion-irradiation in Cu [78], The same activation energy of 0.14 eV was found for both Ar and Xe ions irradiations. This value is close to the one obtained in our study for Cu. For comparison, activation energy for thermal grain growth in Cu is about 1 eV.

It is noticed that the apparent activation energies found are close to the activation energies for self-interstitial diffusion in metals (typically 0.1 eV). This suggests that radiation-enhanced diffusion of interstitials is a possible mechanism of ion-irradiation-induced grain-growth in the temperature dependent regime. However we will see in chapter 5 that point defect migration is likely not the major source of temperature dependence of grain-growth in our case because most irradiations were performed in the recombination-dominated regime except for Au irradiated at 473 K and Pt irradiated at
773 K. The case of Au irradiated with Kr 500 keV at 473 K is the only case of all experiments where we observed voids (bubbles) decorating the grain boundaries, supporting the idea of defects migration to the grain boundary sinks as seen in Figure 4.17.

![Image of Au film irradiated with 500 keV ions at 473 K, at a final dose of $10^{16}$ ions/cm$^2$ showing the formation of faceted bubbles decorating the grain boundaries.]

**Figure 4.17:** Au film irradiated with 500 keV ions at 473 K, at a final dose of $10^{16}$ ions/cm$^2$ showing the formation of faceted bubbles decorating the grain boundaries.

### 4.5 Effects of the material melting point / cohesive energy

Since in the low-temperature regime, grain-growth kinetics are independent of the substrate temperature, a legitimate question is whether ion-irradiation-induced grain-growth in this regime is not purely collisional (i.e. ballistic). If this is the case, then materials with similar collisional properties (i.e. damage energy linear density $F_D$ and recoil energy spectra) should exhibit similar grain-growth kinetics. If this is not the case than materials properties must be affecting grain-growth and therefore they should be taken into account in the model.
Thus the purpose of this section is to investigate the influence of the material properties of the target materials on the grain growth kinetics. Pt and Au were chosen as the target materials. Both materials have a fcc crystallographic structure at room temperature and, as mentioned previously, Au (atomic mass=196.97) and Pt (atomic mass=195.08) are adjacent elements in the periodic table of element and SRIM calculations show that they have similar recoil energy spectra under the same irradiation conditions as shown in Figure 5.5. However they have very different melting points, thermal conductivities, cohesive energies (i.e. atomic jump activation energies) as shown in Table 4.7. As a consequence, by comparing their grain growth kinetics we can highlight the specific influence of these material properties on grain-growth.
Table 4.7: Material properties of Pt and Au and their collisional characteristics obtained from SRIM2003 code for simulations of irradiations of 80 nm thick films irradiated with 500 keV Ar ions with an incident angle of 15 degrees (from Appendix 1).

<table>
<thead>
<tr>
<th>Element</th>
<th>Crystal structure at room temperature</th>
<th>Atomic mass (amu)</th>
<th>Atomic density (10^{22} \text{ cm}^{-3})</th>
<th>(\Delta H_{\text{coh}}) (eV/at)</th>
<th>Melting point (K)</th>
<th>Heat capacity (C_0) (J/mol-K)</th>
<th>Thermal conductivity (K_0) (W/m-K)</th>
<th>Deposited damage-energy (eV/ion-Å)</th>
<th>Disp. rate (dpa/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>fcc</td>
<td>195.08</td>
<td>6.60</td>
<td>5.84</td>
<td>2041</td>
<td>25.9</td>
<td>72</td>
<td>120</td>
<td>0.0128</td>
</tr>
<tr>
<td>Au</td>
<td>fcc</td>
<td>196.97</td>
<td>5.90</td>
<td>3.81</td>
<td>1337</td>
<td>25.42</td>
<td>320</td>
<td>100</td>
<td>0.0119</td>
</tr>
</tbody>
</table>
Figure 4.18: Average grain size is plotted versus the dose in dpa. The plot shows the
effect of intrinsic materials properties on ion beam induced grain growth in Pt thin films
compared with Au. Both materials have similar collisional properties but different
material properties. The Pt film was irradiated with 500 keV Ar ions at room temperature
which falls in the “temperature-independent” regime for Pt. The Au foil was irradiated
with 500keV Ar ions at 50K which also falls in the temperature-independent regime.

Figure 4.18 shows the grain-growth curves for Pt and Au films both irradiated
with 500 keV Ar ions in the low-temperature regime where the kinetics of grain-growth
are independent of temperature. The plots show that both grain-growth rate and final size
are about two times larger in the Au films than in the Pt films although both materials
have similar recoil spectra and are both irradiated in the temperature-independent regime.
The SRIM calculations show similar overall deposited energy per ion per unit length (100
eV/ion-Å for Au and 120 eV/ion-Å for Pt). This means that collisional properties such as the deposited damage energy cannot explain alone grain growth kinetics; materials properties such as the melting-point and cohesive energy of the target materials must play a determining role too and should be taken into account when modeling grain-growth under ion-irradiation. Indeed the difference in grain-growth kinetics between Au and Pt could come from the difference in material properties such as their melting-temperature/cohesive energy (and related properties such as formation and migration energies of defects) of the two materials.

This result agrees with similar observations in the literature. For instance, Liu observed significant variations in grain growth rates among alloys that exhibit similar collisional damage behavior, and suggested that a purely collisional model is inadequate for describing ion-induced grain growth [106]. It was proposed that ion-irradiation induced-grain-growth may be related to “thermal spike” effects, the thermal spike diffusion being characterized by its short diffusion time, high temperature and localized liquid-like diffusion region as described in chapter 1. The ion-induced grain-boundary mobility was first scaled with the number of defects created within thermal spikes (using Vineyard’s analysis[14]) which yielded a dependence on \( \frac{F_D^2}{\Delta H_{coh}^2} \) for a cylindrical spike geometry [106]; this formulation was later corrected by Alexander to a dependence on \( \frac{F_D^2}{\Delta H_{coh}^3} \) [69]. In any case, it should be pointed out that the expression of the grain-boundary mobility dependence derived by Alexander should be associated to the low-temperature regime where grain growth is independent of temperature. In the higher-temperature regime the expression of the mobility should be corrected by a temperature dependent term in order to account for the observed dependence of grain-growth on temperature which we have reported in this chapter.
4.6 Role of solute: Cu-Fe vs. Cu and Zr-Fe vs. Zr.

The non-equilibrium processing of the thin films using sputtering technology results not only in nanocrystalline structure but also in supersaturated solid solutions in the case of alloy systems. As explained in chapters 2 and 3, the formation of alloys and supersaturated solid solutions in nanocrystalline materials which do not exist in coarse-grained polycrystals has been previously reported [66]. Hence we were able to process supersaturated Zr-Fe and Cu-Fe thin films and irradiated them to determine the effect of the alloying elements on ion-irradiation induced grain growth.

In the case of the Zr-Fe system, the diffraction patterns of the as-deposited films could be indexed using only the reflections from the hcp $\alpha$-Zr phase. Because of the rapidity of the effective quench during thin film deposition, no second phase was formed, although RBS analysis confirmed an iron content in the Zr-Fe films well beyond the solubility limit of Fe in Zr (in the order of ppm) [92]. In the case of Cu-Fe system, the two elements are reportedly immiscible in solid form. The thin films of Cu supersaturated with iron were processed using the same co-sputtering method mentioned earlier. Figure 4.19 shows the bright field and associated diffraction pattern for both Zr-4.4at%Fe and Cu-3%Fe. As shown in Figure 4.19, the intensity of the diffracted rings is even around their circumference, indicating no in-plane texture for either system. In the case of the Zr-Fe films, the grains were preferentially oriented with the basal plane perpendicular to the foil surface, as verified by the high 002 intensity in Figure 4.19 (bottom right). This texture differs from that observed in previous experiments [95]. For Cu-Fe films, the relative intensity of the diffracted rings was as expected for coarse-grained Cu with no preferential orientation.
Figure 4.19: Bright fields and associated diffraction patterns of Cu-3%Fe and Zr-4.4%Fe films as deposited. The films are nanocrystalline with diffraction patterns characteristic of the pure metal: the rings of the Cu-Fe films were all indexed as fcc Cu rings and the rings of the Zr-Fe films were all indexed as hcp α-Zr rings.

Figure 4.20 shows the average grain size for pure Zr and for Zr-4.4%Fe irradiated with 500 keV Kr ions in the low-temperature regime where the grain-growth kinetics do not depend on the irradiation temperature. The supersaturated solid-solutions showed smaller and slower ion-beam induced grain growth than that seen in pure Zr. Indeed the presence of alloying element Fe slows down the grain growth rate (slope of the curve at the origin) and results in smaller final average size. Solute drag and/or precipitate formation could be responsible for slowing down grain-growth, since, as shown in chapter 3, Zr-Fe intermetallics (mainly Zr$_2$Fe) form during ion-irradiation as indicated by the diffraction patterns [110]. In the case of Cu-3%Fe thin films irradiated with 500keV
Kr ions, grain-growth was also slowed relative to that observed in pure Cu. Figure 4.21 shows the average grain size for pure Cu and for Cu-3%Fe irradiated in the same conditions (at 300 K, with 500 keV Kr ions). The Fe-containing films showed slower grain growth than the pure Cu films. However, since no second phase precipitate could be detected in the diffraction patterns, it is likely that solute drag is the mechanism for slowing down the ion-irradiation induced grain growth in the Cu-3%Fe thin films.

Figure 4.20: Average grain size in Zr and Zr-4.4%Fe films irradiated in situ with 500 keV Kr ions plotted versus the dose in dpa in the temperature-independent regime.

The solute drag effect in the Cu-Fe thin-films is not very pronounced at low doses whereas in the Zr-Fe thin films, as soon as the Zr$_2$Fe precipitates form (early in the irradiation experiment), the kinetics of grain-growth is slowed down relative to the grain-
growth rate in the pure material (see Figure 4.20). This is indicative that second-phase-particle drag effects ("Zener drag") are more effective at slowing down grain-growth than solute drag effects.

Figure 4.21: Average grain size in Cu and Cu-3%Fe films irradiated in situ at room temperature with 500 keV Kr ions plotted versus the dose in dpa. The plot highlights the effect of alloying element on ion-beam induced grain growth.

Table 4.8 reports the fitting parameters for grain-growth curves for Cu-Fe irradiated with 500 keV Kr ions and Zr-Fe irradiated with 500 keV ions. The higher exponents than those shown in Table 4.12 indicate that grain-growth is slowed in the alloys. In the case of Zr-Fe the drag effect by second-phase particles (Zr2Fe precipitates) is expected to play an important role in the grain-growth process and therefore the
kinetics parameters should be affected. This is most likely the reason for the higher grain-growth exponent which is synonymous with slower kinetics. Similarly, solute drag effect impacts the kinetics parameters in the case of Cu-Fe.

Table 4.8: Least squares error curve fit parameters determined for ion induced grain-growth data at room temperature for the different films. The measured grain size $D$ and ion dose $\Phi$ were fit to Eq. 4.5 in the dose range from 0 to 100 dpa.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion type / Energy</th>
<th>Temperature (K)</th>
<th>Fit parameters</th>
<th>Coefficient of determination $R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Fe</td>
<td>Kr/500 keV</td>
<td>Room temperature</td>
<td>$D_0$ (nm) 15.47, $n$ 5.95, $K$ (nm$^n$/dpa) 4.14$x10^6$</td>
<td>98.2%</td>
</tr>
<tr>
<td>Zr-Fe</td>
<td>Kr/500keV</td>
<td>423</td>
<td>15.61, 5.71</td>
<td>4.08$x10^6$ 98.2%</td>
</tr>
<tr>
<td>Cu-Fe</td>
<td>Kr/500 keV</td>
<td>473</td>
<td>15.63, 4.90</td>
<td>3.5$x10^6$ 92.4%</td>
</tr>
</tbody>
</table>

Finally, it is noted that in the theory of solute drag effect on grain growth it is usually assumed that the drag force is independent of the grain size. This should be a valid approximation for usual coarse polycrystalline materials (with grain sizes in the micron range). However in the case of nanocrystalline materials this approximation may no longer hold [111]. The relationship between the solute drag term and grain size is being determined by the evolution of the difference between the concentration of solute atoms segregated in the grain boundaries and that of solute atoms dissolved in the crystallites. This concentration difference evolves upon grain growth and solute migration to the boundary. In the case of nanocrystalline materials, this change is more dramatic than in the case of coarse grained materials.
Chapter 5

Thermal Spike Model of Grain Growth under Ion-Irradiation

In this chapter, a theoretical model is developed to help rationalize the experimental observations of grain growth. The main question is how to relate the microstructure evolution observed to the processes of damage creation by ion-matter interaction and or how to predict microscopic changes (i.e. changes at the micron scale) from atomic scale elementary effects of radiation. The difficulty comes from the gap in time and length scales between what is happening at the atomic scale and the related effects on a microscopic scale. The purpose of this chapter is therefore to develop a model which shows how the atomic jumps induced by thermal spikes on the microstructure level can explain ion-irradiation induced grain-growth.

Generally grain growth in polycrystalline materials is understood as a result of the universal thermodynamic principle that a system is most stable when it is in its lowest free-energy state. Because grain boundaries contain interfacial energy, polycrystals are at best thermodynamically metastable, the ideal thermodynamical stability being reached when the material has been converted to a monocrystal. Therefore, the driving force associated with grain growth is the reduction of the system energy by reducing the total grain boundary surface area. The mechanism governing grain growth is usually assumed to be grain-boundary migration, driven by the grain-boundary curvature [46]. As a consequence of such migration the grain boundary curvature is reduced and so is the total grain boundary area per unit volume as a result of the growth of the bigger grains at the detriment of the smaller ones. For a constant volume, this results in the increase of the mean grain size and the decrease of the number of grains in the system, the larger ones growing at the expense of the small ones. In conventional grain growth, the atomic jumps involved in the grain boundary migration leading to grain growth are thermally induced. In the case of ion-irradiation induced grain growth the driving force is expected to be the
same, however the mechanisms for atomic jumps are different: atomic jumps are induced by the ion collisions and related thermal spikes. This allows for grain growth to occur also at cryogenic temperatures where thermal grain growth is not observed.

5.1 Driving force for grain-boundary migration:

The main driving force for grain-boundary migration is the curvature of the grain-boundary, which was derived by analogy to soap bubble growth. Indeed, if the grain-boundary energy is assumed to be independent of boundary orientation, then the grain-boundary behaves like a soap film. If a grain boundary is curved, then it is subject to a pressure (i.e. force per unit area of grain-boundary) of magnitude:

$$P = \frac{2\gamma}{r_{\text{curv}}}$$  \hspace{1cm} \text{Eq. 5.1}

where $\gamma$ is the grain-boundary surface energy per unit area of grain-boundary, directed towards the center of curvature of the boundary. Eq. 5.1 can be rewritten as:

$$P_{\text{curv}} = \frac{4\gamma}{D}$$  \hspace{1cm} \text{Eq. 5.2}

where $D$ is the diameter of the grain (grain-size).

In three dimensional configuration, the only way that the boundary tensions will balance is if the boundary is planar i.e. $r_{\text{curv}} = \infty$ or if it is curved with equal radii in opposite directions. A metastable equilibrium at a junction between three grains can exist, in which case the angles at the triple junction must be 120°; for grain boundaries meeting at a corner formed by four grains, the metastable equilibrium angle is 109° 28′. If these conditions or similar ones are satisfied then a metastable equilibrium can be established at all grain boundary junctions. However for the whole polycrystalline structure to be in total metastable equilibrium the surface tensions must also balance over all the boundary faces between the junctions.
For simplicity we consider the two-dimensional case. For topological reasons if less than six boundaries surround the grain, then each boundary must be concave. In this case, the forces exerted on the boundaries are directed inward (with respect to the grain center) and will cause the grain to shrink. On the other hand larger grains (with larger number of grain boundaries) can have convex boundaries and will grow.

As a result of grain-boundary migration the total number of grains decreases. Under thermal conditions, this grain growth usually occurs at temperatures above \(0.5 \, T_m\) when grain-boundaries have enough mobility. Under ion-irradiation the phenomenon can happen at lower temperatures, even at cryogenic temperatures where thermal diffusion processes should be negligible.

By analogy with soap bubble growth the pressure difference caused by a curved grain-boundary creates a difference in free energy across the boundary, \(\Delta G\). When a unit area of grain-boundary moves by a distance \(dx\) the number of moles of material that enter the growing grain is \(\frac{dx \cdot 1}{V_{\text{mol}}}\) and thus the free energy release associated with the grain boundary migration is \(\frac{\Delta G \cdot dx}{V_{\text{mol}}}\). The process can be thought of as a force per unit area that pulls the grain boundary towards the grain with the higher energy. The work of such a force (per unit area) or pressure is:

\[
P \cdot dx = \frac{\Delta G \cdot dx}{V_{\text{mol}}}
\]

Eq. 5.3

where \(P\) is in N per unit of grain-boundary area. The force can therefore be expressed as:

\[
P = \frac{\Delta G}{V_{\text{mol}}} \quad \text{(in N.m}^{-2}\text{)}
\]

Eq. 5.4

which is basically the free energy difference per unit volume of material. We note that:
Using Eq. 5.2, the chemical potential difference resulting from the grain boundary curvature $\Delta G$ can therefore be written as:

$$\Delta G_{\text{curv}} = \frac{4\gamma V_{\text{mol}}}{D}$$  \hspace{1cm} \text{Eq. 5.6}$$

where $\Delta G$ is in units of J.mol$^{-1}$, the molar volume $V_{\text{mol}}$ is in m$^3$.mol$^{-1}$, the grain-boundary surface energy $\gamma$ is in J.m$^{-2}$, and the average grain size (or diameter) $D$ is in m. If $\Delta G_{\text{curv}}$ is expressed per atom then:

$$\Delta G_{\text{curv}} = \frac{4\gamma V_{\text{at}}}{D}$$  \hspace{1cm} \text{Eq. 5.7}$$

5.2 Grain-boundary migration under thermal annealing:

This section discusses the case where grain-boundary migration occurs under thermal annealing alone [112]. Figure 5.1 shows the grain-boundary configuration. Due to its curvature, the grain-boundary is subjected to a difference of free energy $\Delta G$ across the grain-boundary (of width $\delta$) expressed as Eq. 5.7.
Figure 5.1: Grain configuration: the free-energy gradient across the grain-boundary is due to the curvature driving force [69].

In order for an atom to break away from a grain and jump to another site it needs to overcome an energy barrier $E_a$ defined as the sum of the activation energy for vacancy formation and the activation energy for vacancy migration:

$$ E_a = E_v^f + E_v^m $$

Eq. 5.8
The probability that an atom overcomes this energy barrier thermally is
$$\exp\left(-\frac{E_a}{k_BT}\right)$$. If the atoms of grain 1 vibrate with a frequency $\nu_1$ and $n_1$ is the number of atoms per unit area of grain boundary, the jump rate is $n_1\nu_1 \exp\left(-\frac{E_a}{k_BT}\right)$ (in $\text{m}^{-2}\text{s}^{-1}$) with:

$$\nu = \nu_0 \exp\left(-\frac{\Delta S_v + \Delta S_m}{k_B}\right)$$  \hspace{1cm} \text{Eq. 5.9}

where $\nu_0$ is the Debye frequency and $\Delta S_v$ and $\Delta S_m$ are the entropies of vacancy formation and vacancy migration respectively. If $A_2$ is the probability that an atom that has overcome the grain boundary energy barrier finds an empty site in grain 2, then the effective flux of atoms from grain 1 to grain 2 per unit area of grain-boundary is:

$$\varphi_{1\rightarrow2} = A_2n_1\nu_1 \exp\left(-\frac{E_a}{k_BT}\right)$$ (in $\text{m}^{-2}\text{s}^{-1}$)  \hspace{1cm} \text{Eq. 5.10}

A similar flux exists in the opposite direction but if the curvature of the boundary between grain 1 and grain 2 is such that atoms of grain 2 have a lower free energy they will also have to overcome the free energy difference across the grain boundary $\Delta G$. Hence the flux of atoms from grain 2 to grain 1 is:

$$\varphi_{2\rightarrow1} = A_1n_2\nu_2 \exp\left(-\frac{\Delta G}{k_BT}\right) = A_1n_2\nu_2 \exp\left(-\frac{E_a + \Delta G}{k_BT}\right)$$  \hspace{1cm} \text{Eq. 5.11}

When the surface is flat $\Delta G=0$ then the boundary is under (metastable) equilibrium, hence

$$\varphi_{1\rightarrow2} = \varphi_{2\rightarrow1}$$  \hspace{1cm} \text{Eq. 5.12}

thus:

$$A_2n_1\nu_1 = A_1n_2\nu_2$$  \hspace{1cm} \text{Eq. 5.13}
The net flux of atoms from grain 1 to grain 2 is then expressed as:

\[
J_{\text{net}}^{1 \rightarrow 2} = \varphi_{2 \rightarrow 1} - \varphi_{1 \rightarrow 2} = A_2 n_1 \nu_1 \exp\left(-\frac{E_a}{k_B T}\right) \left[1 - \exp\left(-\frac{\Delta G}{k_B T}\right)\right]
\]  

Eq. 5.14

Usually $\Delta G << k_B T$ therefore

\[
\exp\left(-\frac{\Delta G}{k_B T}\right) \approx 1 - \frac{\Delta G}{k_B T}
\]  

Eq. 5.15

Hence, Eq. 5.14 can be written as:

\[
J_{\text{net}}^{1 \rightarrow 2} = \frac{\Delta G}{k_B T} A_2 n_1 \nu_1 \exp\left(-\frac{E_a}{k_B T}\right)
\]  

Eq. 5.16

The velocity of the grain boundary can then be expressed as:

\[
v = J_{\text{net}}^{1 \rightarrow 2} \cdot V_{\text{at}} = V_{\text{at}} A_2 n_1 \nu_1 \exp\left(-\frac{E_a}{k_B T}\right) \frac{\Delta G}{k_B T}
\]  

Eq. 5.17

where $V_{\text{at}}$ is the atomic volume. Eq. 5.17 can also be written as:

\[
v = \frac{A_2 n_1 \nu_1 V_{\text{at}}^2}{k_B T} \exp\left(-\frac{E_a}{k_B T}\right) \frac{\Delta G}{V_{\text{at}}}
\]  

Eq. 5.18

where $\frac{\Delta G}{V_{\text{at}}} = P_{\text{curv}}$ according to Eq. 5.5.

The grain-boundary mobility $M$ defined from the relationship:

\[
v = M \cdot \mathbf{P}
\]  

Eq. 5.19

can be identified in Eq. 5.18 with the following expression:

\[
M_{\text{th}} = \frac{A_2 n_1 \nu_1 V_{\text{at}}^2}{k_B T} \exp\left(-\frac{E_a}{k_B T}\right)
\]  

Eq. 5.20
This is the grain-boundary mobility expression under purely thermal conditions. It is defined as the grain boundary velocity under unit driving force (the driving force being per unit area) and has the units of m$^3$s$^{-1}$N$^{-1}$ or m$^4$s$^{-1}$J$^{-1}$.

5.3 Grain-boundary migration under ion-irradiation:

In this section, we modify the derivation of purely thermal behavior to describe grain-growth under ion irradiation.

5.3.1 Low-temperature regime:

The observation of a temperature regime where the substrate temperature does not affect the kinetics of ion-irradiation-induced grain-growth was reported in chapter 4. This suggests that at low temperatures the phenomenon is primarily controlled by irradiation-effects. However the results have shown a considerable variation in grain-growth within metals (Pt and Au) with similar collisional behavior. This suggests that collisional atomic displacements alone cannot describe ion-irradiation induced grain-growth and that intrinsic material properties should be taken into account. This can be done by using the concept of thermal spikes. More precisely it was proposed that ion-irradiation induced grain growth is induced by the atomic motion within the thermal spikes. As mentioned before, the concept of thermal spike effects was already used in the early eighties to explain the some heavy ion induced phenomena such as ion-beam mixing in multilayers [9, 113-117]. This concept was proposed to describe ion-irradiation induced grain growth originally by Liu et al. [106] and was further developed by Alexander’s work on multilayers and co-evaporated alloys [107].

The idea behind the thermal spike model of ion-irradiation induced grain growth is the following. As described in chapter 1, after the collisional phase of a displacement cascade, the remaining of the kinetics energy of the recoil atoms is thermalized within the crystal lattice. As a result, each primary recoil atoms causes a temperature increase or
“temperature spike” in a very localized region. If this spike occurs in the direct vicinity of a grain boundary, atoms which are thermally activated within the thermal spike region can jump across the boundary. If a net number of atom jumps occur in one direction across the boundary, the boundary migrates in the opposite direction (after the thermal spike region has come back to thermal equilibrium with the surroundings). The local driving forces present (e.g. chemical concentration gradients and grain boundary curvature) then cause the net number of atom jumps to be in one direction rather than the opposite.

Two important assumptions lie behind the model proposed to describe grain-growth under ion-irradiation in the low-temperature regime.

5.3.2 Assumption 1:

*Only defects created in the direct vicinity of grain-boundaries participate in their migration.*

This assumption is supported by the absence of observation that grain-growth does not depend on substrate temperature in this regime. This implies that long range thermal diffusion is not significant. This assumption also underlay previous studies of grain-growth: Atwater assumed that only elastic collisions occurring near or at the grain boundaries lead to enhanced grain growth [70]. Atwater argued that thermally-induced migration of irradiation-induced defects created within the bulk of the grain was not the rate limiting step in the process of grain boundary migration during ion-irradiation-induced grain-growth “since the measured activation energies for grain-boundary migration during ion bombardment were small (~0.15 eV/at) but non-zero”[70]. Although defect production and migration occur through the bulk of grains, the defects that participate in the grain-growth process are the ones created at or near the grain-boundary. (However his model, which was primarily ballistic in nature and did not involve thermal spikes, failed to explain quantitatively the grain growth kinetics observed experimentally).

Evaluation of the relative rates of recombination and absorption at sinks.:
The very large number of displacements created by irradiation is eliminated by the reaction of these defects with other defects and defect sinks. In the case of vacancy and interstitial reaction this process is dubbed “recombination” and results in the annihilation of both defects. The absorption of defects at sinks can cause processes such as dislocation climb, void growth, etc. to occur.

Depending on the displacement rate, the temperature, sink strengths, the majority of the defects could be eliminated by recombination (“recombination-dominated regime”) or by absorption at sinks (sink-dominated regime).

If the irradiation is conducted in a recombination-regime, no effect of long range diffusion would be expected.

It is possible using rate theory [118] to evaluate which regime is operational. In fact, we have performed calculations based on rate-theory concepts, which show that at the temperatures of interest we are in recombination-dominated regime. Indeed, by estimating parameter the E defined in Eq. 5.21 one can determine the regime type (sink dominated or recombination dominated). The parameter E compares the defect losses to vacancy-interstitial recombination (numerator) with the defect losses to fixed-sinks such as voids, dislocations, grain-boundaries, and free surfaces (denominator). E is defined as:

$$E = \frac{4K_v K_{iv}}{\left( \sum_x k_{iv}^2 D_x \right) \left( \sum_x k_{vi}^2 D_v \right)}$$  \hspace{1cm} \text{Eq. 5.21}

where \(K_v\) is the defect formation rate i.e. the displacement rate (in displacements per atom dpa per sec), \(K_{iv}\) is the rate of interstitial-vacancy recombination and is defined as follows:

$$K_{iv} = \frac{4\pi \cdot r_{iv} (D_v + D_i)}{V_{at}} = K_{iv} \left( D_i + D_v \right)$$  \hspace{1cm} \text{Eq. 5.22}

In Eq. 5.22 \(V_{at}\) is the atomic volume, \(D_v\) and \(D_i\) are the diffusion coefficients for vacancies and interstitials, and \(K_{iv} = \frac{4\pi \cdot r_{iv}}{V_{at}}\) where \(r_{iv}\) is the annihilation radius i.e. the distance within which an interstitial and a vacancy inevitably recombine. In order to
determine $r_{iv}$ it is useful to consider the fact that the recombination volume $\frac{4\pi \cdot r_{iv}^3}{3}$ is of the order of $100V_{at}$.

$k_{id}^2$ and $k_{vd}^2$ (in Eq. 5.21) are the sink-strengths for interstitials and vacancies respectively. In Eq. 5.21 the sums (in the denominator) occur over all possible point-defect sinks “s”, such as voids, dislocations, grain-boundaries, free surfaces etc. These are given in Table 4.6.

If $E << 1$, we are in sink-dominated regime, and when $E >> 1$ we are in recombination dominated regime.

<table>
<thead>
<tr>
<th>Defect sink type</th>
<th>Sink strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dislocations</td>
<td>$k_{id}^2 = z_i \rho_d$ where $z_i$ is the dislocation bias for interstitials ($\sim 1.02$), and $\rho_d$ is the dislocation density $k_{vd}^2 = z_v \rho _d$ where $z_v$ is the dislocation bias for vacancies ($\sim 1$)</td>
</tr>
<tr>
<td>Voids</td>
<td>$k_{iv}^2 = k_{sv}^2 = 4\pi R_v N_v$ where $R_v$ is the radius of the void and $N_v$ is the density of voids.</td>
</tr>
<tr>
<td>Grain-boundaries</td>
<td>$k_{gb}^2 = \left( \frac{3}{2R^2} \right) \left( 5 + \sqrt{21} \right) = \frac{14.4}{R^2}$</td>
</tr>
<tr>
<td>Free-surface</td>
<td>$k_{iSurf}^2 \propto \frac{S_i}{L}$ and $k_{vSurf}^2 \propto \frac{S_v}{L}$ where $k_{sc}^2$ is the sink strength from all the microstructure within the foil of thickness $2L$, $S_v = \frac{K_{vSurf}}{D_v}$ and $S_i = \frac{K_{iSurf}}{D_i}$ ($K_{iSurf}$ and $K_{vSurf}$ being the transfer velocities across the foil surface for interstitial and vacancies respectively).</td>
</tr>
</tbody>
</table>

For the case of nanocrystalline thin-films, the sink strength for dislocations voids should be low, since the dislocation density is low; as a matter of fact no dislocations were observed on the bright-field micrographs. Instead, the main sinks for defects are
going to be the free surfaces of the foil and the grain-boundaries because, unlike usual commercial alloys which are coarse-grained, in nanocrystalline materials, grain-boundaries are likely to occupy more than 50% of the volume. For simplicity, these sinks are homogenized over the foil. Expressions for the sink strength of free-surfaces were derived for the case of thin-films[119]. In our case, since we are dealing with nanocrystalline materials, the free-surfaces can be considered as the collection of grain-boundaries respectively of the top layer and the bottom layer of grains therefore if we consider grain-boundaries as perfect sinks, the strength of free surfaces (as sinks for defects) is already taken into account in the grain-boundary sink strength term. Thus, in the case where only grain-boundary sinks are considered, $E$ is written:

$$E = \frac{4K_0K_{iv}}{k_{iGB}D_i \cdot k_{vGB}^2D_v} = \frac{4K_0K_{ivs}}{k_{iGB}^2 \cdot k_{vGB}^2} \cdot \left( \frac{1}{D_i} + \frac{1}{D_v} \right)$$  \hspace{1cm} \text{Eq. 5.23}$$

It is well known that interstitials tend to move much faster than vacancies in crystals hence $D_i \gg D_v$ so that the parameter $E$ can be re-written as:

$$E \approx \frac{4K_0K_{ivs}}{k_{iGB}^2k_{vGB}^2} \cdot \frac{1}{D_v}$$  \hspace{1cm} \text{Eq. 5.24}$$

In Eq. 5.24, $K_0$ is determined by the irradiation experimental conditions (irradiating particle flux and displacement cross-sections obtained from SRIM2003 reported in Table 2.2).

The very complex expression for the grain-boundary sink strength $k_{GB}^2$ derived by Bullough [119] simplifies when the defect losses to the sinks in the bulk of grains (e.g. voids, dislocations) are negligible when compared with the defect losses to the grain-boundaries; $k_{GB}^2$ can then be expressed as:

$$k_{gb}^2 \approx \frac{14.4}{R^2}\quad \text{Eq. 5.25}$$
In order to estimate $E$, $k_{GB}^2$ was evaluated at the beginning of the irradiation when grains are smaller and $k_{GB}^2$ is the highest. The diffusion coefficient for vacancies is defined as:

$$D_v = D_{vs} \exp \left( -\frac{E^m_v}{k_B T} \right) \tag{Eq. 5.26}$$

where $E^m_v$ is the activation energy for vacancy migration. Values of $E^m_v$ found in the literature for the different elements are reported in Table 5.2 and range from 0.7 to 1.45 eV/atom. The generic value of $10^{-2}$ cm$^2$/sec was used for $D_{vs}$. Table 5.2 summarizes the values of parameters which are relevant to the determination of $E$. Using these values $E$ is computed plotted versus irradiating temperature for the different systems: Au irradiated with 500 keV Ar ions, Cu 500 keV Kr, Pt 1 MeV Kr, and Zr 500 keV Kr. The curves shown in Figure 5.2 clearly indicate that at the temperatures of interest, the system is in the recombination-dominated regime since the values of $E$ are very large values. This is true even though this value was computed for the initial conditions, where the grain-boundary sink-strength is the highest. This means that at these temperatures the diffusion length is shorter than the recombination radius, supporting the idea that only defects created at the grain-boundary direct vicinity participate in grain-growth in the low-temperature regime.
Table 5.2: Parameters values for the determination of E.

<table>
<thead>
<tr>
<th>Material/foil thickness (nm)</th>
<th>Vₜₐₜ (cm³/atom)</th>
<th>Kᵥₐ (cm⁻²)</th>
<th>Eᵥₐ (activation energy for vacancy migration) (eV/atom)</th>
<th>Ion type/flux</th>
<th>Displacement rate K₀ (dpa/s)</th>
<th>Initial average grain-size (cm)</th>
<th>Initial k²</th>
<th>4K₀ Kᵥₐ k² GB⁻¹ kᵥ GB⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr 80 nm</td>
<td>2.34x10⁻²³</td>
<td>4.42x10⁻¹⁶</td>
<td>1.4[120]</td>
<td>Kr 500keV</td>
<td>0.0213</td>
<td>1.45x10⁻⁶</td>
<td>2.74x10¹³</td>
<td>5.03x10⁻¹²</td>
</tr>
<tr>
<td>Cu 90 nm</td>
<td>1.18x10⁻²³</td>
<td>6.98x10⁻¹⁶</td>
<td>0.71[121], 0.82[122], 0.9[123]</td>
<td>Kr 500keV</td>
<td>0.0232</td>
<td>1.55x10⁻⁶</td>
<td>2.40x10¹³</td>
<td>1.13x10⁻¹¹</td>
</tr>
<tr>
<td>Pt 80 nm</td>
<td>1.51x10⁻²³</td>
<td>5.92x10⁻¹⁶</td>
<td>1.45[121], 1.35[123]</td>
<td>Kr⁺⁺ 1MeV</td>
<td>0.0185</td>
<td>1.35x10⁻⁶</td>
<td>3.16x10¹³</td>
<td>4.39x10⁻¹²</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ar 500keV</td>
<td>0.0128</td>
<td></td>
<td></td>
<td>3.04x10⁻¹²</td>
</tr>
<tr>
<td>Au 80 nm</td>
<td>1.69x10⁻²³</td>
<td>5.48x10⁻¹⁶</td>
<td>0.83[121], 0.71[122], 0.85[123]</td>
<td>Ar 500keV</td>
<td>0.0119</td>
<td>1.50x10⁻⁶</td>
<td>2.56x10¹³</td>
<td>4.01x10⁻¹²</td>
</tr>
</tbody>
</table>
Figure 5.2: E parameter plotted on logarithmic scale as a function irradiation temperature for Au irradiated with 500 keV Ar ions, Pt irradiated with 1 MeV Kr ions, Zr irradiated with 500 keV Kr ions and Cu irradiated with 500 keV Kr ions.
5.3.3 Assumption 2:

*Displacements resulting from isolated elastic collisions need not be taken into account, i.e. only atomic jumps occurring within thermal spikes are responsible for the grain-growth observed.*

In theory, all displacements occurring at the grain-boundary (including those resulting from “isolated” elastic collisions) modify the local topography of the grain-boundary. However, in order for those atomic-scale processes occurring at the grain-boundary to result in the migration of the boundary and modify its curvature “macroscopically” a high local density of those defects is needed, which is the case for thermal spikes. In other words, at low temperatures, grain growth occurs only when irradiation-induced thermal-spikes are involved.

This assumption stems from the observation that no grain-growth was observed during the 1 MeV-electron irradiation of Zr-Fe thin films which were carried out in the High Voltage Electron Microscope at the CEA at Saclay (France). Indeed, in the case of electron irradiation, the displacements are homogeneously created, without cascades and therefore without thermal spikes. Samples were irradiated to 180 dpa without grain growth occurring. A bright-field image of a Zr-Fe foil irradiated at room temperature to 80 dpa is shown in Figure 5.3.
Figure 5.3: Bright-Field image of a Zr-Fe thin-film irradiated with 1MeV electron-irradiation to a dose of 80 dpa.

Hence it is assumed that displacements created outside the thermal spike (i.e. along the path of the ions) as isolated elastic collisions need not be taken into account even if those atomic jumps occur near or at the grain-boundary. In such a model, the number of atomic jumps created within thermal spikes and the size of these thermal spikes should play a crucial role on grain growth. Therefore they need to be evaluated.

In summary: **In the low-temperature regime, ion-irradiation grain growth is most likely caused by the thermal spike induced displacements. These atomic jumps must occur close enough to the grain-boundary and with a high local density; in other words grain growth occurs only when displacement spikes are involved and the thermal spikes actually participating in the grain-boundary migration are only those triggered at the grain-boundaries.**
This picture of grain-growth under ion irradiation is supported by molecular dynamics simulations of 5 keV cascades in nanocrystalline-Ni samples of 5 and 10 nm initial grain by Voegeli et al. [84]. As reported in chapter 1, it was found that ion-induced grain growth is observed only if the thermal spike volume is larger than the grain volume or overlaps the grain-boundary area, in which case the shrinkage or growth of grains is accumulated over several events. If the spike volume does not reach the grain-boundary area, ion-induced grain-growth is not observed.

5.3.4 Derivation of the grain-growth rate equation:

Figure 5.4 shows a schematic representation of the cascade structure induced by an ion transversing a polycrystalline thin-film. As the ion interacts with the matter, primary knock-on atoms are displaced from their lattice sites with some kinetic energy. The high energy ones subsequently dissipate their energy through displacement (sub)cascades which result in local thermal spikes. Some of these spikes occur within the bulk of grains, others hit grain-boundaries. Only the latter contribute to grain-boundary migration and grain-growth in this regime of low-temperatures.

---

Figure 5.4: Schematic representation of the cascade structure induced by an ion transversing a polycrystalline thin-film.
If $\chi$ is the average number of thermal spikes triggered by one ion per unit depth in the thin-film, then the number of thermal spikes per unit volume of material when non-overlapping cascades are assumed is given by

$$\Phi \frac{[#\text{ions/cm}^2]}{[#\text{spikes/ion - cm}]}$$  \hspace{1cm} \text{Eq. 5.27}

Among these thermal spikes, only those created close enough to the grain-boundary will participate in growth of the grains. If the probability of a random spike hitting the grain-boundary is $P_{GB}$, the number of spikes (per unit volume) occurring at a grain-boundary is

$$P_{GB} \Phi \chi$$  \hspace{1cm} \text{Eq. 5.28}

If $\eta$ is the number of displacements within a thermal spike ($\eta$ being a function of the energy dissipated in the spike), the number of atomic jumps induced by thermal spikes located at grain-boundaries (per atom) is given by

$$\frac{P_{GB} \Phi \chi \eta}{N_{at}}$$  \hspace{1cm} \text{Eq. 5.29}

Eq. 5.30 gives the number of atomic jumps per atom involved in grain-boundary migration (and hence in grain-growth). These atomic jumps when biased in one direction displace the grain-boundary by a distance $\delta$ which is basically the grain-boundary width. Hence, after a dose increment $\Delta \Phi$, grain-boundaries move by

$$\Delta L = \frac{P_{GB} \Delta \Phi \chi \eta}{N_{at}} \delta$$  \hspace{1cm} \text{Eq. 5.31}

Therefore the grain-boundary migration distance per unit dose is given by:

$$\frac{\Delta L}{\Delta \Phi} = \frac{P_{GB} \chi \eta}{N_{at}} \delta$$  \hspace{1cm} \text{Eq. 5.32}

If the ion flux $\Phi$ (in ions/cm$^2$-s) is constant, Eq. 5.32 becomes:

$$\frac{\Delta L}{\Delta t} = \frac{\dot{\Phi} \chi}{N} P_{GB} \eta \delta$$  \hspace{1cm} \text{Eq. 5.33}
Eq. 5.33 gives the expression of the velocity of the grain boundary. In the frame of an “average grain” model Eq. 5.33 is the grain growth rate \( \frac{d\bar{D}}{dt} \):

\[
\frac{d\bar{D}}{dt} = \Phi \frac{\chi}{N_{at}} P_{GB} \eta \delta
\]

Eq. 5.34

Eq. 5.34 is the fundamental equation determining the kinetics of ion-irradiation-induced grain-growth in the temperature-independent regime. Although the grain-growth rate is determined by the irradiation conditions, this model is not purely collisional because the parameter \( \eta \) depends on the intrinsic properties of the irradiated material and therefore differs even for materials which have similar collisional properties, as shown below.

Note: In the above description, subcascades are implicitly considered isolated one from another, which means that the mean free path of the recoil is larger than the size of a spike. The energy dissipated in the thermal spike is the energy of the recoil that gave birth to it, and the size of the thermal spike region is that of the subcascade.

**Determination of \( P_{GB} \)**

The probability of a thermal spike occurring at or near a grain-boundary \( P_{GB} \) is proportional to the grain-boundary density and to the radius of the thermal spike (in case a spherical geometry is assumed for the spikes) according to:

\[
P_{GB} = \rho_{GB} \left[ \frac{\text{# cm}^2 \text{ GB}}{\text{cm}^3} \right] r_{\text{spike}} \text{[cm]}
\]

Eq. 5.35

In a population of spherical grains of average size \( D \), the density of grain boundary per unit volume of target material is given by:

\[
\rho_{GB} = \frac{\text{Surface of the average grain}}{\text{Volume of the average grain}} = \frac{6}{D}
\]

Eq. 5.36
Therefore $P_{GB}$ becomes:

$$P_{GB} = \frac{3d_{\text{spike}}}{D} \quad \text{Eq. 5.37}$$

where $d_{\text{spike}}$ is the diameter of the average thermal spike. Eq. 5.37 reflects the fact that as grains grow, the probability of thermal spikes occurring at the grain-boundaries decreases, resulting in the saturation effects observed at high doses.

**Determination of the number of displacements ($\eta$) induced in a thermal-spike of energy $Q$**

The determination of the number of displacements ($\eta$) induced in a thermal-spike of energy $Q$ is based on Vineyard’s analysis of thermal spikes and activated processes in the frame of thermal spike model of the radiation interaction with matter [14]. This analysis is based on the assumption that energy is deposited instantaneously in a very small region, producing a localized increase of temperature which spreads and cools according to the laws of classical heat conduction in a homogeneous continuum. If an activated process (e.g. migration of atoms) is energized by the spike, then the number of elementary steps (such as atomic jumps) caused by one spike can be expressed as an integral over space and time of the rate expression of the atomic jumps in the spike. The temperature is given by a function of space and time characteristic of the spike.

**Thermal spike in an infinite medium under no driving force**

We assume that the energy of a thermal spike is that of the initial recoil atom (PKA) which gave rise to it through successive atomic collisions. If we consider that the energy of the spike $Q$ is initially introduced at a point in the medium, the subsequent dissipation of this energy results in the temperature distribution $T(r,t)$ in the thermal spike region. Since MD studies show that a spherical geometry would be more appropriate to describe cascades and subcascades, a spherical cascade is assumed here. Vineyard
derived an expression for $T(r,t)$ by solving the heat conduction equation in cylindrical geometry considering an initial deposited energy distribution expressed as $Q\delta^3(r)$, where $\delta^3(r)$ is the 3-D delta function. A simple power law dependence is assumed for the thermal conductivity $\kappa$, and the heat capacity $c$ on temperature such that

$$\kappa = \kappa_0 T^{n-1} \quad \text{and} \quad c = c_0 T^{n-1} \quad \text{with} \quad n \geq 1 \quad \text{Eq. 5.38}$$

Note that with such an expression the thermal diffusivity given by the ratio $\frac{\kappa}{c}$ is still constant and independent of temperature. The time-dependent solution for the temperature variation as a function of radial distance from the initial point source is given by:

$$T(r,t) = \left(\frac{nQc_0^{1/2}}{(4\pi\kappa_0 t)^{3/2}}\right)^{1/n} \exp\left(-\frac{c_0 r^2}{4n\kappa_0 t}\right) \quad \text{Eq. 5.39}$$

where $r$ is the radial distance from the initial point of energy deposition, $t$ is time and $\kappa_0$ and $c_0$ are respectively the values of the thermal conductivity and the heat capacity at ambient temperature. It should be noted that in such a treatment, the target macroscopic temperature or “ambient temperature” is taken as absolute zero. If an ambient temperature is added, the integration of the equations cannot be achieved analytically.

According to Vineyard’s analysis of thermal spikes, atomic motion within the spike is promoted thermally and these thermally activated atomic jumps are assumed to obey a directionally random Arrhenius law such that the jump rate is given by [14]:

$$R(r,t) = A \exp\left(-\frac{E_a}{k_B T(r,t)}\right) \quad \text{Eq. 5.40}$$

where $E_a$ is the activation energy for atomic jump in the thermal spike, $k_B$ is Boltzmann’s constant, and $A$ is a constant independent of temperature. $T(r,t)$ is the temperature distribution within the spike.
Hence the total number of atomic jumps induced in one thermal spike $\eta$ is obtained by using $T(r,t)$ from Eq. 5.39 in Eq. 5.40 and integrating over time and space according to

$$\eta = \int_0^\infty dV \int_0^\infty R(r,t) dt$$  \hspace{1cm} \text{Eq. 5.41}$$

where $dV$ is the infinitesimal volume and $R(r,t)$ is the atomic jump rate per unit volume. In the absence of driving forces, and if the cascade is assumed spherical then $\eta$ is expressed as:

$$\eta = \int_0^\infty 4\pi r^2 dr \int_0^\infty A \exp \left(-\frac{E_a}{k_B T(r,t)}\right) dt$$  \hspace{1cm} \text{Eq. 5.1}$$

The details of the integration are given in Appendix 3. As a result, the total number of atomic jumps occurring in a thermal spike of energy $Q$, as it develops and cools, is:

$$\eta = \frac{3}{10} \pi n^{8/3} Q^{5/3} \left(\frac{k_B}{E_a}\right)^{\frac{5n}{3}} \Gamma\left(\frac{5n}{3}\right)$$  \hspace{1cm} \text{Eq. 5.42}$$

where $\Gamma\left(\frac{5n}{3}\right)$ is the gamma function of argument $\frac{5n}{3}$. It should be noted that Eq. 5.42 does not take into account the effect of local driving force on the atomic jumps. Indeed, Vineyard’s expression of $R(r,t)$ in Eq. 5.40 is for random jumps and does not include the biasing effects of local driving-forces (i.e. chemical potential gradients) on atomic migration. Examples of those chemical-potential gradients include grain-boundary curvature and solute concentration gradients.
Incorporating the driving force due to grain-boundary curvature:

When the local chemical-potential gradient is incorporated to describe atomic motion within thermal spikes, similarly to Eq. 5.16, the rate of atomic jumps per unit volume \( R(r,t) \) becomes:

\[
R(r,t) = \frac{\Delta G}{k_B T(r,t)} N_{at} \nu \exp \left( - \frac{E_a}{k_B T(r,t)} \right)
\]

Eq. 5.43

assuming that the atomic density near the grain boundary is the same as in the bulk material. When the local chemical potential gradient is due to grain-boundary curvature, Eq. 5.7 can be incorporated in Eq. 5.43 which then becomes:

\[
R(r,t) = \frac{4\gamma V_{at}}{Dk_B T(r,t)} N_{at} \nu \exp \left( - \frac{E_a}{k_B T(r,t)} \right)
\]

Eq. 5.44

The total number of jumps within the thermal spike is then given by the integral:

\[
\eta = \int_0^\infty 4\pi r^2 dr \int_0^\infty \frac{4\gamma V_{at} N_{at}}{Dk_B T(r,t)} \nu \exp \left( - \frac{E_a}{k_B T(r,t)} \right) dt
\]

Eq. 5.45

The details of the integrations are given in Appendix 3. The results indicate that the total number of atomic jumps within a thermal spike in the presence of the grain-boundary driving force (from Eq. 5.7) is

\[
\eta_{\text{driving force}} = \frac{4\gamma V_{at} N_{at} \sqrt{\frac{3}{5} \frac{n^{8/3}}{10\pi C_0^{2/3} \kappa_0}} \left( \frac{k_B}{E_a} \right)^{\frac{5n+1}{3}} \Gamma \left( \frac{5n}{3} + 1 \right)}{Dk_B}
\]

Eq. 5.46

If \( n=1 \) (i.e. if the heat capacity and heat conductivity are assumed constant within the spike), \( \eta \) becomes:

\[
\eta = \frac{4\gamma V_{at} N_{at} \sqrt{\frac{3}{5} \frac{8}{3} \Gamma \left( \frac{8}{3} \right) k_B^{8/3} Q^{5/3}}}{10\pi C_0^{2/3} \kappa_0 E_a^{8/3}}
\]

Eq. 5.47
We note that the activation energy for atomic jump can be scaled with the cohesive energy of the material [124] according to:

$$E_a = \beta \Delta H_{coh}$$  \hspace{1cm} \text{Eq. 5.48}

Thus, $\eta$ is proportional to $\frac{Q^{5/3}}{\Delta H_{coh}^{(8/3)}}$.

Finally, by incorporating Eq. 5.37 and Eq. 5.47 into Eq. 5.34, the grain-boundary velocity expression becomes:

$$v = \frac{dD}{dt} = \frac{\Phi \chi \delta}{N_{at}} \frac{3d_{cas}}{D} \left[ \frac{4\gamma V_{at} N_{at} \sqrt{\frac{3}{5}} \Gamma \left( \frac{8}{3} \right) k_B^{8/3}}{Dk_B 10\pi C_0^{2/3} \kappa_0 E_a^{8/3}} \right]$$  \hspace{1cm} \text{Eq. 5.49}

It is noted that Eq. 5.49 relates the time-evolution of the average grain-size with material properties such as the specific heat, thermal conductivity, atomic volume, Debye frequency, grain-boundary energy, and the cohesive energy, and with irradiation parameters such as the ion flux, the energy and size and number of thermal spikes induced by the ions. It can thus explain the differences in grain-growth kinetics observed in materials with similar collisional properties.

5.3.4 Determination of the grain-boundary mobility in the ballistic regime:

Using Eq. 1.8, we can identify the grain-boundary mobility in the ballistic regime $M_{irr}$, in Eq. 5.49:

$$M_{irr} = \frac{3d_{spike}}{D} \frac{\Phi \chi \delta}{3d_{cas}} \frac{V_{at} \sqrt{\frac{3}{5}} \Gamma \left( \frac{8}{3} \right) k_B^{5/3}}{10\pi C_0^{2/3} \kappa_0 E_a^{8/3}}$$  \hspace{1cm} \text{Eq. 5.50}

Eq. 5.50 shows that $M_{irr}$ depends on the grain size and on irradiation parameters, such as the thermal spike size and density.
5.3.5 The grain growth equation:

Eq. 5.49 gives the grain-growth rate and can be re-written as:

\[
D^3 dD = \left[ 12 \gamma d_{spike} \Phi \chi \delta \frac{V_a v}{10 \pi C_0^{2/3} \kappa_0} \frac{\sqrt{\frac{3}{5} \Gamma \left( \frac{8}{3} \right) k_B^{5/3}}}{Q^{5/3} E_a^{8/3}} \right] dt \quad \text{Eq. 5.51}
\]

After integration:

\[
\frac{1}{3} D^3 - \frac{1}{3} D_0^3 = \left[ 12 \gamma d_{spike} \Phi \chi \delta \frac{V_a v}{10 \pi C_0^{2/3} \kappa_0} \frac{\sqrt{\frac{3}{5} \Gamma \left( \frac{8}{3} \right) k_B^{5/3}}}{Q^{5/3} E_a^{8/3}} \right] t \quad \text{Eq. 5.52}
\]

And finally, we obtain the grain-growth equation for the thermal spike model:

\[
D^3 - D_0^3 = \left[ 36 \gamma d_{spikes} \chi \delta \frac{V_a v}{10 \pi C_0^{2/3} \kappa_0} \frac{\sqrt{\frac{3}{5} \Gamma \left( \frac{8}{3} \right) k_B^{5/3}}}{Q^{5/3} E_a^{8/3}} \right] \Phi = K \Phi \quad \text{Eq. 5.53}
\]

Eq. 5.53 is of the form of Eq. 4.5 to which the grain-growth curves were fitted. The exponent value of 3 obtained theoretically for the ballistic regime is a very satisfying value, since the fitting of the grain-growth curves given in Table 4.2 and Table 4.1 showed an exponent close to 3 in the low-temperature regime. As mentioned before, an exponent of 3 agrees with results from previous studies of grain-growth under irradiation in elemental films by Atwater and Liu and in alloy films by Alexander [70, 83, 106, 107] since in those studies, in spite of some scatter, the exponent values had an average value of 3. However, that exponent (~3) was mainly supposed to be a deviation (possibly due to impurities or internal stresses) from Hillert’s parabolic law of grain-growth, which was taken as the operating model. The present study suggests that the exponent of 3 is an inherent feature of grain-growth under ion –irradiation. Although, this study does not
exclude drag effects possibly due to the morphology of the film nor residual stresses remaining from the fabrication process, or impurity effects, it is proposed that if these effects occur, they result in a deviation of the exponent value from the value of 3 rather than 2 (cf. Table 4.2 and Table 4.1). In the case of pure elemental materials, the expected value for the ion-irradiation-induced grain-growth exponent is n=3.

It is noted that, the exponent value of 3 originates from the introduction of the probability term $P_{GB}$. Although previous studies agreed on the idea that only atomic displacements created at the grain-boundaries participate in their migration hence in grain-growth [69, 70, 106, 125], no such correcting term was introduced. Without such a term, Alexander’s model resulted in the prediction of the parabolic law, which is in disagreement with experiments.

*Note: What would be the effect of a 2-D microstructure on the probability of cascades hitting grain-boundaries?*

As the grain size increases, the geometry of the system changes; grains may go from a sphere-like shape inside the foil (3-D geometry) to a plaque spanning the foil thickness (2-D). In that case, $P_{GB}$ calculation is slightly different. In 3-D geometry, $P_{GB}$ is given by Eq. 5.37. In 2-D, the grain-boundary density becomes:

$$
\rho_{GB} = \frac{\text{Surface of the grain boundary}}{\text{Volume of the average grain}} = \frac{4}{D}
$$

Eq. 5.54

and $P_{GB}$ becomes

$$
P_{GB} = \frac{2d_{spike}}{D}
$$

Eq. 5.55

Hence the grain growth rate equation Eq. 5.49 becomes:

$$
\frac{dD}{dt} = \frac{\Phi}{N_{at}} \frac{\chi}{D} \frac{2d_{cas}}{\eta \delta}
$$

Eq. 5.56

and Eq. 5.53 becomes
\[
\begin{align*}
\hat{D}^3 - \hat{D}_0^3 = & \left[ \frac{24\gamma d_{\text{spikes}}\chi\delta}{10\pi C_0^{2/3} \kappa_0} \right] \left[ \frac{V_{\text{at}}^{3/5} \left( \frac{3}{5} \right)^{8/3}}{C_10^{3/2} \kappa_1} \right] \frac{Q^{5/3}}{E_a^{8/3}} \Phi = K \Phi \\
\end{align*}
\]

Eq. 5.57

The factor \( K \) in the 2-D case is smaller than the \( K \) in the 3-D case by a factor of 2/3. In the case where we go from a 3-D microstructure at the beginning of the irradiations to a 2-D configuration at high doses, this geometrical transition can accentuate the saturation effects.

5.3.6 Theory versus experiment:

Given that the theoretical value of the grain-growth exponent \( (n=3) \) is in good agreement with experimental results, it should be possible using Eq. 5.53 to correctly predict the experimentally observed grain-growth kinetics in the pure elemental thin-films (Au, Pt, Zr, Cu). To evaluate \( K \), we need to estimate the average number of thermal spikes per ion \( (\chi) \) and the average thermal-spike energy \( (Q) \), and the size of the average spike \( d_{\text{cas}} \). This is done in the following sections.

**Estimate of the average number of thermal spikes per ion \( (\chi) \) and the average thermal-spike energy \( (Q) \)**

As mentioned before, when an ion travels through matter, it triggers atomic displacements, referred as the primary knock-on atoms (PKA). Some of these PKAs have enough energy to trigger a collisional cascade which can, at the end, result in a liquid-like thermal spike, while others do not. The latter do not need to be taken in consideration in this analysis. We therefore need to find the recoil spectra and only count those which have a high-enough energy to trigger a thermal spike.

SRIM2003 was used to generate the recoil spectra. The SRIM2003 runs were performed for 10000 ions in order to obtain good statistics. The values of the
displacement energy thresholds and other conditions for the SRIM2003 runs are reported in Appendix A. During each run of the Monte Carlo simulation SRIM2003 keeps track of all the recoils generated, and writes them in a large text file. A program was written which sorts through the SRIM2003 outputs and collects the recoil data to generate the recoil spectra. The program written in C++ language is presented in Appendix B. Figures 5.5 shows the calculated recoil energy-spectra for all cases of interest in this study: Au irradiated with 500 keV Ar ions, Cu irradiated with 500 keV Kr ions, Pt irradiated with 1 MeV Kr ions and 500 keV Ar ions, Zr irradiated with 500 keV Kr ions, and Zr irradiated with 500 keV Ar ions.

![PKA energy distributions](image)

Figure 5.5: Recoil energy-spectrum calculated using the PKA-energy data generated by SRIM2003 for simulations running 10000 ions for: 80 nm Au foil irradiated with 500 keV Ar ions, 90 nm Cu foil irradiated with 500 keV Kr ions, 80 nm Pt foil irradiated with 1 MeV Kr ions, 80 nm Pt foil irradiated with 500 keV Ar ions, 80 nm Zr foil irradiated with 500 keV Kr ions, and 80 nm Zr foil irradiated with 500 keV Ar ions.
It can be noted that the recoil spectra for Au and Pt irradiated with 500 keV Ar ions are very similar, which was expected, since the two elements have very similar atomic mass. Yet the grain-growth kinetics proved to be very different for the two elements as reported in chapter 4; this confirms the idea that ion-irradiation-induced grain-growth is not a purely collisional phenomenon and that the model should include effects of material intrinsic properties.

For all recoil energy spectra about 40% of the primary knock-on recoils are created with energies less than 100 eV. According to the Kinchin Pease model they could only create at most two Frenkel pairs if the displacement energy threshold is 25 eV. These PKAs clearly need not be taken into account for they cannot give rise to a thermal spike and will not influence grain growth. Furthermore, as reported previously, irradiation with 1 MeV electrons, which can create recoils of ~100 eV did not cause grain-growth to occur in Zr-Fe, which means that such recoil energies are not enough to create thermal spikes.

To determine the average number of thermal spikes created per ion ($\chi$), and the average energy of a thermal spike $Q$, we use the following assumptions:

a. We consider an energy threshold $E_{\text{threshold}}^1$ above which a PKA gives rise to a thermal spike and below which it can be disregarded. This recoil energy threshold for cascade formation is not known for most metals and is an ill-defined quantity. It should depend on the incident irradiating particle, the target material and depth. Fenn-Tye & Marwick have evaluated it to be 5 keV to 10 keV, in their study of cascade mixing in Pd films using energetic heavy ions such as 100 keV Ne, 200 keV Ar and Kr, and 400 keV Xe[126]. In this study, we will take the same energy threshold $E_{\text{threshold}}^1$ for all materials to be 2 keV, (knowing that this may result in an underestimation of the average thermal spike energy).

b. At the other end of the PKA energy distribution, primary recoils can be generated with energies up to hundreds of keV, depending on the ion energy and target atomic mass. However both Monte Carlo calculations and TEM [127] studies have shown that high energy cascades break up into subcascades. For instance, Jenkins and English [128] estimated that in Cu$_3$Au, PKAs of energy higher than 30 keV are divided
into subcascades. In a study of irradiation damage created in high energy displacement cascades in Cu and Au, Proennecke et al. have observed the formation of subcascades for high energy PKAs; they also reported that the recoils of higher energy would only produce a higher number of subcascades. Thus, literature suggests the existence of a second threshold energy $E_{\text{threshold}}^2$ above which a PKA will break into subcascades. Proennecke et al. have calculated this threshold energy for the formation of the subcascades for gold to be between 200 keV and 300 keV and the separation distance was found to be about 50 nm. Rossi and Nastasi [16] have formulated a similar idea differently using fractal geometry concepts. They argued that for self-ion cascades, a spike composed of a single dense cascade could develop only when the kinetic energy of a recoil falls below a given critical value $E_C$ which was related to the mass and density of the target through empirical relationships obtained using the Biersack Ziegler potential [129]. For an initial recoil energy $E$ greater than $E_C$, the cascade would form $n = E/E_C$, subcascades until the collision energy in the cascade reaches the value of $E_C$.

In light of the above arguments, we make an estimate of the average number of thermal spikes per ion $\chi$ and the average energy $Q$ of the thermal spikes by sorting through the outputs generated by SRIM and applying the following algorithm:

$\Rightarrow$ If $E_{\text{PKA}} < E_{\text{threshold}}^1$ then the PKA can be disregarded: the number of spikes generated by this PKA is $n=0$.

$\Rightarrow$ If $E_{\text{threshold}}^1 < E_{\text{PKA}} < E_{\text{threshold}}^2$ then the PKA gives rise to one spike of energy $E_{\text{PKA}}$: $n=1$.

$\Rightarrow$ If $E_{\text{PKA}} > E_{\text{threshold}}^2$ then the PKA energy is broken into $n = \frac{E_{\text{PKA}}}{E_{\text{threshold}}^2}$ subcascades of energy $E_{\text{threshold}}^2$.

Although the above model can result in fractional subcascades (e.g. $n=1.45$ subcascades of energy $E^2$), it is considered to be a better description of the phenomenon, since it allows for taking into account subcascades formation which is a general feature of energetic PKAs, (moreover the energy conservation is respected).
The main difficulty is to agree on reasonable values for the energy thresholds used in the algorithm. As mentioned before, these values should depend on the material. In this study, we will take the same energy thresholds for all materials. As mentioned before, $E^1$ will be set to 2 keV, and $E^2$ will be set to 200 keV.

For each ion, we can calculate the number of spikes it induces and their energy according to the rules described above. When averaged over the number of ions for which the SRIM2003 runs were done (i.e. 10000 ions), this gives the number of thermal spikes triggered by the ion $\chi$ which is given by:

$$\chi = \frac{\sum_{i} n_i}{N_{\text{ions}}}$$  

Eq. 5.58

where $n_i$ is the number of spikes triggered by ion # $i$, and $N_{\text{ions}}$ is the total number of ions (in our case the SRIM2003 simulations were run for $N_{\text{ions}}=10000$).

An overall average energy for spikes created in a given system i.e. (for a given material and a given ion type/energy) can also be estimated, according to:

$$Q = \frac{\sum_{i} n_i \bar{E}_i}{\sum_{i} n_i}$$  

Eq. 5.59

where $\bar{E}_i$ is the average energy of the spikes created by ion # $i$. The average thermal spike energy $Q$ is then used to estimate the size of the average thermal-spike. In their study of computer simulation of defect production by displacement cascades in metals[130], Bacon et al. have shown that the maximum size of the liquid-like region (aka thermal spike) in defect cascades of energies up to 5 keV was given by:

$$d_{\text{spike}} = 6a_0(Q)^{1/3}$$  

Eq. 5.60

where $d_{\text{spike}}$ is the diameter of the thermal spike in nm, $a_0$ is the lattice parameter of the material in nm, and $Q$ is the energy of the cascade in keV. Eq. 5.60 was found to apply for higher energy cascades as well. In studies of cascade formation in Fe [131] and in Ni$_3$Al [132] where cascade energies higher than 10 keV were simulated, the predicted
values of $d_{\text{spike}}$ obtained with Eq. 5.60 for $Q=10$ keV and 30-50 keV were close to the values found in the simulations, and the range of large $d_{\text{spike}}$ size for higher energies was entirely consistent with experimental data [127, 128]. This suggests that we may use this expression to estimate the size of the thermal spike at low temperatures.

Using the methodology described above, we were able to evaluate the parameters involved in the expression of $K$ in Eq. 5.53. The values of the material properties involved in calculating Eq. 5.53 are listed in Table 5.3 and the values of the irradiation parameters are listed in Table 5.4.

Table 5.3: Values of material properties involved in the thermal spike model of grain-growth under ion irradiation for Zr, Cu, Pt, and Au [133]

<table>
<thead>
<tr>
<th>Element</th>
<th>$\nu$ Debye frequency (Hz)</th>
<th>$V_{\text{at}}$ Atomic volume (cm$^3$)</th>
<th>$\kappa_0$ Thermal conductivity (eV/cm-K)</th>
<th>$c_0$ Heat capacity (eV/cm$^3$-K)</th>
<th>$\Delta H_{\text{coh}}$ Cohesive energy (eV/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>3.80x10$^{13}$</td>
<td>2.34x10$^{-23}$</td>
<td>1.44x10$^{18}$</td>
<td>1.12x10$^{19}$</td>
<td>6.25</td>
</tr>
<tr>
<td>Cu</td>
<td>4.48x10$^{13}$</td>
<td>1.18x10$^{-23}$</td>
<td>2.50x10$^{19}$</td>
<td>2.15x10$^{19}$</td>
<td>3.49</td>
</tr>
<tr>
<td>Pt</td>
<td>3.14x10$^{13}$</td>
<td>1.51x10$^{-23}$</td>
<td>4.50x10$^{18}$</td>
<td>1.78x10$^{19}$</td>
<td>5.84</td>
</tr>
<tr>
<td>Au</td>
<td>2.16x10$^{13}$</td>
<td>1.69x10$^{-23}$</td>
<td>2.00x10$^{19}$</td>
<td>1.56x10$^{19}$</td>
<td>3.81</td>
</tr>
</tbody>
</table>

Table 5.4: Irradiation parameters used to calculate $K$

<table>
<thead>
<tr>
<th>Element</th>
<th>Ion type / energy</th>
<th>Flux (#ions/cm$^2$-s)</th>
<th>$E_{\text{threshold}}^1$</th>
<th>$E_{\text{threshold}}^2$</th>
<th>$\chi$</th>
<th>$Q$ (eV)</th>
<th>$d_{\text{cas}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>Kr 500keV</td>
<td>2.5 10$^{12}$</td>
<td>2 keV</td>
<td>200 keV</td>
<td>6.51</td>
<td>20300</td>
<td>5.3</td>
</tr>
<tr>
<td>Cu</td>
<td>Kr 500keV</td>
<td>2.5 10$^{12}$</td>
<td>2 keV</td>
<td>200 keV</td>
<td>13.7</td>
<td>18800</td>
<td>5.7</td>
</tr>
<tr>
<td>Pt</td>
<td>Ar 500keV</td>
<td>2.5 10$^{12}$</td>
<td>2 keV</td>
<td>200 keV</td>
<td>5.84</td>
<td>13900</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>Kr 1MeV</td>
<td>1.25 10$^{12}$</td>
<td>2 keV</td>
<td>200 keV</td>
<td>10.9</td>
<td>22000</td>
<td>6.6</td>
</tr>
<tr>
<td>Au</td>
<td>Ar 500keV</td>
<td>2.5 10$^{12}$</td>
<td>2 keV</td>
<td>200 keV</td>
<td>4.78</td>
<td>14500</td>
<td>6.0</td>
</tr>
</tbody>
</table>
We have been able to fit our experimental data with Eq. 5.53 by using the same energy thresholds for the determination of the average number of spikes per ion and the average spike energy and by using the activation energy for atomic jumps within a spike $E_a$ as the only variable. Indeed, it was reported that this value scales with the cohesive energy of the target material according to $E_a = \beta \Delta H_{coh}$ (Eq. 5.48). Values of $\beta$ in ion-beam mixing experiments are found to be around 0.14. In ion-irradiation-induced grain-growth experiments this parameter was found to be between 0.05 and 0.15 depending on the experiment [83]. In our case, we were able to get a good fit of the grain growth curves by using the values of $\beta$ reported in Table 5.5. As pointed out in [83], the fact that the value of $\beta$ was different only by a factor of 1 to 2 is remarkable since these values were obtained from experimental data studying different phenomena.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>0.11</td>
</tr>
<tr>
<td>Cu</td>
<td>0.07</td>
</tr>
<tr>
<td>Pt</td>
<td>0.04</td>
</tr>
<tr>
<td>Au</td>
<td>0.020</td>
</tr>
</tbody>
</table>

Figures 5.6 - 5.10 show the experimental data (i.e. average grain-size evolution with ion dose) versus the data predicted by the model using the values in Tables 5.3-5.5. The grain-growth curves obtained from the model showed a good agreement with the experimental data bringing further validation of the model.
Figure 5.6: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Pt irradiated with Ar 500 keV ions at 298 K.

Figure 5.7: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Pt irradiated with 1 MeV Kr ions at 50 K and 298 K.
Zr, 500 keV Kr, 20 K
Average grain size vs. ion dose:
Experiment vs. Model

Figure 5.8: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Zr irradiated with 500 keV Kr ions at 20 K.

Cu, 500 keV Kr, 50 K
Average grain size vs. ion dose:
Experiment vs. Model

Figure 5.9: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Cu irradiated with 500 keV Kr ions at 50 K.
Figure 5.10: Average grain-size versus ion dose: Experimental data vs. Model in the temperature-independent regime: Au irradiated with 500 keV Ar ions at 50 K.

5.4 Thermally assisted regime

The experimental results showed a temperature range where both grain growth rate and the final size were enhanced with higher irradiating temperatures, which revealed that both thermal effects and irradiation effects control the grain-boundary migration in this regime. The transition between the temperature-independent regime and this thermally assisted regime was found to depend on the material, but when scaled with the melting temperature of the material it fell in the same range \(0.14 \text{ to } 0.22 T_m\).
5.4.1 Temperature dependence of grain-growth under ion-irradiation

Grain-growth is a thermal process that occurs purely thermally at high enough temperatures. Under ion irradiation it was observed to occur at very low temperatures where thermal diffusion is limited. In fact the experimental results showed a low-temperature regime where the kinetics of grain-growth under irradiation are independent of temperature and a higher temperature range where both grain growth rate and the final size are enhanced with higher irradiating temperatures with respect to both the low-temperature regime and the purely thermal grain-growth. The transition between the temperature-independent regime and this thermally assisted regime was found to depend on the material, but when scaled with the melting temperature of the material it fell in the same range \(0.14 \text{ to } 0.22T_{\text{melt}}\). Figure 5.11 presents a schematic summary of the dependence of grain-growth kinetics with respect to irradiation temperature which emphasizes the different temperature regimes. As a matter of fact, a lot of irradiation effects are described by Figure 5.11, where the diffusion coefficient or another kinetics-parameter characteristic of the phenomenon studied is plotted versus the inverse of temperature. The plot divides in three regions with respect to the temperature:

- A low-temperature regime where the kinetics are independent of temperature: irradiation effects control the kinetics of the process.
- A high-temperature regime where thermal effects control the process and the thermal equilibrium defect concentration dominates the total defect concentration. Such high temperatures were not reached during our experiments. For Zr thin films, temperatures higher than 973 K were not investigated because of possible damage to the sample. Already at 973K, thermal stresses induced some tearing or “wrinkles” of some regions and the sample stuck to the washers used in the sample holder.
- In between the two regimes there is a range of intermediate temperatures where the kinetics of grain-growth are enhanced with increasing temperature. This regime may further be divided in two sub-ranges if we consider whether thermal grain-growth was observed in the non irradiated areas or not:
(i) thermal grain-growth is not observed at the given temperature in the non-irradiated area, however temperature has an effect on the kinetics; it was the case for Zr at all temperatures investigated in the temperature dependent regime; it was the case for Au and Cu at room temperature where thermal grain-growth was not observed in the non-irradiated areas yet showed enhanced grain-growth under ion irradiation compared to the ballistic regime;

or

(ii) the onset for purely thermal grain-growth was reached and the kinetics were enhanced compared to both purely thermal grain-growth and purely ballistic regime. It was the case for Au and Cu at 473 K and 573 K: thermal grain-growth was observed in both cases in the non-irradiated areas but under irradiation the kinetics were found to be enhanced.

---

**Figure 5.11:** Schematics of the temperature dependence of grain growth under ion irradiation.
Usually, thermal processes which occur under irradiation at lower temperatures than the temperatures at which they usually occur purely thermally are interpreted in the frame of the radiation-enhanced diffusion theory. So it is only legitimate that the first step in the analysis of the grain-growth results in the thermally-assisted regime was to look at how radiation-enhanced diffusion concepts might explain the kinetics observed. The question is whether the enhancement of the phenomenon is due to intercascade processes or to thermal-enhancement of intracascade processes: in other words, are higher grain-growth rates and larger final grain-sizes a result of radiation-enhanced diffusion? or are they a result of intracascade effects related to the ambient temperature?

The question is all the more legitimate than apparent activation energies were found to be similar to activation energies for the migration of interstitials (typically 0.1 eV), suggesting that radiation-enhanced diffusion of interstitials is a possible mechanism of ion-irradiation-induced grain-growth in the temperature dependent regime.

5.4.2 Ion-irradiation-induced grain-growth and radiation-enhanced diffusion:

First of all, because most of our experiments were conducted in the recombination-dominated regime, long-range diffusion plays no role. Moreover, if grain-growth under ion-irradiation was controlled by radiation-enhanced diffusion, a dependence on ion flux should be observed experimentally, which was not observed. During our irradiations of Zr-Fe thin-films with 500 keV Kr ions, after varying the ion flux by a factor of two, no changes were observed as far as the grain size. In [78], grain-growth was also observed to be independent of the flux in Cu foils irradiated with 200 keV Ar ions at room temperature (therefore in the thermally-assisted regime) after changing the ion-flux by a factor of 20. The same observation was done in a study of Au films irradiated with 200 keV Xe ions at two different fluxes (different by a factor of 10) [70]. This means that the grain size is a function of ion dose not ion flux. This suggests that ion-irradiation-induced grain-growth is not a radiation-enhanced diffusion process after the collision cascades have returned to their thermal equilibrium states.
Similar conclusions were made from ion-beam mixing results – it is always interesting to compare ion-beam induced grain-growth with ion-beam mixing results because although the phenomena studied are different, they both involve the same ion-matter interaction processes. Activation energies found in ion-beam mixing experiments are close to activation energies for self-interstitial diffusion in metals (typically 0.1 eV) suggesting that radiation-enhanced diffusion of interstitials is a possible mechanism of ion-beam mixing in the temperature dependent regime. For instance, in their study of ion-beam mixing in Ni-Si [134] Averback et al. found an apparent activation energy of 0.09 eV. Based on their analysis of the experimental results using chemical rate theory - which considered all cases (no-sink, no recombination, recombination-dominated, sink-dominated), The no-sink regime was the only one for steady state conditions in which the activation enthalpy of the process was determined by the faster moving species (interstitials). However the no-sink requirement was unreasonable. It was also argued that in the case of recombination dominated regime, the thickness of the mixed layer should be inversely proportional to the square-root of the ion flux. Therefore, after varying the flux by a factor of 22 in the mixing of Ni-Si at 80K and 373K, they expected the thickness of the mixed layer to change by a factor of 2.2; the experiment though showed no effect at either temperatures. It was concluded that the observed temperature-dependence of ion-beam mixing is not associated with the migration energy of point defects, i.e. radiation-enhanced diffusion of interstitial is not the mechanism responsible for the low activation energies observed experimentally.

The discussion above shows that the atomic motion involved in ion-irradiation-induced grain-growth process in the thermally-assisted regime is not a conventional radiation-enhanced diffusion process but rather an intra-cascade phenomenon.

This leads to the question of the effect of irradiation temperature on the primary damage cascade, which could explain the temperature-dependence of the grain-growth kinetics in the intermediate temperature range. Indeed, it is proposed that the temperature dependence of grain growth in the thermally assisted regime could arise from the temperature dependence of the primary stage of damage formation i.e. the size of the thermal spike itself. This is all the more relevant since our model proposes that the
process of grain-boundary migration itself occurs during the thermal spike. Therefore it is proposed that the dependence of grain-growth kinetics on \( T_{irr} \) arises from the dependence of the thermal spike process itself on \( T_{irr} \), that is thermal spike size increases with higher substrate temperature. Literature is scarce on this topic and shows that this is an area where further work definitely needs to be done. However, the main studies published to date give us a general idea and a confirmation to the present study.

5.4.3 Effects of \( T_{irr} \) on the primary stage of damage formation (cascade process):

In most molecular dynamics simulations reported in the literature, the PKA is generated in a lattice equilibrated at 100 K or less [17, 18]. An important feature of these studies was the indication of a transient local melting in the core of the cascade and that a liquid-drop model represents at least the qualitative features of the process. This suggested that atomic mixing in cascade-induced thermal spikes could be accounted for by quasi-liquid diffusion in a locally melted region. This was confirmed by other more detailed studies [130-132, 135-137]. Hsieh and Averback performed molecular dynamics simulations of 3 keV displacement cascades in Cu [138] and found that most atomic displacements occurred in the quasi-molten core region that develops at \( t \sim 0.5 \) ps and persists for a few ps. The mixing was found to increase modestly at 300 K compared to 0K, and more rapidly at higher temperatures. By varying the ambient temperature of the lattice \( (T_{irr}=0, 300, 500, \text{ and } 700 \text{ K}) \), the size and the lifetime of the molten region increased with irradiation temperature and the instantaneous diffusion coefficients in the cascade melt were in agreement with those in equilibrium liquid.

Gao and Bacon performed MD simulations of cascades in \( \alpha-\text{Fe} \) [131] and Ni\(_3\)Al [132]. These studies [131, 132, 135, 136] demonstrated the need to incorporate heat transfer as accurately as possible when the quantitative details of irradiation temperature are of concern in the description of defect production. In the case of \( \alpha-\text{Fe} \) [131], the effect of the lattice temperature on defect production associated with displacement cascades was studied with simulations of cascades of either 2 or 5 keV at 100 K, 400 K, 600 K, and 900K. For the same PKA energy, the size of the thermal spike was larger at the
lattice temperature of 600 K than at 100 K. In the case of Ni$_3$Al [132], the molecular dynamics simulations provided detailed information on defect production and disordering produced in cascades of energy 10 keV, as a function of irradiation temperature $T_{irr}$. The results were consistent with those obtained for Fe, i.e. the total number of atomic jumps within the thermal spike was found to increase with $T_{irr}$, and the maximum size $d_{spike}$ of the melted zone was larger at $T_{irr}=900$ K than at $T_{irr}=100$K, reflecting the increase in intensity and lifetime of the thermal spike. $d_{spike}$ is shown as a function of $T_{irr}$ in Figure 5.12. We note that $d_{spike}$ at 900K (~half of the melting point of Ni$_3$Al) is about 1.4 times size at 100K.

![Figure 5.12](image)

**Figure 5.12**: Mean diameter of the “molten zone” $d_{melt}$ as a function of initial lattice temperature in a 10 keV cascade induced in Ni$_3$Al.

Hsieh and Averback also performed molecular-dynamics simulations of intra-cascade mixing to evaluate the mixing rate with increasing $T_{irr}$[138]. The results of the study showed that the maximum diameter of the molten sphere increases with the substrate temperature (from 0 to 700K). Rossi and Nastasi [16] derived an empirical relationship between the size of the spike and $T_{irr}$ using the results of the molecular dynamics study in [138]. $d_{spike}$ was expressed as follows:
where $\lambda$ is a constant, $d_b$ a ballistic constant depending on the element, $T_{irr}$ the initial substrate temperature, and $T_s$ a characteristic temperature depending on the target. $\lambda$ and $d_b$ depend on the spike energy the cohesive energy and the thermal properties of the substrate. In fact $d_b$ has the unit of length and could be interpreted as the size of the spike at 0K so that

$$D_{\text{spike}}(T_{irr}) = D_{\text{spike}}^{0K} \left[ 1 + \lambda \exp\left(-\frac{T_s}{T_{irr}}\right) \right]$$

Eq. 5.62

For Cu, the values found for $d_b$ (i.e. $D_{\text{spike}}^{0K}$), $T_s$, and $\lambda$ are 16 Å, 617 K, and 1.95, respectively, with a correlation coefficient of 1.

The information reported above supports the idea that the temperature dependence observed in the thermally assisted regime is the direct reflection of the temperature dependence of the cascade formation process itself; thus the apparent “activation energies” measured in the thermally assisted regime should in fact be a measure of the temperature dependence of the thermal spike size.

Also, higher irradiation temperatures result in higher number of atomic jumps within the thermal spikes as verified by the MD simulations mentioned above. However it is not possible to derive an analytical expression for this increase of $\eta$. Indeed, the derivation of $\eta$ (presented above and in Appendix 3), depend on the derivation of the temperature distribution within the thermal spike $T(r,t)$. $T(r,t)$ is obtained from solving the heat conduction equation. As pointed out before, the analytical solution of this equation is only possible if assume a substrate temperature $T_{irr}$=0K; if not, finite element discretization is necessary. However, the MD simulations published to date do confirm an increase of atomic jumps at the peak of damage with $T_{irr}$. MD simulations would therefore be helpful to quantitatively determined the effect of $T_{irr}$ on $d_{\text{spike}}$ and $\eta$.

Our data at high temperatures is limited. The model was derived for the case of pure elemental thin-films i.e. no drag effect was considered taken into account in the model. In the case of Zr-Fe, data is available at higher temperatures but the precipitation
reaction occurring concomitantly with grain-growth affects the kinetics; therefore it would be unappropriate to apply the model without correcting for the second-phase particle drag effect. For Cu, Au, and Pt, Table 5.6 shows the values of the spike size required if the dependence of the spike-size on $T_{irr}$ were to explain alone the grain-growth increase resulting from going from 50 K (temperature-independent regime) to respectively 300 K for Au and Cu, and to 773 K for Pt (ignoring the effect of $T_{irr}$ on $\eta$).

Table 5.6: Size of cascade in the thermally assisted regime

<table>
<thead>
<tr>
<th>Material</th>
<th>Ion type/energy</th>
<th>$d_{cas}$ (nm) at 50K</th>
<th>$T$ (K) / Homologous temperature</th>
<th>$d_{cas}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Ar 500 keV</td>
<td>6.0</td>
<td>473/ 0.22</td>
<td>12.0</td>
</tr>
<tr>
<td>Cu</td>
<td>Kr 500 keV</td>
<td>5.7</td>
<td>298/ 0.22</td>
<td>7.5</td>
</tr>
<tr>
<td>Pt</td>
<td>Kr 1MeV</td>
<td>6.6</td>
<td>773/ 0.37</td>
<td>15.0</td>
</tr>
</tbody>
</table>

We note that for Cu, an increase in average thermal spike size of 30% would be enough to account for the enhanced kinetics at room temperature (which is in the thermally assisted regime); this seems reasonable. In the case of Au and Pt, the spike size should be increased by a factor of 2 and 2.2 respectively to account alone for the enhancement of the kinetics at 473 K and 773 K respectively whereas the literature shows variations of 30-40%.

However the biggest discrepancy comes in the two experiments performed at the highest temperatures. For these experiments, we may be operating in the sink-dominated regime, as shown in Figure 5.2, thus the flux of mobile point defects annihilating at the grain-boundary could enhance grain-growth at the higher $T_{irr}$ relative to the lower temperature case. Additional evidence that this may be the case is provided by the observation of void formation decoring the grain-boundaries in Au irradiated at 573 K indicating that point defects are arriving grain boundary sinks for those irradiation conditions.

Another aspect of the cascade structure which could be playing a role in the enhancement of the kinetics at higher temperature is the possibility of thermal spikes overlap, in which case the resulting size of the combined overlapping spikes would
enhance grain-growth. In an attempt to examine the role of intracascade processes in ion mixing, Rossi and Nastasi considered how cascade structure and sub-cascade overlapping influence ion mixing and the onset temperature for temperature-dependent ion mixing [16]. The results of their Monte Carlo simulations of ion-mixing in bilayers at 0 K showed the influence of spike diameter, $d_s$, and spike overlap on the evolution of the mixed layer thickness as a function of number of spikes. Ion-beam mixing (i.e. the interdiffusion layer thickness) was observed to increase with the number of spikes and the mixing rate depended strongly on the spike diameter. When spikes (sub-cascades) were allowed to overlap, the mixing rate increased. When temperature effects were included in the simulations, it was observed that the size of the sub-cascades increased with increasing temperature and that, neighboring sub-cascades, which were isolated at lower temperatures, would overlap. Our model did not account for this possible effect because knowledge on thermal spike overlap is limited but it could play a role at higher temperatures, due to the increase in size.

To summarize: the enhanced grain-growth under ion irradiation in the thermally assisted regime, is primarily caused by thermal spike size increase and increase of atomic jumps within thermal spikes due to higher substrated temperature. At the highest temperatures point defects fluxes to the grain-boundaries and thermal spike overlap may also contribute.
Chapter 6

Conclusions and Suggestions for Future Work

The microstructural evolution of nanocrystalline metallic thin-films under ion irradiation, especially grain growth and second-phase precipitation, was studied with detailed in situ experiments, and a theoretical model was developed to explain the results of grain-growth. Free-standing Zr, Pt, Cu and Au, Cu-Fe, and Zr-Fe nanocrystalline thin films prepared by sputter deposition were irradiated in-situ at the Intermediate Voltage Electron Microscope (IVEM) at Argonne National Laboratory with Ar and Kr ions to fluences in excess of $10^{16}$ ion/cm$^2$ at temperatures ranging from 20 to 773 K. The microstructure evolution of the thin-films (grain-growth and second-phase precipitation in the alloys) was followed by systematically recording bright field images and diffraction patterns at successive ion-irradiation doses. The main conclusions are as follows:

1. Grain growth was observed as a result of irradiation in all samples at all irradiation temperatures, even below 50 K where thermal diffusion is minimal and thermal grain-growth is not observed. The average grain size $D$ increased monotonically with ion dose $\Phi$ according to the equation: $D^n - D_0^n = K\Phi$.

The results indicate the existence of three temperature regimes for grain growth in nanocrystalline materials:

(i) A low temperature regime (below $\sim 0.2$ $T_{\text{melt}}$) where “collisional” effects dominate the grain growth process; in this regime, grain-growth kinetics do not depend on the irradiation temperature and the grain-growth exponent is found to be $\sim 3$.

(ii) An intermediate-temperature regime or “thermally assisted regime” where both the grain-growth rate and the final grain size increase with increasing irradiation temperature.
(iii) A high temperature regime or “purely thermal regime”, where thermal effects dominate over ion-beam effects.

2. The effect of solute addition on grain-growth was investigated using supersaturated solid solutions of Zr(Fe) and Cu(Fe) irradiated with 500 keV Kr ions. In the case of Zr-Fe, the formation of Zr$_2$Fe precipitates occurred during irradiations performed at room temperatures and above. In the case of Cu(Fe), no second-phase precipitate (i.e. no Fe precipitation) occurred. The grain-growth rate and final size decreased with respect to the pure metallic films as a result of both solute drag (Cu-Fe) and second-phase particle pinning i.e. Zener drag effect (Zr-Fe).

3. Neither grain-growth nor the intermetallic precipitation occurred under 1 MeV electron irradiation of Zr-Fe thin-films. This means that a minimum density of defects (such as formed in the cascades created by ion irradiation) is needed for either the Zr$_2$Fe precipitation or grain-growth to occur. This indicates that only defects created within dense subcascades (i.e. thermal spikes) influence grain-growth kinetics, i.e. isolated defects do not contribute to grain-growth. Also, rate theory calculations show that most of the irradiations were performed in the recombination-dominated regime, which means that long-range diffusion of point defects does not play a role in grain-growth under ion irradiation.

4. A model of grain-growth under ion irradiation in the temperature-independent regime was developed, based on the direct impact of irradiation-induced thermal spikes on grain-boundaries. The model describes grain growth driven solely by the reduction of grain boundary area. In the model, grain-boundary migration occurs by atomic jumps within the thermal spikes biased by the local grain-boundary curvature driving force. In contrast with previous models of grain-growth under ion-irradiation which ignored the nature of the cascade structure, this model incorporates cascade structure features such as subcascade formation, and the probability of subcascades occurring at grain-boundaries. The model yields a power law expression relating the average grain-size with the ion dose, where the exponent is 3 in good agreement with the experimental data. In contrast with previous studies, this work showed that the grain-growth exponent of 3 is an inherent feature of grain-growth under ion irradiation.
5. In the thermally assisted regime, the increased of grain-growth rate and final grain-size is explained within the framework of the same model, by the increased thermal spike size and the increase of atomic jumps within thermal spikes at higher temperature with higher substrate temperature. At the highest temperatures, other effects such as subcascade overlap and point defect migration to sinks may also enhance the process.

**Future work:**

Ideas for future work include:

a. Incorporating the recoil-energy distribution even more directly in the model by using fitting expressions for \( \chi(E_{\text{PKA}}) \) as proposed in Appendix 4.

b. It would also be beneficial to conduct careful experiments in the thermally assisted regime to determine the exact dependence of grain-growth in this regime. Such experiments should also include a study of the flux dependence at high temperatures. The study would benefit from experiments conducted specifically in recombination-dominated regime and in sink-dominated regime, respectively.

c. The process of grain-boundary pinning by precipitates or the reduction of grain-growth by means of solute drag could also be included in the model for the case of alloys under ion irradiation.

d. The modeling of grain-growth would also benefit from advances in the understanding of cascade structure. It should be noted that, in any case, the study of grain-growth under ion irradiation will remain within the limitations of the present knowledge of the exact nature of the irradiation-induced cascade structure, which is expected to vary considerably among different ion-target combinations and in turn lead to varying grain-growth behavior. A quantitative description of the energy threshold for sub-cascade formation is still lacking. Subcascade overlap effects were mentioned in this study but little is know on this subject, which could have an impact on the process of grain-growth. Finally, knowledge of the temperature dependence of (sub)cascade formation is still lacking. Particularly, the exact nature of temperature dependence of the spike-size with \( T_{\text{irr}} \) for the different materials is not known. This is a question which
needs more investigation. Molecular dynamics studies could help, although they are limited by the energy range for which they can be performed nowadays. This aspect is all the more relevant to the study of grain-growth since the process of grain-boundary migration under ion-irradiation itself was shown to relate directly to the thermal spike phase of the cascades. In any case, the present study has highlighted the role of cascade structure in grain-growth under ion-irradiation.
Bibliography


Appendix A

SRIM2003 irradiation simulations

Input data for the various ion-irradiations is reported in the tables along with the results. All irradiations simulations were run in full cascade mode with 5000 ions to have good statistics. Input data include the displacement energy threshold, target material, density, thickness of slab, ion type and energy and angle of incidence. The results of interest such as the number of ion transmitted, the sputtering yields, the energy loss repartition between electrons and nuclei, and the damage production cross-sections are reported.

<p>| Target layer composition (at%)/ Thickness(Å) | Cu 900 Å |
| Displacement Energies: | $E_d$(Cu)=25eV Angle=15 degrees |
| Density calculated by TRIM (g/cm³) | 8.92 |
| Ion type / Energy: | Kr / 500 keV |
| Number of ions: | 5000 |
| Backscattered ions: | 5 |
| Transmitted ions: | 3316 |
| Type of calculation: | Full cascade |
| Energy from the ions: | 291 keV/ion (323 eV/ion/Ang) |
| Energy to the recoils: | 291 keV/ion |
| Sputtering yield: | Atoms/ion eV/ion |
| Cu | 7.99 170.82 |
| Energy loss (%): | Ions Recoils |
| Ionization | 17.14 13.97 |
| Vacancies | 0.09 6.41 |
| Phonons | 0.29 62.10 |
| Damage: | Displacements/ion: 7116 (7.906disp/ion-A) |
| Vacancies/ion: 6727 (7.474vac/ion-A) |
| Replacement collisions/ion: 389 (0.432rep/ion-A) |</p>
<table>
<thead>
<tr>
<th>Target layer composition (at%)/Thickness(Å)</th>
<th>Pt 800 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement Energies:</td>
<td>E_d(Pt)=25eV angle=15</td>
</tr>
<tr>
<td>Density calculated by TRIM (g/cm³)</td>
<td>21.450</td>
</tr>
<tr>
<td>Ion type / Energy:</td>
<td>Kr / 1000 keV</td>
</tr>
<tr>
<td>Number of ions:</td>
<td>5000</td>
</tr>
<tr>
<td>Backscattered ions:</td>
<td>150</td>
</tr>
<tr>
<td>Transmitted ions:</td>
<td>4234</td>
</tr>
<tr>
<td>Type of calculation:</td>
<td>Full cascade</td>
</tr>
<tr>
<td>Energy from the ions:</td>
<td>294 keV/ion (367 eV/ion/Ang)</td>
</tr>
<tr>
<td>Energy to the recoils:</td>
<td>294 keV/ion</td>
</tr>
<tr>
<td>Sputtering yield:</td>
<td>Atoms/ion eV/ion</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td>Ions Recois</td>
</tr>
<tr>
<td></td>
<td>Ionization</td>
</tr>
<tr>
<td></td>
<td>Vacancies</td>
</tr>
<tr>
<td></td>
<td>Phonons</td>
</tr>
<tr>
<td>Damage:</td>
<td>Displacements/ion:</td>
</tr>
<tr>
<td></td>
<td>Vacancies/ion:</td>
</tr>
<tr>
<td></td>
<td>Replacement collisions/ion:</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Target layer composition (at%)/Thickness(Å)</th>
<th>Pt 800 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement Energies:</td>
<td>E_d(Pt)=25eV angle=15</td>
</tr>
<tr>
<td>Density calculated by TRIM (g/cm³)</td>
<td>21.450</td>
</tr>
<tr>
<td>Ion type / Energy:</td>
<td>Ar / 500 keV</td>
</tr>
<tr>
<td>Number of ions:</td>
<td>5000</td>
</tr>
<tr>
<td>Backscattered ions:</td>
<td>318</td>
</tr>
<tr>
<td>Transmitted ions:</td>
<td>4201</td>
</tr>
<tr>
<td>Type of calculation:</td>
<td>Full cascade</td>
</tr>
<tr>
<td>Energy from the ions:</td>
<td>96.4 keV/ion (120 eV/ion/Ang)</td>
</tr>
<tr>
<td>Energy to the recoils:</td>
<td>96.4 keV/ion</td>
</tr>
<tr>
<td>Sputtering yield:</td>
<td>Atoms/ion eV/ion</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td>Ions Recois</td>
</tr>
<tr>
<td></td>
<td>Ionization</td>
</tr>
<tr>
<td></td>
<td>Vacancies</td>
</tr>
<tr>
<td></td>
<td>Phonons</td>
</tr>
<tr>
<td>Damage:</td>
<td>Displacements/ion:</td>
</tr>
<tr>
<td></td>
<td>Vacancies/ion:</td>
</tr>
<tr>
<td></td>
<td>Replacement collisions/ion:</td>
</tr>
<tr>
<td>Target layer composition (at%)/ Thickness(Å)</td>
<td>Zr 800 Å</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Displacement Energies:</td>
<td>$E_d$(Zr)=25 eV angle=15</td>
</tr>
<tr>
<td>Density calculated by TRIM (g/cm$^3$)</td>
<td>6.49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion type / Energy:</th>
<th>Ne / 500 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of ions:</td>
<td>5000</td>
</tr>
<tr>
<td>Backscattered ions:</td>
<td>22</td>
</tr>
<tr>
<td>Transmitted ions:</td>
<td>4277</td>
</tr>
<tr>
<td>Type of calculation:</td>
<td>Full cascade</td>
</tr>
<tr>
<td>Energy from the ions:</td>
<td>8 keV/ion ( 10 eV/ion/Ang)</td>
</tr>
<tr>
<td>Energy to the recoils:</td>
<td>8 keV/ion</td>
</tr>
<tr>
<td>Sputtering yield:</td>
<td>Atoms/ion</td>
</tr>
<tr>
<td></td>
<td>Zr 156</td>
</tr>
<tr>
<td></td>
<td>eV/ion</td>
</tr>
<tr>
<td></td>
<td>1208.41</td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td>Ions</td>
</tr>
<tr>
<td></td>
<td>Ionization</td>
</tr>
<tr>
<td></td>
<td>90.58</td>
</tr>
<tr>
<td></td>
<td>1.63</td>
</tr>
<tr>
<td></td>
<td>Vacancies</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>0.60</td>
</tr>
<tr>
<td></td>
<td>Phonons</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>7.01</td>
</tr>
</tbody>
</table>

| Damage:                                   | Displacements/ion: |
|                                          | 177 (0.221 disp/ion-A) |
|                                          | Vacancies/ion:       |
|                                          | 168 (0.21 vac/ion-A) |
|                                          | Replacement collisions/ion: |
|                                          | 9 ( 0.011 rep/ion-A) |

<table>
<thead>
<tr>
<th>Target layer composition (at%)/ Thickness(Å)</th>
<th>Zr 800 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement Energies:</td>
<td>$E_d$(Zr)=25 eV angle=15</td>
</tr>
<tr>
<td>Density calculated by TRIM (g/cm$^3$)</td>
<td>6.49</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ion type / Energy:</th>
<th>Kr / 600 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of ions:</td>
<td>5000</td>
</tr>
<tr>
<td>Backscattered ions:</td>
<td>18</td>
</tr>
<tr>
<td>Transmitted ions:</td>
<td>4682</td>
</tr>
<tr>
<td>Type of calculation:</td>
<td>Full cascade</td>
</tr>
<tr>
<td>Energy from the ions:</td>
<td>144 keV/ion ( 180 eV/ion/Ang)</td>
</tr>
<tr>
<td>Energy to the recoils:</td>
<td>144 keV/ion</td>
</tr>
<tr>
<td>Sputtering yield:</td>
<td>Atoms/ion</td>
</tr>
<tr>
<td></td>
<td>Zr 2.71</td>
</tr>
<tr>
<td></td>
<td>eV/ion</td>
</tr>
<tr>
<td></td>
<td>973.42</td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td>Ions</td>
</tr>
<tr>
<td></td>
<td>Ionization</td>
</tr>
<tr>
<td></td>
<td>30.41</td>
</tr>
<tr>
<td></td>
<td>14.74</td>
</tr>
<tr>
<td></td>
<td>Vacancies</td>
</tr>
<tr>
<td></td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>4.45</td>
</tr>
<tr>
<td></td>
<td>Phonons</td>
</tr>
<tr>
<td></td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>50.10</td>
</tr>
</tbody>
</table>

<p>| Damage:                                   | Displacements/ion: |
|                                          | 2601 (3.251 disp/ion-A) |
|                                          | Vacancies/ion:       |
|                                          | 2467 (3.083 vac/ion-A) |
|                                          | Replacement collisions/ion: |
|                                          | 134 (0.167 rep/ion-A) |</p>
<table>
<thead>
<tr>
<th>Target layer composition (at%)/Thickness(Å)</th>
<th>Zr 800 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement Energies: E_d(Zr)=25eV angle=15</td>
<td></td>
</tr>
<tr>
<td>Density calculated by TRIM (g/cm³) 6.49</td>
<td></td>
</tr>
<tr>
<td>Ion type / Energy: Ar / 500 keV</td>
<td></td>
</tr>
<tr>
<td>Number of ions: 5000</td>
<td></td>
</tr>
<tr>
<td>Backscattered ions: 49</td>
<td></td>
</tr>
<tr>
<td>Transmitted ions: 4898</td>
<td></td>
</tr>
<tr>
<td>Type of calculation: Full cascade</td>
<td></td>
</tr>
<tr>
<td>Energy from the ions: 37.6 keV/ion (47 eV/ion/Ang)</td>
<td></td>
</tr>
<tr>
<td>Energy to the recoils: 37.6 keV/ion</td>
<td></td>
</tr>
<tr>
<td>Sputtering yield:</td>
<td></td>
</tr>
<tr>
<td>Atoms/ion eV/ion</td>
<td></td>
</tr>
<tr>
<td>Zr 0.877 1970.15</td>
<td></td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td></td>
</tr>
<tr>
<td>Atoms/ion eV/ion</td>
<td></td>
</tr>
<tr>
<td>Ions 69.77 5.83</td>
<td></td>
</tr>
<tr>
<td>Ionization 0.05 1.94</td>
<td></td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td></td>
</tr>
<tr>
<td>Atoms/ion eV/ion</td>
<td></td>
</tr>
<tr>
<td>Ions 69.77 5.83</td>
<td></td>
</tr>
<tr>
<td>Ionization 0.05 1.94</td>
<td></td>
</tr>
<tr>
<td>Phonons 0.22 22.19</td>
<td></td>
</tr>
<tr>
<td>Damage:</td>
<td></td>
</tr>
<tr>
<td>Displacements/ion: 755 (0.944 disp/ion-A)</td>
<td></td>
</tr>
<tr>
<td>Vacancies/ion: 717 (0.896 vac/ion-A)</td>
<td></td>
</tr>
<tr>
<td>Replacement collisions/ion: 39 (0.048 rep/ion-A)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Target layer composition (at%)/Thickness(Å)</th>
<th>Zr 800 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement Energies: E_d(Zr)=25eV angle=15</td>
<td></td>
</tr>
<tr>
<td>Density calculated by TRIM (g/cm³) 6.49</td>
<td></td>
</tr>
<tr>
<td>Ion type / Energy: Kr / 500 keV</td>
<td></td>
</tr>
<tr>
<td>Number of ions: 5000</td>
<td></td>
</tr>
<tr>
<td>Backscattered ions: 20</td>
<td></td>
</tr>
<tr>
<td>Transmitted ions: 4473</td>
<td></td>
</tr>
<tr>
<td>Type of calculation: Full cascade</td>
<td></td>
</tr>
<tr>
<td>Energy from the ions: 155 keV/ion (194 eV/ion/Ang)</td>
<td></td>
</tr>
<tr>
<td>Energy to the recoils: 155 keV/ion</td>
<td></td>
</tr>
<tr>
<td>Sputtering yield:</td>
<td></td>
</tr>
<tr>
<td>Atoms/ion eV/ion</td>
<td></td>
</tr>
<tr>
<td>Zr 3.08 835.31</td>
<td></td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td></td>
</tr>
<tr>
<td>Atoms/ion eV/ion</td>
<td></td>
</tr>
<tr>
<td>Ions 24.67 15.65</td>
<td></td>
</tr>
<tr>
<td>Ionization 0.07 4.84</td>
<td></td>
</tr>
<tr>
<td>Phonons 0.25 54.55</td>
<td></td>
</tr>
<tr>
<td>Damage:</td>
<td></td>
</tr>
<tr>
<td>Displacements/ion: 2932 (3.665 disp/ion-A)</td>
<td></td>
</tr>
<tr>
<td>Vacancies/ion: 2781(3.476 vac/ion-A)</td>
<td></td>
</tr>
<tr>
<td>Replacement collisions/ion: 151 (0.188 rep/ion-A)</td>
<td></td>
</tr>
<tr>
<td>Target layer composition (at%) / Thickness(Å)</td>
<td>Au 800 Å</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Displacement Energies:</td>
<td>$E_d(Au)=25\text{eV}$ angle=15</td>
</tr>
<tr>
<td>Density calculated by TRIM (g/cm$^3$)</td>
<td>19.311</td>
</tr>
<tr>
<td><strong>Ion type / Energy:</strong></td>
<td>Ar / 500 keV</td>
</tr>
<tr>
<td>Number of ions:</td>
<td>5000</td>
</tr>
<tr>
<td>Backscattered ions:</td>
<td>313</td>
</tr>
<tr>
<td>Transmitted ions:</td>
<td>4420</td>
</tr>
<tr>
<td>Type of calculation:</td>
<td>Full cascade</td>
</tr>
<tr>
<td>Energy from the ions:</td>
<td>80 keV/ion (100 eV/ion/Ang)</td>
</tr>
<tr>
<td>Energy to the recoils:</td>
<td>80 keV/ion</td>
</tr>
<tr>
<td>Sputtering yield:</td>
<td>Atoms/ion eV/ion</td>
</tr>
<tr>
<td>Au</td>
<td>4.29 362.48</td>
</tr>
<tr>
<td>Energy loss (%):</td>
<td>Ions Recoils</td>
</tr>
<tr>
<td>Ionization</td>
<td>54.55 15.50</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.07 3.33</td>
</tr>
<tr>
<td>Phonons</td>
<td>0.26 26.30</td>
</tr>
<tr>
<td>Damage:</td>
<td>Displacements/ion: 2263 (3.828disp/ion-A)</td>
</tr>
<tr>
<td></td>
<td>Vacancies/ion: 2001 (2.501vac/ion-A)</td>
</tr>
<tr>
<td></td>
<td>Replacement collisions/ion: 262 (0.327rep/ion-A)</td>
</tr>
</tbody>
</table>
Appendix B

C++ program used to sort through the SRIM2003 outputs to generate the PKA energy distribution presented in Figure 5.5

// Multi_cutoff_E.cpp : Defines the entry point for the console application.

#include "stdafx.h"
#include "math.h"
#include "stdio.h"

//#using <mscorlib.dll>
#define Number_of_energies 70
#define Number_of_ions 10000
#define Number_of_rows 10000
#define total_size 3000000

//using namespace System;
char collision [20], cutoffenergies [20],output_file [20];
double cutoff_energy[Number_of_energies];
double energy[Number_of_rows][Number_of_ions];
double read_energy[total_size];

int N_of_row, N_of_col, N_of_energy;

void input_file();

void main(void)
{
    FILE *fout;

    int n_o_e, row, col, count;
    double total_sum;

    input_file();

    fout = fopen("Output_file.xls", "w");

    n_o_e = 1;
    col = 1;

    while(n_o_e <= N_of_energy)
    {
        printf(fout,"
%i   %le 
", n_o_e, cutoff_energy[n_o_e]);

        while(col <= N_of_col)
        {
            row = 1;
count = 0;
total_sum = 0;
while(row <= Number_of_rows)
{
    if(energy[139][col] >= cutoff_energy[n_o_e])
    {
        total_sum += energy[139][col];
        printf("\n\t energy[\%i][\%i] --> \%le", row, col,
        energy[139][col]);
        //fprintf(fout,"\n\t energy[\%i][\%i] --> \%le",
        row, col, energy[139][col]);
        count++;
    }
    row++;
}
printf("\n the average of \%i th ion set is \%le \n", col,
    total_sum/count);
    //fprintf(fout,"the number of cascades of \%i th ion is \%i,
    and the average cascade energy is \%le \n", col, count,
    total_sum/count);
    fprintf(fout,"\%i \%i \%le \n", col, count, total_sum/count);
    col++;
}
    n_o_e++;
    col=1;
}
fclose (fout);
return ;

void input_file()
{
    int i = 1, col=1, row=1, zero, k = 1;
    FILE *fin;
    FILE *fin1;
    FILE *fout_1;
    fin = fopen ("collision","r");
    fin1 = fopen ("cutoffenergies","r");
    fout_1 = fopen("Output_input.xls", "w");

while(k <= Number_of_energies)
{
    fscanf (fin1,"%le ", &cutoff_energy[k]);
    if (cutoff_energy[k] <= 0) break;
    N_of_energy = k;
    k++;
}
while(i <= total_size)
{
fscanf (fin,"%le ", &read_energy[i]);
if (read_energy[i] > 0)
{
    energy[139][col] = read_energy[i];
    printf(" energy(%i)(%i) = %le \n", row, col, energy[139][col]);
    fprintf(fout_1,"%le \n", read_energy[i]);
    row++;
}
if (read_energy[i] < 0)
{
    break;
}
zero=1;
if (read_energy[i] == 0)
{
    col++;
    row = 1;
    while(zero <= 11)
    {
        fscanf(fin,"%le ", &read_energy[zero]);
        zero++;
    }
    fprintf(fout_1, "-----------\n");
}
i++;
}
N_of_col = col;
//N_of_row = row;
printf("\n %i %i", N_of_row, N_of_col);

fclose(fin);
fclose(fin1);
fclose (fout_1);
Appendix C

Number of displacements created in a thermal spike

C.1 Thermal spike in an infinite medium under no driving force:

In the thermal spike model of the interaction of energetic radiation with matter, it is assumed that energy is deposited instantaneously in a very small region, producing a localized increase of temperature which spreads and cools according to the laws of classical heat conduction in a homogeneous continuum. If an activated process (e.g. migration of atoms, evaporation of atoms from a surface etc) is energized by the spike the number of elementary steps caused by one spike can be expressed as an integral over space and time of the rate expression for the process in which the temperature is given by a function of space and time characteristic of the spike. Vineyard examined the case of thermal spikes of cylindrical and spherical geometries and derived an expression for the temperature distribution within the thermal spike for both geometries [14].

If the energy of the spike Q is initially introduced at a point in the medium, the subsequent dissipation of this energy results in the temperature distribution T(r,t) in the thermal spike region which is assumed to be either spherical or cylindrical. Since MD studies show that a spherical geometry would be more appropriate to describe cascades and subcascades, only the spherical case will be treated here. Vineyard derived an expression for T(r,t) by solving the heat conduction equation in cylindrical geometry considering an initial deposited energy distribution as Qδ³(r) where δ³(r) is the 3-D delta function. A simple power law dependence is assumed for the thermal conductivity κ, and the heat capacity c on temperature such that κ=κ₀T^{n-1} and c=c₀T^{n-1}(n≥1). However it is noticed that with such expression the thermal diffusivity given by the ratio κ /C is still constant and independent of temperature.
\[
T(r, t) = \left( \frac{nQc_0^{1/2}}{(4\pi\kappa_0 t)^{3/2}} \right)^{1/\alpha} \exp \left( -\frac{c_0 r^2}{4n\kappa_0 t} \right) \quad \text{Eq. 3.1}
\]

where \( r \) is the radial distance from the initial point of energy deposition, \( t \) is time and \( \kappa_0 \) and \( c_0 \) are respectively the ambient values of the thermal conductivity and the heat capacity. It is to be noted that in such a treatment, the target macroscopic temperature or “ambient temperature” is taken as absolute zero. If an ambient temperature is added, the integration of the equations can not be achieved.

Atomic motion within the spike is promoted thermally and these thermally activated atomic jumps are assumed to obey a directionally random Arhenius law as follows[14]:

\[
R = A \exp \left( -\frac{E_a}{k_B T(r,t)} \right) \quad \text{Eq. 3.2}
\]

where \( E_a \) is the activation energy for atomic jump, \( k_B \) is Boltzmann’s constant, and \( A \) is a constant independent of temperature. \( T(r,t) \) is the temperature distribution within the spike.

Hence the total number of atomic jumps induced in one thermal spike \( \eta \) is obtained by incorporating \( T(r,t) \) from Eq. 3.1 into Eq. 3.2 and integrating over time and space according to:

\[
\eta = \int_0^\infty dV \int_0^\infty R(r, t) dt \quad \text{Eq. 3.3}
\]

where \( dV \) is the infinitesimal volume and \( R(r, t) \) is the atomic jump rate per unit volume. The expression of \( R(r, t) \) depends on the driving forces used to describe atomic motion within thermal spikes. In the absence of driving forces, and if the cascade is assumed spherical then \( \eta \) is expressed as:

\[
\eta = \int_0^\infty 4\pi r^2 dr \int_0^\infty A \exp \left( -\frac{E_a}{k_B T(r,t)} \right) dt \quad \text{Eq. 3.4}
\]
We pose:

\[ r = \frac{n^{5/6}Q^{1/3}}{c_0^{1/3} \pi^{1/2}} \left( \frac{k_B}{E_a} \right)^{\left(\frac{n}{3}\right)} \tau^{\left(\frac{n}{3}\right)} \ln^{1/2}(\rho) \quad \text{and} \quad \frac{dr}{\rho \ln^{1/2}(\rho)} = \frac{n^{5/6}Q^{1/3}}{2c_0^{1/3} \pi^{1/2}} \left( \frac{k_B}{E_a} \right)^{\left(\frac{n}{3}\right)} \tau^{\left(\frac{n}{3}\right)} \frac{d\rho}{\rho \ln^{1/2}(\rho)} \]

\[ t = \frac{n^{2/3}Q^{2/3}}{4\pi \kappa_0 c_0^{2/3} \pi^{3/2}} \left( \frac{k_B}{E_a} \right)^{\left(\frac{2n}{3}\right)} \tau^{\left(\frac{2n}{3}\right)} \quad \text{and} \quad \frac{dt}{\rho \ln^{1/2}(\rho)} = \frac{n^{5/3}Q^{2/3} c_0^{1/3}}{6\pi \kappa_0} \left( \frac{k_B}{E_a} \right)^{\left(\frac{2n}{3}\right)} \tau^{\left(\frac{2n-1}{3}\right)} d\tau. \]

\( \eta \) then becomes:

\[ \eta = \int_{\rho}^{\infty} \frac{An^{25/6}Q^{5/3}}{3 \kappa_0 c_0^{2/3} \pi^{3/2}} \left( \frac{k_B}{E_a} \right)^{\left(\frac{5n}{3}\right)} \ln^{1/2}(\rho) d\rho \int_{0}^{\infty} \frac{\tau^{\left(\frac{5n-1}{3}\right)}}{\tau^{\left(\frac{5n}{3}\right)}} \exp(-\rho \tau) d\tau \quad \text{Eq. 3.5} \]

which equals:

\[ \eta = \int_{\rho}^{\infty} \frac{An^{25/6}Q^{5/3}}{3 \kappa_0 c_0^{2/3} \pi^{3/2}} \left( \frac{k_B}{E_a} \right)^{\left(\frac{5n}{3}\right)} \frac{\Gamma\left(\frac{5n}{3}\right) \ln^{1/2}(\rho)}{\rho^{\left(\frac{5n-1}{3}\right)}} d\rho \quad \text{Eq. 3.6} \]

After a further change of variables posing \( u = \ln(\rho) \) and \( du = \frac{d\rho}{\rho} \), \( \eta \) becomes:

\[ \eta = \frac{An^{25/6}Q^{5/3}}{3 \kappa_0 c_0^{2/3} \pi^{3/2}} \left( \frac{k_B}{E_a} \right)^{\left(\frac{5n}{3}\right)} \Gamma\left(\frac{5n}{3}\right) \int_{0}^{\infty} u^{\frac{1}{2}} e^{\left(\frac{5n}{3} u\right)} du \quad \text{Eq. 3.7} \]

Finally, the total number of atomic jumps induced by one spherical thermal spike of energy \( Q \) in the absence of chemical forces (driving forces) is given by:

\[ \eta_{\text{no driving force}} = \sqrt{\frac{3}{5}} \frac{An^{8/3}Q^{5/3}}{10\pi C_0^{2/3} \kappa_0} \left( \frac{k_B}{E_a} \right)^{\left(\frac{5n}{3}\right)} \Gamma\left(\frac{5n}{3}\right) \quad \text{Eq. 3.8} \]
C.2 Considering the driving force due to grain-boundary curvature:

When the local driving force due to grain-boundary curvature from Eq. 5.7 is incorporated into describe atomic motion within the thermal spike, the rate of jumps within the thermal spike per unit volume is then given by:

\[ R(r, t) = \frac{4\gamma V_{at}}{Dk_B T(r, t)} N_{at} v \exp \left( -\frac{E_a}{k_B T(r, t)} \right) \]  \hspace{1cm} \text{Eq. 3.9} 

and the total number of jumps within the thermal spike is then given by:

\[ \eta = \int_0^\infty 4\pi r^2 dr \int_0^\infty \frac{4\gamma V_{at}}{Dk_B T(r, t)} N_{at} v \exp \left( -\frac{E_a}{k_B T(r, t)} \right) dt \]  \hspace{1cm} \text{Eq. 3.10} 

which can be written as:

\[ \eta = \int_0^\infty 4\pi r^2 dr \int_0^\infty \frac{A}{T(r, t)} \exp \left( -\frac{E_a}{k_B T(r, t)} \right) dt \]  \hspace{1cm} \text{Eq. 3.11} 

where

\[ A = \frac{4\gamma V_{at} N_{at} v}{Dk_B} \]  \hspace{1cm} \text{Eq. 3.12} 

It is assumed that during the lifetime of the thermal spike the grain size is constant. The integrations are then accomplished after change of variable as above and \( \eta \) becomes:

\[ \eta = \int_1^\infty \frac{An^{25/6} Q^{5/3}}{3\kappa_0 c_0^{2/3} \pi^{3/2}} \left( \frac{k_B}{E_a} \right)^{5n/3} \left( \frac{5n}{3} + 1 \right) \ln^{1/2} (\rho) d\rho \int_0^\infty t \left( \frac{5n}{3} \right) \exp (-\rho t) dt \]  \hspace{1cm} \text{Eq. 3.13} 

which equals:

\[ \eta = \int_1^\infty \frac{An^{25/6} Q^{5/3}}{3\kappa_0 c_0^{2/3} \pi^{3/2}} \left( \frac{k_B}{E_a} \right)^{5n/3} \left( \frac{5n}{3} + 1 \right) \ln^{1/2} (\rho) \frac{\Gamma \left( \frac{5n}{3} + 1 \right)}{\rho^{(\frac{5n}{3}+1)}} d\rho \]  \hspace{1cm} \text{Eq. 3.14}
After a further change of variables posing \( u = \ln(\rho) \) and \( du = \frac{d\rho}{\rho} \), \( \eta \) becomes:

\[
\eta = \frac{A_n^{25/6} Q^{5/3}}{3\kappa_0 c_0^{2/3} \pi^{3/2}} \left( \frac{k_B}{E_a} \right)^{\left( \frac{5n+1}{3} \right)} \Gamma\left( \frac{5n}{3} + 1 \right) \int_0^\infty u^{1/2} e^{-\left( \frac{5n}{3} u \right)} du
\]

Eq. 3.15

Finally:

\[
\eta = \frac{\sqrt{3}}{10\pi c_0^{2/3} \kappa_0} \left( \frac{k_B}{E_a} \right)^{\left( \frac{5n+1}{3} \right)} \Gamma\left( \frac{5n}{3} + 1 \right)
\]

Eq. 3.16

We note that

\[
\eta = \left( \frac{k_B}{E_a} \right) \left( \frac{5n}{3} \right) \eta_{\text{no driving force}}
\]

Eq. 3.17

If \( n = 1 \) (i.e. if the heat capacity and heat conductivity are assumed constant within the spike), \( \eta \) becomes:

\[
\eta = \frac{4\gamma V_{at} N_{at} \sqrt{3}}{Dk_B} \frac{\sqrt{5} \Gamma\left( \frac{8}{3} \right) k_B^{8/3}}{10\pi c_0^{2/3} \kappa_0} \frac{Q^{5/3}}{E_a^{8/3}}
\]

Eq. 3.18

We note that since \( E_a = \beta \Delta H_{coh} [124] \), \( \eta \) is in fact proportional to \( \frac{Q^{5/3}}{\Delta H_{coh}^{(8/3)}} \).
Appendix D

Incorporation of the recoil energy distribution in the thermal spike model

In this appendix, attention is brought to how the “average thermal spike model” could be further improved. The recoil-energy distributions presented in Figure 5.5 show that the number of recoils of low energies is much larger than the number of recoils of larger energies. Given that it is the high energy recoils which contribute the most to grain growth according to Eq. 5.53, therefore a simple arithmetic average value of the recoil energy as expressed in Eq. 5.59 would give more weight to the small energy recoils than they should and on the other hand it would bring down the actual contribution of the high-energy recoils. In order to correct for that effect, the recoil energy distribution could be somewhat incorporated in the analysis. This would be possible if the recoil energy distributions were accurately fitted by expressions of the type: $\chi(E) = AE^B$, for instance, where $A$ and $B$ are constants. Then Eq. 5.53 can be written as:

$$\frac{D^3 - D_0^3}{\Phi} = \chi Q^{5/3} d_{cas} \text{ where } C = \left[ \frac{V_m \sqrt{3 - \frac{2}{5} \Gamma \left( \frac{8}{3} \right) k_n^{5/3}}}{10 \pi C_0^{2/3} \kappa_0 E_n^{8/3}} \right]$$ Eq. 4.1

where $\chi$ is the average number of spikes per ion, $Q$ are the average energy of spikes, and $d_{cas}$ is the size of the average spike of energy $Q$. Now, if we incorporate the recoil energy distribution (which should result in a cascade size distribution) into the model in a more comprehensive way, and using the same approach for recoils of energy higher than $E_2$ as described earlier (page 33 of this chapter) we obtain:

$$\frac{D^3 - D_0^3}{C \Phi} = \int_{E_1}^{E_2} \chi(Q) Q^{5/3} d_{cas}(Q) dQ + \int_{E_2}^{E_{\text{max}}} \chi(Q) \frac{Q}{E_2} E_2^{5/3} d_{cas}(E_2)$$ Eq. 4.2
where $E_{\text{max}}$ is determined by the maximum-energy transfer parameter

$$\Lambda = \frac{4M_iM_{\text{ion}}}{(M_1 + M_{\text{ion}})^2}$$

according: $E_{\text{max}} = \Lambda E_{\text{ion}}$. Using Eq. 5.60 for the estimate of $d_{\text{cas}}(Q)$ where $Q$ was expressed in keV, Eq. 5.54 becomes:

$$\frac{D^3 - D_0^3}{C\Phi} = \int_{E_1}^{E_2} A Q^n Q^{5/3} 6a_0 \left( \frac{Q}{1000} \right)^{1/3} dQ + \int_{E_1}^{E_2} A Q^n Q_{E_2} E_2^{3/3} 6a_0 \left( \frac{E_2}{1000} \right)^{1/3} dQ \quad \text{Eq. 4.3}$$

(here $Q$ is in eV). Eq. 4.4 can also be written as:

$$\frac{D^3 - D_0^3}{C\Phi} = \frac{6a_0 A}{1000^{1/3}} \left[ \int_{E_1}^{E_2} Q^{2+n} dQ + E_2^{\text{max}} \right] \quad \text{Eq. 4.5}$$

After integration, Eq. 5.56 becomes:

$$\frac{D^3 - D_0^3}{C\Phi} = \frac{6a_0 A}{1000^{1/3}} \left( \frac{1}{3 + B} \left[ E_{2}^{3+n} - E_{1}^{3+n} \right] + \frac{1}{2 + B} E_{2}^{\text{max}} \right) \quad \text{Eq. 4.6}$$

Note: Although this approach seems more accurate, there are limitations to it, which arise from the fact that finding the right fitting expression for the whole spectrum seems difficult. An expression of the type: $\chi(E) = AE^B$ tend to overestimate the end tail of the distribution. Moreover, Eq. 5.60 which is used to estimate $d_{\text{cas}}(Q)$ is an empirical expression obtained from MD simulations for low energy cascades in materials of cubic structure and may not be accurate for the higher energy recoils (more than 100 keV). This being said, this brief discussion highlights once again the role of cascade structure in grain-growth under ion-irradiation.
VITA

Djamel Kaoumi

Djamel Kaoumi was born in Marseille (France) on the 28th of March 1977. He completed his undergraduate education (in Physics) at the Ecole Nationale Superieure de Physique de Grenoble (ENSPG) (Grenoble, France) in 1999 with honors. He obtained his Masters degree in Nuclear Engineering with a minor in Materials Science and Engineering at the University of Florida (Gainesville, FL) in 2001. He enrolled for a PhD degree in Nuclear Engineering at the Pennsylvania State University in 2001 with a Fellowship of the Dean of the College of Engineering.