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**Object kinetic Monte Carlo simulations of
irradiated tungsten for nuclear fusion reactors**

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Resumen

El wolframio es considerado como el principal candidato para revestimientos de materiales expuestos a plasmas, tanto para materiales de primera pared en el caso de reactores de fusión por confinamiento inercial como para recubrimiento de ciertas partes del divertor en el caso de reactores de fusión por confinamiento magnético. Esto es debido a sus propiedades, tales como alto punto de fusión, alta conductividad térmica, bajo coeficiente de erosión y baja retención de tritio. Sin embargo, además de los altos requerimientos termomecánicos, el wolframio tendrá que soportar la irradiación iónica de helio e hidrógeno entre otros, la cual puede dar lugar a efectos perjudiciales de origen atómico, tales como el agrietamiento, exfoliación o hinchamiento.

Todavía se necesitan muchos esfuerzos para desarrollar un material basado en tungsteno que sea capaz de soportar las condiciones realistas de irradiación en las futuras plantas de fusión nuclear, en particular, los pulsos de alta intensidad que se espera tengan lugar. El modelo multiescala secuencial se muestra como una buena metodología para el estudio de la irradiación de helio o hidrógeno en wolframio, ya que ayuda a comprender los procesos clave de los efectos físicos que se observan experimentalmente. En el modelo multiescala secuencial, los resultados de un determinado paso son los datos de entrada del siguiente. Gracias al uso combinado de la teoría de la densidad del funcional (DFT), la dinámica molecular (MD), la aproximación de colisiones binarias (BCA) y el Monte Carlo cinético de objetos (OKMC), el modelo multiescala cubre un amplio espectro en las escalas temporal y espacial, desde $\sim$ nm y $\sim$ ps hasta μ m y horas o incluso días.

El estudio que se presenta en esta tesis está basado principalmente en simulaciones con OKMC de irradiación de helio o hidrógeno en wolframio, utilizado como material de revestimientos de materiales expuestos a plasmas. El estudio cubre diferentes aspectos de la irradiación iónica: la naturaleza de los iones (helio o hidrógeno) y el flujo (bien continuo o pulsado) en wolframio tanto con baja como con alta densidad de bordes de grano (wolframio monocristalino o nanocristalino respectivamente). Dado que la metodología OKMC necesita como datos de entrada tanto la energía de unión como la energía de migración, estos parámetros se obtuvieron gracias a cálculos de DFT. Como resultado, se presenta una completa parametrización tanto para irradiación de hidrógeno como de helio en wolframio. Las cascadas de daño producidas en el wolframio debido a la irradiación iónica son también datos de entrada para los códigos de computación de OKMC. Con el objetivo de determinar si las cascadas obtenidas con BCA son realistas o no, se ha realizado una comparación con unas cascadas obtenidas con MD. Aunque la técnica MD tiene en

cuenta tanto la evolución de la temperatura como la migración, aglomeración y recombinación de defectos, el tiempo de computación requerido y las limitaciones temporales y espaciales de simulación hacen que sea muy atractivo el uso de un método mucho más rápido como el BCA. Los resultados obtenidos muestran que, en el caso de irradiación con iones ligeros (los cuales producen PKAs de baja energía), las cascadas obtenidas con BCA son suficientemente adecuadas para ser utilizadas en un posterior cálculo con OKMC. El código de computación de OKMC utilizado en esta tesis fue un código abierto recientemente desarrollado, el código MMonCa. Por ese motivo, se hizo una validación previa del código para el caso de irradiación iónica en wolframio y se obtuvieron resultados similares a aquellos obtenidos con otros códigos y que habían sido encontrados en la literatura.

Por un lado, el flujo iónico que llegará al wolframio en fusión por confinamiento inercial es pulsado por naturaleza. Por otro lado, en fusión por confinamiento magnético, los efectos más nocivos provienen de las pulsos iónicos debidos a los llamados modos localizados de borde (ELMs). Sin embargo, muchos estudios experimentales se llevan a cabo en instalaciones de irradiación convencionales, que operan en modo continuo. La comparativa entre ambos modos de irradiación muestra que en el caso de irradiación pulsada de helio hay más retención de He, los átomos de He están retenidos en aglomerados de He-V con un menor número de vacantes y que esos aglomerados de He-V se localizan en un volumen mucho menor. Por ello, se espera una peor respuesta del wolframio ante irradiación pulsada de He. El efecto del flujo ha de ser tenido en cuenta cuando se estudie el wolframio para revestimientos de materiales expuestos a plasmas.

Con el objetivo de mitigar los efectos perjudiciales de la irradiación de helio, se están investigando nuevos materiales basados en el uso de wolframio nanoestructurado (NW). En el caso de irradiación con helio, las simulaciones de OKMC mostraron que el helio está atrapado en aglomerados de He-V mayores y con menor relación He/V que en el caso de wolframio monocristalino (MW). Es más, con el aumento de la fluencia, aumenta la diferencia de la energía de tensión elástica total. En el caso de irradiación con hidrógeno, se reprodujeron mediante simulaciones OKMC experimentos a diferentes condiciones de irradiación (sólo irradiación de hidrógeno e irradiación de C e H, tanto simultánea como secuencial) tanto en MW como en NW. Los resultados mostraron que, de nuevo, la densidad de bordes de grano tiene un claro efecto en la aniquilación entre vacantes y átomos intersticiales de W. Más aún, de la comparativa entre los experimentos y las simulaciones en el caso de NW, se infirió que los bordes de grano actúan como caminos preferenciales para la difusión de hidrógeno. Los estudios tanto de helio como de hidrógeno

en MW y NW mostraron que el NW se comporta de un modo diferente al MW con respecto a la irradiación iónica y que una mejor respuesta se espera en el caso de NW.

Por último, se ha estudiado la irradiación de helio en condiciones que tendrán lugar en los futuros reactores de fusión por confinamiento magnético. Con estas condiciones de irradiación, una nanoestructura muy poco densa (el llamado fuzz) se ha observado experimentalmente, pero únicamente dentro de una ventana de temperaturas definida (desde 900 hasta 2000 K). Gracias a un nuevo modelo implementado en MMonCa, este efecto pudo ser estudiado. Los resultados mostraron que el proceso es dominado por el atrapamiento y emisión de los átomos de He en las vacantes. A bajas temperaturas, el He es atrapado en aglomerados de He-V muy estables. A temperaturas intermedias, estos aglomerados atrapan y emiten átomos de He, que dan lugar finalmente a mayores aglomerados de He-V, que son los que provocan el crecimiento del fuzz. Para terminar, a alta temperatura, el He es emitido de los aglomerados de He-V que se forman, terminando en una falta de retención de He y, por consiguiente, una falta de formación de fuzz.

Abstract

Tungsten is considered the main candidate for plasma facing material applications, for both the first-wall in inertial confinement fusion reactors and divertor regions in magnetic confinement fusion reactors. This is due to its properties such as high melting point, high thermal conductivity, low sputtering coefficient and low tritium retention. However, in addition to the high thermomechanical requirements, tungsten will have to deal with ion irradiation, helium and hydrogen among others, which results in detrimental effects of atomistic origin such as cracking, exfoliation or blistering.

Many efforts are still needed to develop a tungsten-based material capable of dealing with realistic irradiation conditions in future power plants, in particular, the expected intense ion pulses. Sequential multiscale modelling is a powerful methodology to study helium or hydrogen irradiation in tungsten, since it helps to understand the driving processes of the physical effects observed experimentally. In the sequential multiscale modelling, the results of one step are the input data for the next one. Thanks to the combined use of density functional theory (DFT), molecular dynamics (MD), binary collision approximation (BCA) and object kinetic Monte Carlo (OKMC), the multiscale modelling covers a wide range of spatial and temporal scales, from $\sim$ nm and $\sim$ ps to μ m and hours or even days.

In this thesis, a study mainly based on OKMC simulations of helium or hydrogen irradiation in tungsten as a plasma facing material is presented. The study covers different aspects of ion irradiation: ion nature (helium or hydrogen) and flux (continuous or pulsed modes) on tungsten with low or high grain boundary density (monocrystalline or nanocrystalline, respectively). Since OKMC makes use of binding and migration energies as input data, these parameters were obtained from density functional theory calculations. As a result, a complete parameterization of hydrogen or helium irradiation in tungsten is presented. Damage cascades generated in tungsten due to ion irradiation are also input for OKMC codes. In order to determine whether BCA damage cascades are realistic or not, a comparison with cascades obtained by means of MD was done. Although MD takes into account temperature evolution and defect migration, clustering and recombination, the computational time needed and the limited spatial and temporal accessible ranges makes attractive the use of a fast method such as BCA. The results showed that, for light ion irradiation (which generates low energy PKAs), BCA cascades are accurate enough to be used as input for the OKMC calculations. The OKMC code used in this thesis was a newly developed open-source code, the MMonCa code. Thus, a previous validation of the code

for ion irradiation in tungsten was done, obtaining similar results than those from other codes found in the literature.

On the one hand, the ion flux that will reach tungsten in inertial fusion confinement is pulsed by the nature. On the other hand, in magnetic confinement fusion, the most detrimental effects stem from ion pulses due to so called edge localized modes (ELMs). However, many experimental studies use conventional irradiation facilities that operate in continuous mode. The comparison between both modes of irradiation showed that in the case of pulsed helium irradiation, there is more He retention, He atoms are retained in He-V clusters with a lower number of vacancies and that these He-V clusters are located in a much smaller volume. Thus, a worse response of tungsten under pulsed He irradiation is expected. The flux effect should be taken in account when studying tungsten for plasma facing material purposes.

In order to mitigate the deleterious effects under helium irradiation, new approaches based on the use of nanostructured tungsten (NW) are being investigated. In the case of helium irradiation, OKMC simulations showed that helium is trapped in larger He-V clusters with lower He/V ration in the case of NW, as a result of the influence of GBs on the annihilation process between vacancies and self-interstitial atoms (SIAs). Thus, these He-V clusters are less pressurized than the equivalent ones in monocrystalline tungsten (MW). Moreover, the higher the fluence, the higher the difference of the total elastic strain energy. In the case of hydrogen irradiation, experiments with different irradiation conditions (single H irradiation and C and H simultaneously and sequentially irradiated) were reproduced with OKMC simulations in both MW and NW. The results showed that, again, the grain boundary density has a clear effect on the annihilation between vacancies and SIAs. Furthermore, from the comparison between experiments and simulations in the case of NW, it was inferred that GBs act as preferential paths for H diffusion. Both helium and hydrogen studies on MW and NW showed that NW behaves in a different way as compared to MW regarding ion irradiation and that a better response is expected in the case of NW.

Finally, helium irradiation in conditions that will take place in magnetic fusion confinement reactors was studied. At these irradiation conditions, an underdense nanostructure (so called “fuzz”) has been observed experimentally, but only in a defined temperature window (from 900 to 2000 K). Thanks to a new model implemented in MMonCa, this effect could be studied. The results showed that the process is driven by the trapping/detrapping of He atoms in vacancies. At low temperatures, He is trapped in very stable He-V clusters. At intermediate temperatures, these clusters trap and emit He atoms, leading to larger He-V clusters which promote fuzz growth. Finally, at high temperature, He is detrapped from the formed He-V clusters, leading to no He atom retention and thus, no fuzz formation.

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Abbreviations

BCA	Binary collision approximation
bcc	Body-centered cubic
CCFC	Culham Center for Fusion Energy
CEA	Commissariat à l'énergie atomique
CESVIMA	Centro de supercomputación y visualización de Madrid
CGW	Coarse-grained tungsten
D	Deuterium
DFT	Density functional theory
EAM	Embedded atom method
ELM	Edge-localized mode
FIA	Foreign interstitial atom
FP	Frenkel pair
GB	Grain boundary
GCA	Generalized gradient approximation
ICF	Inertial confinement fusion
IFN	Instituto de Fusión Nuclear
IMDEA	Instituto Madrileño de Estudios Avanzados
ITER	International Thermonuclear Experimental Reactor
JET	Joint European Torus
LAKIMOKA	Lattice kinetic Monte Carlo
LAMMPS	Large-scale atomic/molecular massively parallel simulator
LLNL	Lawrence Livermore National Laboratory
MCF	Magnetic confinement fusion
MD	Molecular dynamics
MMonCa	Modular Monte Carlo
MW	Monocrystalline tungsten
NIF	National Ignition Facility
NW	Nanocrystalline tungsten
OKMC	Object kinetic Monte Carlo
OVITO	Open visualization tool
PBC	Periodic boundary condition
PFM	Plasma facing material
PKA	Primary knock-on atom
PLATO	Package of linear combination of atomic type orbitals
SEM	Scanning electron microscopy
SIA	Self-interstitial atom
SIESTA	Spanish initiative for electronic simulations with thousands of atoms
SRIM	Stopping and range of ions in matter
T	Tririum
TCL	Tool command language
TDS	Thermal desorption spectroscopy
TEM	Transmission electron microscopy
TOKAMAK	From Russian: тороидальная камера с магнитными катушками
TRIM	Transport of ions in matter
UK	United Kingdom of Great Britain and Northern Ireland
UPM	Universidad Politécnica de Madrid
USA	Unated States of America
V	Vacancy
VASP	Vienna <i>ab initio</i> simulation package

1 Introduction

1.1 Thesis origin

Future fusion power plants would offer a good solution for the increasing demand of electric power, as electricity would be produced without increasing CO₂ emissions to the atmosphere. Moreover, it consumes a much smaller amount of fuel than other sources of energy. For instance, to produce 1000 MWe, a power plant requires annually about 3×10^6 tonnes of coal, or 2×10^6 tonnes of oil or 30 tonnes of UO₂ [1]. In the case of a future fusion power plant, it would need 100 kg of deuterium (D) and 150 kg of tritium (T) [1]: a single D-T fusion reaction produces a neutron of 14.1 MeV and a helium nucleus of 3.5 MeV. In addition to this, fusion energy offers some other advantages [2]: (i) neither SO_x nor NO_x are emitted to the atmosphere, (ii) radioactivity inventory is very limited, (iii) despite transmutation reactions induced by neutrons in the structural materials are unavoidable, they can be strongly limited by using appropriate materials and (iv) the fusion reaction could be easily stopped, if necessary. Moreover, a huge power density can be obtained. However, some scientific and technological issues have to be solved before having this source of energy [3].

Deuterium and tritium have been chosen for the first generation of fusion power plants, because their fusion reaction requires lower temperature comparing, for instance, to deuterium-deuterium [3]. As the D-T plasma must be confined, two schemes are being researched: inertial confinement fusion (ICF) and magnetic confinement fusion (MCF). With regard to ICF, D-T plasma is confined as follows: firstly the lasers deliver energy to heat the outer layer (ablator) of the D-T target. Secondly, the D-T target is compressed by the rocket-like effect, up to a density ~ 100 times higher than its density at the beginning. Thirdly, the first D-T reactions take place at the so called “hot spot”. Then, the ignition starts. Finally, these first D-T fusion reactions heat up the compressed target, with the aid of the produced He (α -heating), starting the fusion of the rest of D-T.

ICF is being researched in facilities such as National Ignition Facility (NIF) in the Lawrence Livermore National Laboratory (LLNL) [4], in the USA, and Laser Mégajoule facility of the Commissariat à l’énergie atomique (CEA) [5], in France.

In the case of MCF, D-T plasma is confined by magnetic fields, which are designed in configurations like tokamak (from Russian, тороидальная камера с магнитными катушками). MCF is being researched in facilities such as JET (Joint European Torus),

which operates via a contract with the Culham Centre for Fusion Energy (CCFE) [6] in the UK, and ITER (International Thermonuclear Experimental Reactor) [7], which is a large-scale international project (European Union, India, Japan, China, Russia, South Korea and the USA). ITER is under construction in Cadarache, France. Another configuration of MFC is the stellarator. A large experimental stellarator has been built by the Max-Planck-Institut für Plasmaphysik in Germany [8].

The development of fusion energy technology depends on the solutions of many issues [3]: plasma heating and confinement, D-T target supply, compatibility of plasma ions and neutrons with the surrounding chamber wall materials, heat removal and fuel breeding in the blanket of the reactor, radiation safety, public acceptance, etc.

A vital area for the development of fusion energy are the plasma facing materials (PFMs), i.e, the materials to withstand the extreme irradiation conditions that will take place in both ICF and MCF, such as high thermal loads and high flux ion irradiation. In ICF, with a laser-driven direct-drive target (typical yield ~ 150 MJ) as an example, PFM will have to deal with irradiation of neutrons, fast ions, debris ions and X-rays in the form of intense pulses [9]. In MCF, the divertor will face the more demanding loads and operating conditions: a stationary heat flux of ~ 10 MW m⁻² and peak particle flux of $\sim 10^{24}$ m⁻² s⁻¹, apart from the much more demanding dynamic events such as edge-localized modes (ELMs) and disruptions [10].

From the thermomechanical point of view, the temperature at the PFM surface will approach 3000 K [10,11] in the case of edge-localized modes (ELMs) or pulsed irradiation with α particles and ion debris in ICF. In Table 1.1, the main characteristic parameters are compared [11] for a typical direct-drive target (yield per shot of 154 MJ) in the case of ICF and conditions assumed for ITER in the case of MCF. The heat flux parameter ($H = E \cdot \Delta t^{1/2}$) takes into account not only energy density (E) but also heat diffusion through the square root of pulse duration (Δt). From the comparison, similar values are obtained for ICF and MCF scenarios, except in the case of disruptions. PFMs must have a large surface area to distribute the energy, and a high thermal conductivity to release the incoming energy and avoid heat accumulation [11].

Table 1.1. Optimistic conditions assumed for ITER divertor and for a typical direct-drive target (yield 154 MJ) [9,11,12].

		Time (s)	Deposited energy (MJ m ⁻²)	Power (MW m ⁻²)	Heat flux parameter (MJ m ⁻² s ⁻¹)	Particle energy (eV)	Flux (m ⁻² s ⁻¹)
Divertor	Steady state	1000	-	5	-	1-30	<10 ²⁴
	<i>ELM</i>	0.2×10^{-3}	1	5×10^3	70	1-30	<10 ²⁴
	Disruption	1×10^{-3}	20	2×10^4	600	1-30	<10 ²⁴
Direct target	α -particles	200×10^{-9}	0.03	1.5×10^5	70	2.1×10^6	1×10^{25}
						avg.	
	DT debris	1.5×10^{-6}	0.06	4×10^4	50	150×10^3	2×10^{22}
						avg.	

Tungsten is proposed as a convenient PFM for both first-wall in ICF [13–17] and divertor regions in MCF [18–23]. W offers several advantages: high melting point (3695 K [24]), high thermal conductivity ($1.75 \text{ W cm}^{-2} \text{ s}^{-1}$ at room temperature [24]), low sputtering coefficient [25] and low tritium retention [23]. In principle, W is supposed to fulfil the majority of the highly demanding requirements, such as transient temperatures and stresses which take place in a ICF chamber [10,26,27] or in divertor region [28]. Nevertheless, the response of W to irradiation damage is known to be compromised by several factors, the most relevant the detrimental effects induced by light species retention in irradiation-generated defects.

Apart from high thermomechanical requirements, W must deal with ion irradiation [29], which creates Frenkel pairs (FPs), i.e., vacancies (V) and self-interstitial atoms (SIAs). The damage in the W lattice increases the accumulation of light species such as hydrogen [30,31] and helium [32,33], which tend to nucleate in the defects. This results in detrimental effects such as cracking, exfoliation or blistering, which are unacceptable for a PFM [34]. Regarding He irradiation, He atoms tend to nucleate inside vacancies as He is not soluble in metals (in particular, in W), which could result in dramatic He bubble formation [35,36]. In general, not only large He bubbles but also He trapped in few vacancies can cause microstructural changes [37,38], even at low energy. Indeed, void formation and underdense W nanostructures (so called “fuzz”) have been observed in irradiation conditions similar to those that will have to face the divertor in MCF [39–42].

Therefore, great efforts are still needed to develop a W-based material suitable as PFM, capable of dealing with He and H irradiation. A possible solution could be the use of nanostructured W [43], due to its high grain boundary (GB) density. Nanostructured W is expected to present higher irradiation tolerance [44], as GBs may act as defect sinks for vacancies, SIAs and light species [45–48]. GBs, on the one hand, might increase the

annihilation rate between vacancies and SIAs and, on the other hand, might trap He and H atoms, decreasing their number in the interior of the grains. Hence, nanostructured W is expected to have a better response to ion irradiation. However, this behaviour is not yet clear, apart from experimentally demonstrated fact that a high GB density has a direct influence on retention of light species in W [49].

Plenty of experiments are being carried out to understand the damage evolution in W due to He and H irradiation. However, sometimes it is difficult to understand the behaviour of defects at such a low scale ($\sim$ nm). At this point, computer simulations reveal as an important tool for the understanding of the experimental results. Ion irradiation effects on W are usually studied by sequential multiscale modelling, i.e., the physical phenomena are studied at very different length and time scales. The sequential multiscale modelling consists of the study of each physical model separately from each other [50], being the results obtained in one step the input data for the next one. Characteristic length and time scales are (i) up to ps and nm in DFT, (ii) up to tens of ns and nm for molecular dynamics, (iii) up to mm in the case of binary collision approximation (no time evolution is simulated in this methodology) and finally (iv) up to hours or even years and $\sim\mu$ m for object kinetic Monte Carlo [50].

This thesis is focused on the study of He and H irradiation in W mainly by means of object kinetic Monte Carlo (OKMC). Note that in order to get useful input parameters for OKMC, other simulation methods are needed (multiscale simulations). The most relevant ones are described in Chapter 2. Initial damage cascades were calculated by means of binary collision approximation (BCA) calculations and most input data for OKMC were calculated by means of density functional theory (DFT). Moreover, in Section 3.4 is described a study of damage cascades by comparing molecular dynamics (MD) and BCA results. Consequently, this thesis covers a wide range of techniques of the multiscale modelling.

1.2 Objectives and original contributions

The aim of this thesis is the study of W as a PFM for both ICF and MCF. Regarding ICF irradiation conditions, nanocrystalline W is proposed as a PFM for the first wall. In order to study the influence of high grain boundary density on He or H retention, a comparison between monocrystalline and nanocrystalline W has been carried out in the case of both He or H irradiation. Regarding MCF, the influence of the temperature on fuzz formation, has been studied, in an attempt to understand the key physical processes that lead to fuzz formation and growth.

The study presented in this thesis is essentially based on object kinetic Monte Carlo (OKMC) and binary collision approximation (BCA) simulations. Furthermore, density

functional theory (DFT) and molecular dynamics (MD) are also simulation techniques used in this thesis. All this implies a comprehensive study of W as PFM, by using several steps of the multiscale modelling.

For this purpose and also being objective of this thesis in itself, a full OKMC parameterization for the study of He and H irradiation in W, in particular for the MMonCa code, has been developed. In a close collaboration with MMonCa developers from IMDEA Materials Institute, thanks to this thesis new physical models have been implemented in the code.

The results have been validated with experiments. The developed methodology has been demonstrated to be useful to understand experiments, make predictions and extract conclusions.

The original contributions of this thesis (contributions that have been published are referenced) are:

- Validation of the MMonCa code to simulate He irradiation in W [51]
- Full parameterization of MMonCa for He or H irradiation in W
- A methodology to create SIAs by using the code SRIM and a comparison of this methodology with damage cascades calculated by means of MD [52]
- Study of the influence of He irradiation flux (continuous and pulsed) on He retention in W [53]
- Study of the influence of high GB density on He retention in W [54]
- Study of the influence of high GB density on H retention in W [55]
- Validation of the MMonCa code to simulate fuzz growth
- Study of the temperature influence on fuzz formation in W under low energy He irradiation [56]

1.3 Structure

Chapter 2 describes the computational methods in this thesis: BCA (Section 2.1), OKMC (Section 2.2), DFT (Section 2.3) and MD (Section 2.4).

In Chapter 3, the OKMC code used in this thesis (the MMonCa code) as well as parameters and calculations related with OKMC simulations are presented. Section 3.1 describes the methodology followed in this thesis to obtain damage cascades from SRIM calculations, in order to get impurities, vacancies and self-interstitial initial positions. These damage cascades are used as input for the MMonCa code. All the input parameters needed for helium and hydrogen irradiation in tungsten, the so called parameterization, are included in Section 3.2. The MMonCa code is presented in Section 3.3, including the definition of objects and the most important commands used in this thesis. In Section 3.4, a study of damage cascades obtained by means of MD or BCA is shown. After describing the results of a theoretical study of PKA damage, a realistic simulation of 625 keV pulsed He irradiation was carried out. Both BCA and MD cascades were used, with the intention to analyse their influence on OKMC results of He irradiation in W.

Section 3.5 includes academic simulations carried out in MMonCa. Firstly, in Section 3.5.1 MMonCa validation by comparing the results with those obtained with another OKMC code (LAKIMOKA) are described. Finally, section 3.5.2 contains an academic study of low energy He irradiation (3 keV) on W. The influence of different flux modes (continuous or pulsed) is analysed. In addition, several temperatures and two different fluences were studied, in order to cover a wide range of parameters apart from the flux mode. A detailed analysis regarding these three parameters is presented in this Section.

After presenting the simulation codes, the input parameters, the MMonCa code itself and some academic results, three different studies are described in the next Chapters.

In Chapter 4, the influence of high GB density on He retention is analysed, by comparing both monocrystalline and nanocrystalline W. A detailed study of the size and type of He-V clusters, depending on the type of W is shown.

In Chapter 5, a similar study is carried out, in the case of H irradiation. In this study, a full comparison with experiments has been done at different irradiation conditions: single H irradiation, C and H simultaneously irradiated and C and H sequentially irradiated in both monocrystalline and nanocrystalline W. Thanks to OKMC simulations, a better understanding of the experiments was possible.

In Chapter 6, a study of the influence of the temperature in fuzz formation in W under low energy He irradiation is presented. A new model was developed in MMonCa, in order to study fuzz formation. After validating the new model with experimental results, fuzz formation in several temperatures (from 700 to 2500 K) was studied.

Finally, Chapter 7 summarises the main achievements of this thesis. In this Chapter, the main conclusions are highlighted and an outlook of the use of tungsten as plasma facing material is included. Moreover, this chapter includes the main working lines for future studies, which could be continued from the work presented in this thesis.

2 Simulation methods

The sequential multiscale methodology consists of modelling different physical processes at several spatial and temporal scales, as described in Chapter 1. In this thesis, density functional theory, molecular dynamics, binary collision approximation and the object kinetic Monte Carlo have been used for modelling helium or hydrogen irradiation in tungsten. In the present Chapter, density functional theory and molecular dynamics are briefly described, paying more attention on the two simulation methods mainly used in this thesis: binary collision approximation and the object kinetic Monte Carlo.

Density functional theory (DFT) has been used to calculate binding energies of helium and hydrogen atoms to vacancies (see Section 3.2). Damage cascades produced in tungsten by helium or hydrogen irradiation have been obtained by means of binary collision approximation (BCA), as described in Section 3.1. Both binding energies and damage cascades are input parameters for object kinetic Monte Carlo (OKMC) simulations. The BCA damage cascades were compared with damage cascades obtained by means of molecular dynamics (see Section 3.4).

The basis of OKMC methodology is included in this Chapter, while a detailed description of the OKMC code used in this thesis (the MMonCa code) can be found in Chapter 3.

2.1 Binary Collision Approximation

The binary collision approximation (BCA) method is applied to the study of the solids under irradiation to calculate the stopping of incoming ions and the transfer of energy to atoms in the solid [57,58]. BCA calculates the events produced by every ion independently of the previous ones. Thus, the lattice of the target material remains unchanged (unlike in OKMC simulations). The path of an incoming ion inside the target material is calculated as a succession of individual and independent collisions between the ion and a selected lattice atom of the target. When the energy transferred to the lattice atom exceeds the displacement threshold energy, the atom will be ejected from its lattice position, creating a Frenkel pair, i.e., a vacancy and a self-interstitial atom (SIA), so called primary knock-on atom (PKA). The incoming ions and the SIAs lose their energy by collisions with other lattice atoms, through elastic and inelastic scattering with the atoms and electrons, respectively. On the one hand, if the transferred energy is low, the PKA will eventually thermalized. On the other hand, if the transferred energy is high enough, i.e., if the PKA gets a kinetic energy higher than the displacement threshold, new atoms will be displaced, generating a damage cascade. In order to simulate radiation damage, the final position of the incoming ions, generated vacancies and SIAs are needed.

A detailed description of the BCA method to calculate damage cascades can be found in Ref. [58].

Figure 2.1. Trajectories of the projectile and target atoms [58].

The interaction between two particles is shown in Figure 2.1, where m_1 is the mass of the projectile atom, m_2 is the mass of the target atom, s is the impact parameter and θ is defined as:

$$\theta = \pi - 2s \int_R^\infty dr [r^2 g(r)]^{-1}, \quad (2.1)$$

where,

$$g(r) = \left[1 - \frac{s^2}{r^2} - \frac{V(r)}{E_r} \right]^{1/2}, \quad (2.2)$$

s is the impact parameter, E_r is the relative kinetic energy, r is the interatomic distance and $V(r)$ is the potential of interatomic force between m_1 and m_2 .

The relative kinetic energy can be written as:

$$E_r = A \frac{E_0}{(1+A)}, \quad (2.3)$$

where E_0 is the incident kinetic energy of the projectile atom and A is the ratio of the mass of the target atom to that of the projectile atom ($A = m_2/m_1$). The integral (2.1) can be solved by means of numerical calculation. One of the most used is the four-point Gauss-Mehler quadrature [59,60].

The equation (2.1) needs a defined interatomic potential $V(r)$ through the equation (2.2). The potential is usually a Coulomb potential, but taking into account the screening effect of the electrons [58]:

$$V(r) = \left(\frac{Z_1 Z_2 e^2}{r} \right) \Phi \left(\frac{r}{a_{12}} \right), \quad (2.4)$$

where $Z_1 e$ and Z_2 are the nuclear charges of the projectile and target atoms, respectively. $\Phi(r/a_{12})$ takes into account the screening effect of the electrons, where a_{12} is a screening length, which depends on the properties of both the projectile and target atoms.

BCA calculates the trajectory of each incident ion independently, i.e., the previous ion has no influence at all in the calculations of the following one. Moreover, no temperature effect is taken into account and, thus, neither the formation of clusters among atoms nor annihilation between vacancies and SIAs is possible. Despite these limitations, BCA codes are widely used to calculate damage produced by ion irradiation. Compared to the more accurate molecular dynamics calculations, BCA consumes several orders of magnitude less computational time. Examples of BCA codes are TRIM/SRIM [61–63] and MARLOWE [58,64]. SRIM considers the material as amorphous. However, its use is appropriate for the simulations presented in this thesis, as the experiments of hydrogen irradiation were carried out considering no channelling (Chapter 5), and the helium irradiation is mainly by pulsed beams (Chapter 4) or at very low energy (Chapter 6).

2.2 Object kinetic Monte Carlo

The use of object kinetic Monte Carlo increases every year, as it is able to simulate experiments in different materials with an excellent agreement [65–73]. OKMC use is widely spread not only in the area of research but also in the industry [74–79]. Object kinetic Monte Carlo can simulate large time scales of the order of hours or even days and simulation boxes of few μm . This is possible because OKMC does not take into account the lattice atoms themselves, as in the case of molecular dynamics (see Section 2.4). On the contrary, it only takes into account the atoms of the material that are out of their lattice position (self-interstitial atoms), impurities (foreign-interstitial atoms), vacancies and clusters of defects. Defects are considered as objects that can migrate, form clusters or be emitted from them, or annihilate in the case of vacancies and SIAs ($V + I \rightarrow \emptyset$). However, OKMC codes are very difficult to be parallelized. Nevertheless, it is worth mentioning that huge efforts are being carried out to obtain a parallel kinetic Monte Carlo [80,81].

The OKMC algorithm follows the dynamic evolution of a system that is out of equilibrium [82,83]. The states are known and are assumed to be Markovian, i.e., the transitions rates r_{ij} depend only on the initial i state and the final j state. Such transitions are independent of time and are input parameters for the algorithm [51]. In the particular case of MMonCa (see Section 3), the transitions are modelled assuming Harmonic Transition State Theory [84] as Arrhenius laws with an activation barrier E_{ij} and a prefactor P_{ij} [51]:

$$r_{ij} = P_{ij} \times e^{-\frac{E_{ij}}{k_B T}}, \quad (2.5)$$

where r_{ij} are the transition rates, k_B the Boltzmann constant and T the temperature of the system in K. In Figure 2.2 it can be observed the meaning of the activation barriers. The energy needed to reach the j state from the i state is:

$$E_{ij} = E_j^f - E_i^f + E_{ij}^b, \quad (2.6)$$

where E_j^f is the formation energy at the j state, E_i^f is the formation energy at the i state and E_{ij}^b is the barrier to reach the j state from the i state. The transition rates r_{ij} are known as they are given as input parameters. The whole set of parameters needed for a certain simulation is called in this thesis parameterization (see Section 3.2). For simplicity, the transition rates are written as r_j , being j the final state achievable from a particular initial state i .

Using this notation, the OKMC direct method [85] is applied as follows [51]:

1. Obtain the cumulative function

$$R_i = \sum_{j=1}^i r_j, \quad (2.7)$$

for $i = 1, \dots, N$, being N the total number of transitions in the given system.

2. Compute two random numbers, r and s , belonging to the interval $(0,1]$.
3. Find the event to perform, i , for which $R_{i-1} < rR_N < R_i$.
4. Perform the event i : transform the particular chosen object from i to j .
5. Increase the total simulated time by

$$\Delta t = \frac{\ln(\frac{1}{s})}{R_N}. \quad (2.8)$$

6. Recalculate the affected rates.
7. Return to the first step.
8. Repeat the process until the requested physical time has been simulated.

Figure 2.2. Energetic diagram for OKMC simulations, showing two states i and j and the formation and barrier energies related with them [51].

2.3 Density Functional Theory

Density functional theory (DFT) is described in a recent review published by Nordlund and Djurabekova [50]. As stated in this reference, DFT uses different approximate functional in order to calculate the total energy of the system. These functional are chosen by comparing

with experiments. For this reason, DFT is not a fully *ab initio* method. However, it reduces the demand of computational time comparing to resolving the true all-electron Schrödinger equation [50]. Two examples of DFT codes are the Vienna *ab initio* simulation package (VASP) [86–88] and the Spanish initiative for electronic simulations with thousands of atoms (SIESTA) [89].

DFT calculations have been used in this thesis, to obtain migration and binding energies needed for the OKMC simulations (see Section 3.2).

2.4 Molecular Dynamics

Molecular dynamics (MD) is a computer simulation method which follows the motion of atoms in time. For this purpose, the classical equations of motion (Newton equations) are solved by means of numerical integration. In order to calculate the position of each atoms in every timestep, the forces, which derive from a potential, have to be calculated [90]. Potentials are usually obtained by comparing to experiments. Examples of potentials are Embedded Atom Method [91,92] and Tersoff potential [93].

MD calculations are very realistic, as they calculate the position of all the lattice atoms in the target material, apart from the position of the irradiated ions. However, these simulations demand large amounts of computational time. As a result, only small simulation boxes of the order of ~nm and time scales of the order of ~ns can be simulated with an MD code [50]. A commonly used MD code is the large-scale atomic/molecular massively parallel simulator (LAMMPS) [94].

MD calculations have been used in this thesis in order to calculate damage cascades of helium irradiation in tungsten and make a comparison with those obtained by means of BCA (see Section 3.4).

3 The MMonCa code

After presenting the fundamentals of object kinetic Monte Carlo (OKMC) simulation in Chapter 2, in this Chapter the main features of the MMonCa code (the OKMC code used in this thesis) are described.

Both migration and binding energies among defects and damage cascades, i.e., the initial position of irradiated ions and the generated Frenkel pairs, are input parameters for OKMC codes. In Section 3.1, a methodology to extract damage cascades (vacancies, self-interstitial atoms and irradiated ions) from the binary collision approximation (BCA) code SRIM is described. In Section 3.2, the parameterization for vacancies, self-interstitial atoms and helium and hydrogen ions used in the MMonCa code are described. In Section 3.3, the MMonCa code is presented.

In order to validate the method for extracting damage cascades from SRIM, a comparison between damage cascades obtained by BCA and molecular dynamics (MD) was carried out. The results show that BCA cascades are accurate enough for the subsequent OKMC simulation in the case of light ion irradiation. The results were published in Ref. [52].

A validation of the MMonCa code itself was done by reproducing the simulation results of another OKMC code (the LAKIMOKA code). As described in Section 3.5.1, there is good agreement between MMonCa and LAKIMOKA results. The results were published in Ref. [51].

Furthermore, a comparison between continuous and pulsed flux modes when irradiating tungsten with 3 keV helium ions was carried out. Several temperatures (from 700 to 1600 K) and two different fluxes (low flux, $2 \times 10^{12} \text{ cm}^{-2}$ per second and high flux, $2 \times 10^{13} \text{ cm}^{-2}$ per second) were studied. From the results, it can be concluded that the pulsed flux turns out to play a major role in ion irradiation of tungsten for plasma facing material purposes. Results presented in Section 3.5.2 were published in Ref. [53].

3.1 Damage cascades

In this thesis, the SRIM code (see Section 2.1) was used to calculate damage cascades of ion irradiation in tungsten. A value of 90 eV was set for the displacement threshold energy of W lattice atoms [95], i.e., 90 eV is the minimum energy that must be transferred to a lattice W to be ejected of its lattice position, creating the corresponding Frenkel pair, i.e., a vacancy and a self-interstitial atom (SIA). SRIM provides the final position of both the incoming ions and the vacancies, but not those of the SIAs. For that reason, the following methodology was developed in this thesis. It is considered that the SIAs will be thermalized at a distance d around the vacancy they produce, when migrating from their lattice position. Thus, they will be placed at x_1 , y_1 and z_1 position, which in spherical coordinates is expressed as:

$$\begin{aligned} x_1 &= x_V + d \cdot \cos\varphi \cdot \sin\theta \\ y_1 &= y_V + d \cdot \sin\varphi \cdot \sin\theta \\ z_1 &= z_V + d \cdot \cos\theta, \end{aligned} \tag{3.1}$$

where x_V , y_V and z_V are the vacancy positions and φ and θ and are the polar and azimuthal angles, respectively. φ and θ angles are randomly selected. To calculate the distance d , a gaussian thermalisation law was considered:

$$x = e^{-\frac{1}{2}\left(\frac{d-R}{S}\right)^2}, \tag{3.2}$$

where x is a random number from 0 to 1, R the range and S the straggling. Since the SIAs are W atoms inside a W lattice, both the range and straggling were calculated by irradiating W ions on a W target at different irradiation energies (E), see Table 3.1.

Table 3.1. Range and straggling obtained by the irradiation of W ions at different energies (E) on a W target, calculated with the SRIM code.

E (eV)	Range	Straggling
$E > 275$	0.7	0.3
$275 \geq E > 250$	0.6	0.3
$250 \geq E > 140$	0.6	0.2
$140 \geq E > 65$	0.5	0.2
$65 \geq E > 45$	0.5	0.1
$45 \geq E > 10$	0.4	0.1
$10 \geq E > 4$	0.3	0.1
$4 \geq E$	0.1	0.1

With this methodology, full cascades (irradiated ions, vacancies and SIAs) can be obtained with SRIM, which are used as input data for OKMC (in this thesis, for the MMonCa code).

3.2 Parameterization

3.2.1 Vacancies and self-interstitial atoms

The parameterization of vacancies (Vs), self-interstitial atoms (SIAs) and their clusters is taken from Ref. [66]. Regarding migration parameters, prefactors and migration energies are summarized in Table 3.2. Unless otherwise indicated, all the prefactors are taken as a constant value of the order of the Debye frequency in this thesis ($\nu_0 = 6 \times 10^{12} \text{ s}^{-1}$ [66]), which is approximately 10% of the Debye frequency of W ($\omega_D = 4.05 \times 10^{12} \text{ s}^{-1}$) [96]. Because of the Arrhenius dependence of both migration and emission of particles from clusters, on the goal is the determination of migration and binding energies [66].

Table 3.2. Migration parameters for vacancies (Vs), SIAs and their clusters: prefactors and migration energies (E^m). Clusters of SIAs (I_m) migrate in 1 dimension, along $\langle 111 \rangle$ direction. The values of the constants are $\nu_0 = 6 \times 10^{12} \text{ s}^{-1}$, $q = 1000$ and $s = 0.5$ [66].

Particle/Cluster	Prefactor (s^{-1})	E^m (eV)
V	ν_0	1.66
$V_{m(m>1)}$	$\nu_0 \cdot (q^{-1})^{m-1}$	1.66
I	ν_0	0.013
$I_{m(m>1)}$	$\nu_0 \cdot m^{-s}$	0.013 (1D)

Regarding migration parameters, it is important to clarify the behaviour of SIAs in body-centered cubic (bcc) metals like W. SIAs are dumbbells, i.e., two atoms of W sharing one crystallographic site [66]. Recent *ab initio* calculations using PLATO [97] and VASP [98] obtained the $\langle 111 \rangle$ as the most stable dumbbell in W. The value of migration energy of a SIA is very low ($E^m(\text{SIA}) = 0.013 \text{ eV}$) [96]. This value is in agreement with the high mobility of SIAs at temperatures as low as 15 K observed experimentally [99]. In Ref. [66] it is indicated that single SIAs move in a 1D motion along $\langle 111 \rangle$ directions, with an activation energy of direction rotation of $E^{\text{rot}} = 0.38 \text{ eV}$. Migration of SIA clusters is described in Ref. [100] as “a rapid transmission of short linear regions of compression (referred to as “crowdion”) along body-diagonals in the body-centered cubic lattice”. In this thesis, a 3D motion for SIAs has been assumed due to the high temperatures of the simulations, high enough to activate E^{rot} . Only for low temperatures ($< 250 \text{ K}$) 1D motion along $\langle 111 \rangle$ directions has been assumed [101].

In the parameterization, the linear dependence of the diffusion coefficient with temperature (demonstrated in Ref. [96]) was not included. Nevertheless, a decreasing law for migration

prefactors of SIA clusters [66] has been included (see Table 3.2), as reported by Osetsky *et al.* in Ref. [102]. They suggest that the diffusion coefficients for the SIA clusters are approximated as the one for a SIA, divided by the square root of clusters size. The values of migration prefactors of SIA clusters are shown in Figure 3.1. The prefactor for I_{50} is almost one order of magnitude lower than the one for a single SIA.

Figure 3.1. Prefactor values for migration of SIA clusters in W [66].

With regard to vacancies, they migrate in a 3D movement with a high migration energy (E^m (V) = 1.66 eV [66]), which agrees with experimental data [103]. This high migration energy implies that at temperatures lower than ~ 600 K, vacancies remain almost immobile. Vacancy clusters move with the same migration energy than single vacancies. However, migration prefactors follow a decreasing law which leads to a negligible movement of vacancy clusters (see Table 3.2), as every additional vacancy incorporated to the cluster leads to a prefactor decrease of three orders of magnitude.

Table 3.3. DFT values for binding energies (E^b) of vacancies and SIAs, up to V_8 and up to I_7 , respectively. Binding energies for larger clusters are calculated with a capillary approximation, with $E^f(V_1) = 3.23$ eV and $E^b(V_2) = -0.1$ eV in the case of vacancies and with $E^f(I_1) = 9.96$ eV and $E^b(I_2) = 2.12$ eV in the case of SIAs [66].

Cluster	E^b (eV)
$V + V \rightarrow V_2$	-0.1
$V + V_2 \rightarrow V_3$	0.04
$V + V_3 \rightarrow V_4$	0.64
$V + V_4 \rightarrow V_5$	0.72
$V + V_5 \rightarrow V_6$	0.89
$V + V_6 \rightarrow V_7$	0.72
$V + V_7 \rightarrow V_8$	0.88
$V + V_{m-1, (m>8)} \rightarrow V_m$	$E^f(V_1) + [E^b(V_2) - E^f(V_1)] \cdot [m^{2/3} - (m-1)^{2/3}] / (2^{2/3} - 1)$
$I + I \rightarrow I_2$	2.12
$I + I_2 \rightarrow I_3$	3.02
$I + I_3 \rightarrow I_4$	3.6
$I + I_4 \rightarrow I_5$	3.98
$I + I_5 \rightarrow I_6$	4.27
$I + I_6 \rightarrow I_7$	5.39
$I + I_{m-1, (m>7)} \rightarrow I_m$	$E^f(I_1) + [E^b(I_2) - E^f(I_1)] \cdot [m^{2/3} - (m-1)^{2/3}] / (2^{2/3} - 1)$

Regarding binding energies, the values for both vacancies and SIAs are shown in Table 3.3. DFT data are only available for small clusters, as simulations are highly time-demanding for large simulation cells. In order to obtain more parameters, a capillary approximation has been used as suggested in Refs. [65,66] (shown in both Table 3.3 and Figure 3.2).

Figure 3.2. DFT and capillary approximation data of binding energies for (a) vacancy clusters and for (b) SIA clusters [66].

It is worth mentioning that the binding energy for two vacancies is negative, i.e., they repel each other [66]. Derlet *et al.* [96] obtained a positive binding energy of 0.41 eV. Moreover, the negative binding energy is likely in conflict with the TEM observation of vacancy

loops [104–107]. Nevertheless, the irradiation produces highly concentrated damage cascades that favour a direct formation of large vacancy clusters, without a previous formation of divacancies [66].

3.2.2 Helium in tungsten

The irradiation of W with He ions leads to three different types of clusters: pure He clusters (He_n), mixed He-vacancy clusters (He_nV_m) and mixed He-SIA clusters (He_nI_m).

With regard to migration parameters, He_nV_m and He_nI_m have been considered as immobile [66], with the only exception of HeV , HeV_2 and HeV_3 [108]. Both single He atoms and He_n clusters can migrate (see Table 3.4).

Table 3.4. Migration parameters of He atoms (He), pure He clusters (He_n) and small HeV_m clusters. Note that $v_0 = 6 \times 10^{12} \text{ s}^{-1}$ [66].

Particle/Cluster	Prefactor (s^{-1})	E^m (eV)
He	$10^{-2} v_0$	0.01
He_2	$10^{-2} v_0$	0.03
He_3	$10^{-2} v_0$	0.05
He_n ($n > 3$)	$10^{-2} v_0$	$E^m(\text{He}_{n-1}) + 0.01$
HeV	v_0	4.83
HeV_2	$v_0/2$	2.04
HeV_3	$v_0/3$	1.94

He migration in tungsten has been extensively studied. Experiments of ^3He and ^4He implantations in W carried out by Wagner *et al.* [109] and Amano *et al.* [110] predicted a value of migration energy for single He atoms in the range of 0.24 to 0.32 eV, as they observed that single He atoms were almost immobile at 90 K but highly mobile at 110 K. However, Becquart *et al.* [111] calculated by means of *ab initio* the migration energy for a single He atom. They obtained a value of ~ 0.06 eV, notably lower than the experimental results. This discrepancy was attributed [66] to He clustering, as He atoms in interstitial positions tend to form small He clusters. Thus, the migration energies obtained experimentally can be attributed to these small He clusters rather than to single He atoms. Moreover, Soltan *et al.* [112] studied He implantation at 5 K with energies from 0.25 to 3 keV into thin films of 80–320 nm of W, followed by isochronal annealing up to 400 K. They observed that He becomes mobile even at temperatures as low as 5 K. Becquart *et al.* [113] obtained a very good agreement between their OKMC calculations and the experimental results of He desorption carried out by Soltan *et al.* [112].

Binding energies for pure He_n clusters were calculated by Becquart *et al.* [66,111]. Results are summarized in Table 3.5. The most stable configuration for He atoms, all of them in interstitial position, is in a platelet configuration at 0 K [66]. The high binding energies indicate that these clusters are stable at temperatures under 500 K. This is in agreement with platelets experimentally observed by Iwakiri *et al.* [45], after irradiating W with 0.25 keV He ions at 293 K, as they observed platelets formed by He atoms.

Table 3.5. DFT values for binding energies (E^b) for a single He atom to pure He_n clusters [66,111].

Cluster	E^b (eV)
$\text{He} + \text{He} \rightarrow \text{He}_2$	1.03
$\text{He} + \text{He}_2 \rightarrow \text{He}_3$	1.36
$\text{He} + \text{He}_3 \rightarrow \text{He}_4$	1.52
$\text{He} + \text{He}_4 \rightarrow \text{He}_5$	1.64
$\text{He} + \text{He}_5 \rightarrow \text{He}_6$	2.09
$\text{He} + \text{He}_6 \rightarrow \text{He}_7$	2.18
$\text{He} + \text{He}_7 \rightarrow \text{He}_8$	2.15
$\text{He} + \text{He}_8 \rightarrow \text{He}_9$	2.11

In the case of mixed He-SIA clusters (He_nI_m), the binding energies proposed by Becquart *et al.* [66] have been used, i.e., single He atoms bind to SIA (I) and SIA clusters (I_n) with a binding energy of 0.94 eV. Regarding binding energies for He-vacancy clusters (He_nV_m), they were calculated by means of *ab initio* calculations [54]. The calculations were carried out using the Vienna *Ab initio* Simulation Package (VASP) [86–88]. The PBE [114] parameterization of the Generalized Gradient Approximation (CGA) for the exchange and correlation functional was used as well as the Plane Augmented Wave pseudopotentials [115], provided by the code. Six valence electrons were considered for W (4 $4d$ and 2 $4s$) and two $1s$ valence electrons for He. Within these approximations, the lattice parameter was estimated to be 3.172 Å, using an energy cutoff for the plane waves of 479 eV. The $5 \times 5 \times 5$ cubic supercell (250 W atoms) used was built repeating the unit cell five times along each direction while 64 k -points sampled the first Brillouin zone. Several He atoms were placed inside the unit cell in combination with n -vacancies (for n up to 4). Each structure was fully relaxed until the forces on all atoms were smaller than 0.025 eV/Å. The general equation giving the formation energy for a system formed by N_W and N_{He} atoms can be written as [116]:

$$E^f = E_{\text{tot}} - N_W \cdot E(W) - N_{\text{He}} \cdot E(\text{He}), \quad (3.3)$$

where E_{tot} is the final total energy obtained in the relaxation of each supercell, $E(W)$ is the atomic energy of one metal atom inside the pure bulk when a $5 \times 5 \times 5$ supercell is used and $E(\text{He})$ corresponds to an isolated He atom located inside an otherwise empty $5 \times 5 \times 5$

box with sides equal to the equilibrium lattice parameter of the pure metal. On the other hand, the binding energy E^b corresponds to the energy released when two objects (in general more) merge to become a mixed one. It is defined as the formation energy difference between a system in which the objects are close together and a system in which the objects are far apart. Therefore, the formation energy of the configurations where the objects are separated is usually calculated individually in a supercell for each object, as defined in Eq. (3.3). The general expression for E^b for a system with N_{def} defects (SIAs, n -vacancies and/or He atoms) can then be written as [116]:

$$E^b(N_{\text{def}}) = \sum_{i_{\text{def}}=1}^{N_{\text{def}}} E^f(i_{\text{def}}) - E^f(N_{\text{def}}). \quad (3.4)$$

Binding energies calculated with this methodology are shown in Table 3.6. The values are very similar to those obtained by other DFT calculations (see Ref. [113]). It is worth mentioning that the binding energy of a He atom to a vacancy, i.e., a He atom trapped inside a vacancy, is 4.67 eV, which is a very high value. This means that a very high temperature would be needed to detrap a He atom from a vacancy.

Table 3.6. Binding energies of a He atom to mixed He_nV_m cluster or to a pure V_m cluster (i.e., formed by adding He atoms) calculated by means of DFT [54]. Binding energies of a V to mixed He_nV_m cluster or to a pure He_n cluster (i.e., formed by adding Vs) were calculated from the DFT values. Similar results were obtained in comparison to those published in Ref. [66].

Cluster (formed by adding He)	E^b (eV)	Cluster (formed by adding V)	E^b (eV)
$\text{He} + \text{V} \rightarrow \text{HeV}$	4.67	$\text{V} + \text{He} \rightarrow \text{HeV}$	4.67
$\text{He} + \text{HeV} \rightarrow \text{He}_2\text{V}$	3.22	$\text{V} + \text{He}_2 \rightarrow \text{He}_2\text{V}$	6.84
$\text{He} + \text{He}_2\text{V} \rightarrow \text{He}_3\text{V}$	3.17	$\text{V} + \text{He}_3 \rightarrow \text{He}_3\text{V}$	8.63
$\text{He} + \text{He}_3\text{V} \rightarrow \text{He}_4\text{V}$	3.23	$\text{V} + \text{He}_4 \rightarrow \text{He}_4\text{V}$	10.25
$\text{He} + \text{He}_4\text{V} \rightarrow \text{He}_5\text{V}$	2.23	$\text{V} + \text{He}_5 \rightarrow \text{He}_5\text{V}$	9.81
$\text{He} + \text{He}_5\text{V} \rightarrow \text{He}_6\text{V}$	2.77	$\text{V} + \text{He}_6 \rightarrow \text{He}_6\text{V}$	9.68
$\text{He} + \text{He}_6\text{V} \rightarrow \text{He}_7\text{V}$	2.35	$\text{V} + \text{He}_7 \rightarrow \text{He}_7\text{V}$	8.94
$\text{He} + \text{He}_7\text{V} \rightarrow \text{He}_8\text{V}$	2.53	$\text{V} + \text{He}_8 \rightarrow \text{He}_8\text{V}$	8.24
$\text{He} + \text{He}_8\text{V} \rightarrow \text{He}_9\text{V}$	2.13	$\text{V} + \text{He}_9 \rightarrow \text{He}_9\text{V}$	7.01
$\text{He} + \text{V}_2 \rightarrow \text{HeV}_2$	4.79	$\text{V} + \text{HeV} \rightarrow \text{HeV}_2$	-0.02
$\text{He} + \text{HeV}_2 \rightarrow \text{He}_2\text{V}_2$	4.93	$\text{V} + \text{He}_2\text{V} \rightarrow \text{He}_2\text{V}_2$	1.69
$\text{He} + \text{He}_2\text{V}_2 \rightarrow \text{He}_3\text{V}_2$	4.08	$\text{V} + \text{He}_3\text{V} \rightarrow \text{He}_3\text{V}_2$	2.6
$\text{He} + \text{He}_3\text{V}_2 \rightarrow \text{He}_4\text{V}_2$	4.15	$\text{V} + \text{He}_4\text{V} \rightarrow \text{He}_4\text{V}_2$	3.52
$\text{He} + \text{V}_3 \rightarrow \text{HeV}_3$	5.43	$\text{V} + \text{HeV}_2 \rightarrow \text{HeV}_3$	0.63
$\text{He} + \text{HeV}_3 \rightarrow \text{He}_2\text{V}_3$	4.98	$\text{V} + \text{He}_2\text{V}_2 \rightarrow \text{He}_2\text{V}_3$	0.68
$\text{He} + \text{He}_2\text{V}_3 \rightarrow \text{He}_3\text{V}_3$	5.14	$\text{V} + \text{He}_3\text{V}_2 \rightarrow \text{He}_3\text{V}_3$	1.74
$\text{He} + \text{He}_3\text{V}_3 \rightarrow \text{He}_4\text{V}_3$	4.33	$\text{V} + \text{He}_4\text{V}_2 \rightarrow \text{He}_4\text{V}_3$	1.92
$\text{He} + \text{V}_4 \rightarrow \text{HeV}_4$	5.67	$\text{V} + \text{HeV}_3 \rightarrow \text{HeV}_4$	0.83
$\text{He} + \text{HeV}_4 \rightarrow \text{He}_2\text{V}_4$	5.34	$\text{V} + \text{He}_2\text{V}_3 \rightarrow \text{He}_2\text{V}_4$	1.2
$\text{He} + \text{He}_2\text{V}_4 \rightarrow \text{He}_3\text{V}_4$	5.13	$\text{V} + \text{He}_3\text{V}_3 \rightarrow \text{He}_3\text{V}_4$	1.2
$\text{He} + \text{He}_3\text{V}_4 \rightarrow \text{He}_4\text{V}_4$	5.21	$\text{V} + \text{He}_4\text{V}_3 \rightarrow \text{He}_4\text{V}_4$	2.08

A clear trend can be observed: the higher the He/V ratio, the lower the binding energy. This trend is clearly observed in Figure 3.3. DFT data are only available for small He_nV_m clusters, as the large number of He configurational positions inside vacancy clusters makes these simulations very tedious and computationally demanding. Nevertheless, in the case of a single vacancy, calculations up to the 9th He atom were feasible. Moreover, one additional He atom was also calculated but the 10th He atom escaped from the vacancy region, which was defined as the free space in the complete $1 \times 1 \times 1$ unit cell. Due to this result, a maximum of 9 He atoms per vacancy inside He_nV_m clusters was set in the parameterization (i.e., $\text{He}/\text{V} = 9$), as pointed out in previous works [117,118]. Molecular dynamics (MD) studies carried out by Henriksson *et al.* [119] did not fix such a limit and, however, they observed that pure He clusters with even only 3 He atoms (He_3) can promote formation of $\langle 111 \rangle$ interstitial crowdion. They explain such a low value by the influence of the nearby surface. In the case of larger clusters, binding energies for clusters of up to 4 He atoms and up to 4 vacancies (He_4V_4 , see Table 3.6) were calculated by means of DFT. DFT values for binding energies are approximated to a power law:

$$E^b(\text{He} \rightarrow \text{He}_{n-1}\text{V}_m) = 4.43 \left(\frac{n}{m} \right)^{-0.28}, \quad (3.5)$$

where $E^b(\text{He} \rightarrow \text{He}_{n-1}\text{V}_m)$ is the binding energy in eV of a He atom to a $\text{He}_{n-1}\text{V}_m$ to form a He_nV_m cluster, n is the number of He atoms in the cluster and m the number of vacancies. Thus, n/m is the He/V ratio of the cluster. This approximation (see Figure 3.3) allows having binding energies for larger clusters than He_4V_4 , as MMonCa requires for input values all the parameters of the clusters that might be formed during the simulation.

Figure 3.3. Binding energy (eV) of a He atom to mixed He_nV_m clusters, as a function of the He/V ratio.

Values given by the power law were considered in the parameterization for clusters of binding energy was not explicitly calculated by DFT. The approximation is in good

agreement with DFT data in the case of high He/V ratio. However, in the case of very low He/V ratio, binding energies are overestimated. In a recent paper [120], Juslin and Wirth studied binding energies by means of molecular dynamics with a new interatomic pair potential for W-He. Their MD results accurately reproduced *ab initio* results of the formation energies and ground state positions of He point defects [120]. They simulated clusters with up to 20 vacancies and 120 He atoms and proposed a maximum binding energy of ~ 6 eV in clusters up to $\text{He}_{m-1}\text{V}_m$ ratio, which is a value close to the formation energy of an interstitial He (6.25 eV according to DFT calculations carried out by González and Iglesias [108]). Thus, this maximum binding energy for a He atom to a He_nV_m cluster was set in the parameterization in this thesis.

3.2.3 Hydrogen in tungsten

The irradiation of W with H ions leads to only two different types of clusters: mixed H-vacancy clusters (H_nV_m) and mixed H-SIAs clusters (H_nI_m). Pure H clusters (H_n) cannot be formed in bulk W due to the large repulsive energy between H atoms, contrary to the behaviour of He in W (described in Section 3.2.2).

With regard to migration parameters, H_nV_m and H_nI_m have been considered as immobile. Although it has been reported that HV cluster can migrate, its migration energy is very high, around 2.52 eV [121,122]. Since the simulations of H irradiation in W in this thesis have been carried out at 300 K, this implies that HV does not migrate effectively. Migration energy of a single H atom was calculated by means of *ab initio*, obtaining a value of $E^m(\text{H}) = 0.205$ eV, which is in perfect agreement with previously published data in Refs. [122,123]. Migration energies for single H atoms, SIAs and vacancies are shown in Table 3.7. At 300 K, both single H atoms and SIAs can migrate. On the contrary, vacancies are not expected to migrate due to their high migration energy.

Table 3.7. Migration energy in eV of single H atoms, SIAs and single vacancies in W.

Particle	E^m (eV)
H	0.205
SIA	0.013 [66]
V	1.66 [66]

Regarding binding energies, H atoms bind to SIAs to form H_nI_m with a binding energy of 0.33 eV [66]. This low value makes the H-SIA trapping mechanism inefficient at 300 K. As noted before, pure H_n clusters cannot be formed in bulk W due to the large repulsive energy between atoms. This has been studied by Henriksson *et al.* [124] by means of both density functional theory (DFT) and molecular dynamics (MD). Two H atoms were inserted at

interstitial sites and the system was allowed to relax to the nearest energy minimum. Because of computer capacity limitations, they were not able to examine a large number of configurations in the DFT calculations. They looked only at two in detail, namely the smaller and larger interatomic distance states. Both DFT and MD indicated the presence of a weakly bound state for two H atoms at a separation of about 2.2 Å, but the binding energy was so low (DFT gave less than 0.1 eV, MD gave 0.3 eV) that it cannot bind the H atoms for significant times even at 300 K [124]. Similar results were obtained by Liu *et al.* [125], obtaining a binding energy between two H atoms of 0.02 eV by means of DFT calculations. As a result, neither SIAs nor another H atom can trap H atoms. Thus, vacancies are the only defect that can trap H atoms in the OKMC simulations carried out in this thesis. In order to obtain binding energies of H atoms to vacancies, a similar methodology as the one used in the case of He atoms described in Section 3.2.2 was carried out. Binding energies for H_nV_m clusters were obtained by performing calculations based on DFT techniques, using the Vienna *Ab initio* Simulation Package (VASP) [86,88,126]. The PBE [114] parameterization of the Generalized Gradient Approximation (GGA) for the exchange and correlation functional was used, as well as the Plane Augmented Wave pseudopotentials [115] provided by the code. In the case of W, six valence electrons were considered (4 $3d$ and 2 $4s$) and 1 $1s$ in the case of H. The lattice parameter was estimated to be 3.172 Å (using an energy cutoff for the plane waves of 479 eV), which is in good agreement with the experimental result of 3.165 Å [127]. A $5 \times 5 \times 5$ cubic supercell (250 W atoms) was built by repeating the unit cell five times along each direction while 8 k -points (a $2 \times 2 \times 2$ mesh) sampled the first Brillouin zone. Up to 10 H atoms were placed in the unit cell in the case of a single vacancy (V) whereas up to 4 H atoms were placed in the case of V_2 , V_3 and V_4 . All the structures were fully relaxed until the forces on all atoms were smaller than 0.025 eV/Å. From the total energy, the formation and binding energies were obtained.

Formation energies (E^f) for a system of a certain number of W and H atoms, N_W and N_H , respectively, were calculated using the equation [128]:

$$E^f = E_{\text{tot}} - N_W \cdot E(W) - N_H \cdot E(H), \quad (3.6)$$

where E_{tot} is the final total energy, $E(W)$ is the atomic energy of one W atom inside the pure bulk when a $5 \times 5 \times 5$ supercell is used and $E(H)$ is the half of the energy of the isolated H_2 molecule [128–130], located inside an otherwise empty $5 \times 5 \times 5$ supercell with sides equal to the equilibrium lattice parameter of the pure W.

The binding energy, E^b , corresponds to the energy released when two (or more) objects merge to become a single one. The general expression for E^b for a system with a number of

defects N_{def} defects (including vacancies, SIAs or H atoms) can be written according to Eq. 3.4.

In Eq. (3.4), the binding energy is defined as the difference between a system in which the objects are close together and a system in which the objects are far apart. For that reason, the formation energy of the configurations where the objects are separated is usually calculated in an individual supercell for each object, as defined in Eq. (3.6). Binding energies for H atoms to V_m and H_nV_m clusters are summarized in Table 3.8.

Table 3.8. Binding energy of a H atom to mixed H_nV_m clusters or to pure V_m clusters calculated by DFT simulations. The values for H atoms in a single vacancy are from Ref. [128].

Cluster (formed by adding H)	E^b (eV)
$H + V \rightarrow HeV$	1.20
$H + HV \rightarrow H_2V$	1.19
$H + H_2V \rightarrow H_3V$	1.07
$H + H_3V \rightarrow H_4V$	0.95
$H + H_4V \rightarrow H_5V$	0.87
$H + H_5V \rightarrow H_6V$	0.52
$H + H_6V \rightarrow H_7V$	0.5
$H + H_7V \rightarrow H_8V$	0.46
$H + H_8V \rightarrow H_9V$	0.17
$H + H_9V \rightarrow H_{10}V$	0.20
$H + V_2 \rightarrow HV_2$	0.97
$H + HV_2 \rightarrow H_2V_2$	0.28
$H + H_2V_2 \rightarrow H_3V_2$	2.60
$H + H_3V_2 \rightarrow H_4V_2$	0.85
$H + V_3 \rightarrow HV_3$	2.01
$H + HV_3 \rightarrow H_2V_3$	1.29
$H + H_2V_3 \rightarrow H_3V_3$	1.00
$H + H_3V_3 \rightarrow H_4V_3$	0.82
$H + V_4 \rightarrow HV_4$	1.87
$H + HV_4 \rightarrow H_2V_4$	1.71
$H + H_2V_4 \rightarrow H_3V_4$	1.11
$H + H_3V_4 \rightarrow H_4V_4$	0.51

In the case of H trapped in a single vacancy (H_nV), the results [128] are in good agreement with previously published data [122,130–133] as observed in Figure 3.4.

Figure 3.4. DFT data of binding energies for H atoms to a single vacancy. Results used in this thesis (Guerrero *et al.* [128]) are compared to those obtained by Johnson *et al.* [131], Heinola *et al.* [132], Ohsawa *et al.* [133], Liu *et al.* [130] and Fernandez *et al.* [122].

DFT values for binding energies are approximated to a power law:

$$E^b(\text{H} \rightarrow \text{H}_{n-1}\text{V}_m) = 1.04 \left(\frac{n}{m}\right)^{-0.43}, \quad (3.7)$$

where $E^b(\text{H} \rightarrow \text{H}_{n-1}\text{V}_m)$ is the binding energy in eV of a H atom to a H_{n-1}V_m to form a H_nV_m cluster, n is the number of H atoms in the cluster and m the number of vacancies. Thus, n/m is the H/V ratio of the cluster. This approximation (see Figure 3.5) allows having binding energies for clusters larger than H_4V_4 . Note that MMonCa requires as input values all the parameters of the clusters that might be formed during the simulation.

Figure 3.5. Binding energy (eV) of a H atom to mixed H_nV_m clusters, as a function of the H/V ratio.

In the case of clusters whose binding energy was not explicitly calculated by DFT, the values given by the power law were used. In the case of H, the approximation is not as good as in the case of He atoms (compare Figure 3.5 to Figure 3.3). As the simulations of H irradiation in W presented in this thesis are at 300 K (see Chapter 5), vacancies do not

migrate. Thus, the great majority of H atoms are retained in monovacancies, which are well parameterized thanks to DFT data.

3.3 Basis of the MMonCa code

The OKMC code used for simulations in this thesis is the open source code MMonCa [51,134]. It has been implemented in C++ with extensions in TCL [135]. TCL is used for programming input scripts, which allows the user to have a simple and well known language as an interface with MMonCa. In the input script the user defines the simulation box, the simulation time, the material, the irradiated ions, the temperature, etc. The use of TCL makes the user interface very flexible, as all the programming capabilities of TCL can be exploited. Figure 3.6 shows the overall structure of the simulator [51].

Figure 3.6. Overall structure of the MMonCa simulator. The user interface relies on a layer of the TCL interpreter, extended to support OKMC. The extension relies on specialized modules to control the space, time and defects [51].

Migration and dissociation of defects are events modelled by an Arrhenius law. The activation energies are, then, the migration energy and the dissociation energy, respectively.

$$\nu = \nu_0 \cdot e^{-\frac{E^a}{k_B T}}, \quad (3.8)$$

where ν_0 is the prefactor, E^a the activation energy (migration or dissociation energy), k_B is the Boltzmann's constant and T is the absolute temperature. The migration length (jump

distance) is defined by the user. The dissociation energy of a certain object from another object is defined as the binding energy between these two objects plus the migration energy of the emitted object.

Once all the activation energies of all transitions that can be take place are defined, the list of all the transitions is generated. Then, one transition is chosen with a probability proportional to its value (see Figure 3.7). Thus, the events with lower activation energies will take place more frequently than those with high activation energies. The Δt associated with the simulation of a certain event is independent on the event itself, as it depends on the whole system. MMonCa simulator does not contain a transition bar with all the rates, but rather a binary tree, where the access time to each rate is not proportional to the number of them N but to $\log_2(N)$. On the one hand, it decreases the access time to the chosen event and, on the other hand, the binary tree implies that the insertion, deletion and modification time is not constant, but it is proportional to $\log_2(N)$. Nevertheless, in the case of large number of rates in the system and more selection of rates than insertions, modifications or deletions, the balance is positive [51].

Figure 3.7. The OKMC algorithm contains a list of all the transitions associated with the objects being simulated. It can be seen graphically that after getting a random number uniformly distributed in $[0, R_n)$, the event selected is “aligned” with such number [51].

Regarding the space, it is divided in small prismatic elements, called “mesh elements”. Inside each “mesh element”, temperature, material, etc. are homogeneous. It allows the simulation of very complex shapes containing different materials. When two consecutive mesh elements are made of different materials, an interface object is built between them to define the properties between both materials [51], see Figure 3.8.

Figure 3.8. Space is divided into small prismatic elements (rectangles in this 2D representation) called “mesh elements”, using a tensor mesh. (a) An interface is the union of all the element faces between adjacent different materials. (b) The capture distance r_c of every particle is defined independently and depends on the reaction. (c) The capture distance of clusters is built as the union of the capture distance of their constituent particles [51].

The definition of objects in MMonCa has changed during the time of this thesis. The objects described in this Section are those of the newest version of MMonCa. There are mainly three different types of defects in MMonCa: mobile particles, multicluster defects and interfaces, described in the next Sections.

3.3.1 Mobile particles

Foreign-interstitial atoms (helium, hydrogen and carbon atoms) as well as self-interstitial atoms (SIAs) and vacancies are defined as mobile particles in MMonCa. Also the combination of helium and hydrogen with and SIAs and vacancies (i.e., He and H in substitutional position) belong to the category of mobile particles (HeV, HeI, HV and HI).

These particles have a defined capture radius. If two particles are at a distance lower than the capture radius, they react. In previous versions, the capture radius only depended on each mobile particle. In the newest version, the capture radius depends on both the mobile particle and the reaction itself. For instance, when a helium atom interacts with a vacancy, a capture radius for this defined reaction is set. In this thesis, the capture radius reported in Table 5 from Ref. [66] were adapted to this new definition in MMonCa.

Mobile particles can migrate, following an Arrhenius law. Thus, a prefactor and migration energy must be defined as input parameters. As stated in Section 3.2, the prefactors are taken of the order of the Debye frequency, unless otherwise indicated [66]. Migration energies are usually calculated by means of density functional theory. The values used in this thesis are indicated in Section 3.2.

In the case of mobile particles with two components, for instance HI, the binding energy between the components has to be defined. Thus, at a temperature high enough, the particles dissociate. For example, the binding energy of HI is 0.33 eV. A temperature of 300 K is high enough to induce HI dissociation, becoming two separate mobile particles (H and I).

It is worth mentioning the singular reaction between SIAs and vacancies. In fact, when a SIA and a vacancy interact, they annihilate.

3.3.2 Multiclusters

Every other combination of mobile particles leads to multiclusters. For instance, He_2 , V_2 , I_2 , HeV_2 , He_2V , etc. are multiclusters in MMonCa. Multiclusters are single objects which can migrate as a whole with a defined migration energy, but they are composed of single mobile particles. The positions of each mobile particle being part of a multicluster are saved and they have their own capture radius when interacting with another particle, regardless the cluster they belong. All the binding energies of particles belonging to a cluster must be defined. Otherwise, the cluster cannot appear in the simulation.

Other two features of multiclusters are shape and migration type. On the one hand, multiclusters can adopt three types of shapes: (i) irregular, when the mobile particles aggregate the cluster without a specific shape, (ii) disc, when the mobile particles forming a cluster are reorganized to adopt the shape of a disc and (iii) void, similar to disc but in this case the shape is a sphere. On the other hand, the migration direction of multiclusters can be selected. Thus, they can migrate in 3D or along defined crystallographic directions, $\langle 111 \rangle$ or $\langle 100 \rangle$ for instance.

3.3.3 Interfaces

Interfaces are objects created between two different materials, or between a material and the outside edge (usually the irradiation surface). When two mesh elements of two different materials share a surface, an interface is automatically created by MMonCa. Interfaces model the change of physical properties between materials. Mobile particles that reach the interface can be annihilated, emitted to both sides (i.e., materials) with defined rates or they can be trapped. Multiclusters can only be annihilated in the interfaces.

In this thesis, a single material has been studied (tungsten). However, even in the case of a single material, the interfaces play a key role: in this case, between the material and the outside edge, the interfaces act as desorption surfaces. Simple surface models have been developed in this thesis. However, MMonCa is suitable for the implementation of complex

models that can account for complex processes (such as grain boundary behaviour, or molecular species desorption).

3.3.4 Ion irradiation and annealing

In this thesis, two types of simulations have been carried out: irradiation and annealing.

In order to simulate ion irradiation, MMonCa needs as input the initial positions of defects (so called damage cascades). In this thesis, damage cascades have been obtained with the SRIM code (see Section 3.1). The command “cascade” is used for this purpose. MMonCa introduces the previously calculated damage cascades at a flux, fluence and temperature defined by the user. Thus, very different irradiation conditions can be simulated, for instance pulsed or continuous flux described in 3.5.2.

Nevertheless, if defects are already present in the material and the effect of the temperature needs to be simulated, the user must choose the “annealing” command. With this command, new defects are not introduced in the simulation box. The material is heated to the desired temperature and time, and MMonCa calculates the defect evolution.

3.4 Damage cascades validation calculated with the SRIM code

3.4.1 Introduction

The first wall in the chamber of inertial fusion reactors operating with direct targets will be subject to ion irradiation, in particular fusion product He ions (born with 3.5 MeV). The average ion energy will be lower (~2.5 MeV) due to thermalization in the compressed target [26]. Such a high energy leads to Frenkel pair production. OKMC depends on the initial damage cascades [136–138], i.e., initial positions upon ion irradiation. In this thesis, damage cascades have been obtained by means of binary collision approximation with the SRIM code, described in Section 3.1. SRIM code takes into account neither the temperature effects nor the possible clusterization or annihilation between vacancies and SIAs. Damage cascades calculated by means of molecular dynamics (MD) are more accurate, because MD does take into account these effects. However, MD demands much more computational time and only small damage cascades can be simulated, since the simulation boxes are typically in the range of tens of nm. The limitation of the BCA method (no temperature effect, clusterization or annihilation process) is compensated by the use of OKMC, that takes into account migration and thus, annihilation and cluster formation of vacancies and SIAs. Therefore, BCA cascades might turn out accurate enough to be used as input for an

OKMC code. To this end, a comparison between damage cascades obtained by means of MD and BCA has been carried out.

3.4.2 Simulation methods

MD simulations were carried out with LAMMPS code [94] with the Tersoff potential for W, modified with ZBL [139]. Simulation box dimensions were $13.2 \times 13.2 \times 13.2 \text{ nm}^3$ (148176 W) or $7.5 \times 7.5 \times 7.5 \text{ nm}^3$ (27648 W). The boxes were thermalized at 300, 1000 and 2000 K. PKA energies from 0.2 to 2 keV were simulated with 1 fs time-step during 21 ps. For this purpose, the velocity (equivalent to the PKA energy) of an atom in the middle of the simulation box was set, while a thermal bath is set in a small region of $\sim 1 \text{ nm}$ thick on the box sides. The temperature was rescaled each 5 fs. MD simulations were carried out in the supercomputer Magerit-CESVIMA (UPM), using 64 cores and a simulation time of about 5 h. Vacancies and SIAs (cascades) were obtained by analysing the results with the space-filling Wigner-Seitz cell method [140,141]. BCA cascades were obtained as described in Section 3.1. Defect cascades obtained by MD or BCA were introduced in MMonCa, at a rate of $10^{13} \text{ cm}^{-2} \text{ s}^{-1}$, up to a fluence of 10^{15} cm^{-2} . MMonCa was parameterized as described in Section 3.2. Continuous and pulsed irradiation was studied. In the case of pulsed irradiation, a single pulse (composed of many cascades, see Section 3.5) was introduced in the simulation box at the beginning of the simulation.

In order to study the influence of the damage cascades on MMonCa results, a comparison of He irradiation in W was carried out, by introducing the damage cascades due to He irradiation in W, obtained by means of BCA or MD. Pulsed He (625 keV) irradiation was simulated, following the experimental conditions published by Renk *et al.* [16]. 80 pulses of He irradiation (10^{13} cm^{-2} per pulse) at $\sim 773 \text{ K}$ were introduced in a simulation box of $1300 (\text{depth}) \times 50 \times 50 \text{ nm}^3$. To accurately reproduce the damage evolution after every pulse, the temperature changes due to the energy deposition ($\sim 1 \text{ J cm}^{-2}$) per pulse during He irradiation was taken into account. Thus, in every pulse, W temperature increases from a base temperature of 773 K up to $\sim 1500 \text{ K}$, followed by a fast cooling back to the base temperature in several tens of μs (see Figure 3.9). The temperature increase due to the deposition of $\sim 1 \text{ J cm}^{-2}$ during 500 ns in W and the subsequent decrease of the temperature was calculated with the free software GNU Octave.

Figure 3.9. Temperature evolution during and after each He pulse. During the 500 ns pulse, the temperature increases due to the incoming 625 keV He ions (red line). After the pulse, the temperature decreases until the base temperature (blue line).

One set of cascades was obtained with the SRIM code [62]. The second one was calculated as follows: PKA position and energy were obtained with SRIM. In those positions, the MD cascades corresponding with the PKA energy were introduced.

3.4.3 Results and discussion

Figure 3.10 shows a comparison between the MD results and previously published data by Setyawan *et al.* [142], Troev *et al.* [143] and Caturla *et al.* [144]. Although the MD results show a higher FP production than in Ref. [142] and a lower FP production than in Ref. [143] the trend is similar. These differences could appear due to the use of different potentials and methodologies. As shown in Ref. [66], the lowest vacancy formation energy is obtained with the potential used in this work. This leads to the highest FP production rate at elevated temperatures as observed in Figure 3.10. Caturla *et al.* [144] obtained the highest values. This is due to the simulation temperatures they used (10 K) at which defect mobility is very small, limiting their recombination. As can be seen in Figure 3.10, the results are similar to those previously published in the literature.

Figure 3.10. Average number of created FP as a function of the PKA energy at different temperatures. The results obtained in this theses by means of MD are compared with previously published data: Setyawan *et al.* [142], Troev *et al.* [143] and Caturla *et al.* [144].

Figure 3.11 shows the number of PFs calculated with MD or with BCA defect cascades. In the case of BCA cascades, SRIM was used to simulate the irradiation of W with W ions at 200, 300, 1000 and 2000 eV, in order to simulate the damage created by PKAs of the same energies inside bulk W. At low PKA energies, BCA results are similar to MD results. However, it can be appreciated that the higher the PKA energy, the higher the overestimation of the BCA results. At high PKA energies (1000 and 2000 eV), the recombination between vacancies and SIAs plays a more important role in the MD calculations, in contrast to the case of BCA cascades, where no recombination is taken into account.

Comparing MD results at 300 and 1000 K, it can be observed that the higher the temperature, the higher the recombination rate. Nevertheless, the difference is low, i.e., the temperature plays a less important role than the PKA energy. At high temperature, the higher defect mobility leads to more recombination, however, vacancies remain practically static in the time scale of the MD simulations [142]. Therefore, no cluster formation is observed with such a low defect density.

Figure 3.11. Average number of created FP as a function of the PKA energy at different temperatures. The results obtained by means of MD are compared with the BCA results.

Both MD and BCA cascades were introduced in MMonCa at two different temperatures (300 and 1000 K), in order to see the influence of the initial cascades in time evolution at a certain temperature. These two temperatures were selected to compare the results when vacancies cannot migrate (300 K) and when they do migrate (1000 K), taking into account that migration energy of a vacancy in W is 1.66 eV. Migration energy of SIAs is very low, 0.013 eV. SIAs can migrate even at 5 K. OKMC results at different temperatures are presented in Figure 3.12. At 300 K, Figure 3.12(a), regardless the PKA energy, the ratio of vacancies obtained with BCA cascades to vacancies obtained with MD cascades (i.e., MC/MD ratio) is of the same order (<1). At this temperature, the PKA energy does not significantly influence the results. The same trend is observed at 1000 K, Figure 3.12(b), but there is a difference depending on the PKA energy: the higher the PKA energy, the higher the difference between results obtained with BCA and MD cascades. At low PKA energies, (200 and 300 eV), there is almost no difference in the vacancy distribution with BCA or MD cascades. At high PKA energies (1000 and 2000 eV), the difference between BCA and MD cascades relies on the formation of vacancy clusters, as vacancies can migrate at these high temperatures. In the case of MD cascades, there are almost no vacancy clusters and a high percentage of vacancies (33.67% and 26.94% at 1000 and 2000 eV, respectively) reach the free surface, i.e., diffuse far away from their initial positions. On the contrary, in the case of BCA cascades, slightly less than 100% of the vacancies belong to large and almost immobile (see Section 3.2) vacancy clusters (V_m). Although in both cases, MD/BCA ratio is lower at 1000 eV than at 2000 eV, data from 60 s

show a decreasing value in the case of 1000 eV, that might lead to a lower value than at 2000 eV at higher dose.

Figure 3.12. Temporal evolution of the number of remaining vacancies obtained with MD cascades divided by the number of vacancies obtained with BCA cascades in OKMC simulations in the case of (a) continuous irradiation at 300 K, (b) continuous irradiation at 1000 K and (c) pulsed irradiation at 300 K, as a function of the PKA energy.

These results imply that at 300 K, when vacancies do not migrate, there are not important differences between MD and BCA cascades. However, at 1000 K the initial differences in

the number of vacancies present in the simulation (see Figure 3.11) do have an influence on OKMC results. The larger number of vacancies present in BCA simulations leads to a higher rate of vacancy clusterization. As vacancy clusters are almost immobile, in the end the overall vacancy concentration turns out higher when BCA cascades are used.

In order to compare the effect of flux (continuous or pulsed), pulsed irradiation at 300 K was simulated in MMonCa with both BCA and MD cascades, see Figure 3.12(c). The difference of the MC/BCA ratio at any PKA energy is negligible and almost equal to 1, i.e., there is no difference between results with BCA or MD cascades. No evolution in time is observed because all the interstitials have disappeared at the very beginning: they annihilate with immobile vacancies or interact with the free surface from the very beginning of the simulation. The comparison with the continuous irradiation mode shows a clear flux effect. In the case of pulsed irradiation, the high number of defects present at the same time promotes FP annihilation instead of interstitial migration. As a consequence, similar vacancy concentrations are present in both MD and BCA.

Table 3.9. PKA energy distribution due to He (626 keV) ion irradiation in W, calculated with SRIM [62].

PKA energy (eV)	Fraction
< 150	0.38
$150 \leq \text{energy} < 250$	0.25
$250 \leq \text{energy} < 400$	0.14
$400 \leq \text{energy} < 750$	0.11
$750 \leq \text{energy} < 1500$	0.06
$1500 \leq \text{energy} < 2500$	0.02
< 2500	0.01

In order to simulate a realistic case, pulsed He (625 keV) irradiation in W was simulated, by using MD or BCA damage cascades, as described in Section 3.1. In Table 3.9, the fraction of PKAs produced by He (625 keV) irradiation in W as a function of PKA energy is shown. More than 75% of PKA have an energy lower than 400 eV. BCA cascades were directly obtained with the SRIM code. MD cascades were built by introducing MD cascades of appropriate PKA energy in the PKA position predicted by SRIM.

In both BCA and MD simulations, 100% of the He atoms are retained after 80 pulses. The range of 625 keV He ions in W is around 1000 nm. All the defects are concentrated in a small volume of about 300 nm in depth around the He range value, which is called in this thesis “damaged volume”. Helium atoms easily find a vacancy to cluster with before reaching the free surface. As a consequence, He desorption is suppressed.

Figure 3.13. Density of pure vacancy clusters (V_m) as a function of their size for comparison of MD and BCA results in the “damaged volume” in the case of He (625 keV) irradiation in W at a fluence of $8 \times 10^{13} \text{ cm}^{-2}$.

Regarding the size of vacancy clusters, the results in Figure 3.13 show that BCA cascades lead to a higher concentration of remaining single vacancies ($\sim 10\%$) and that there are also more larger vacancy clusters, as predicted in the PKA analysis previously described. This can be attributed to the overestimation at high PKA energy and a higher clusterization of vacancies, as the temperature of the simulation is high enough for vacancies to migrate. Although there is a higher FP production in the case of BCA cascades (in the whole simulation 768800 and 375040 FPs with BCA and MD cascades, respectively), the recombination rate is also higher (96.36% and 93.34%, respectively). For this reason, although more vacancies are present in the case of BCA, the difference in the total number of remaining vacancies is not very important.

Figure 3.14. Comparison of MD and BCA results in the “damaged volume” in the case of He (625 keV) irradiation in W at a fluence of $8 \times 10^{13} \text{ cm}^{-2}$. The density of mixed He_nV_m clusters as a function of their He/V ratio is compared.

Figure 3.14 shows the mixed He_nV_m cluster concentration inside the “damaged volume”, as a function of their He/V ratio, i.e., the number of He atoms per vacancy. There is almost no

difference between results with BCA and MD cascades, only a slightly higher number of clusters with low He/V ratio in the case of BCA cascades, as was expected due to the presence of larger vacancy clusters.

3.4.4 Conclusions

The results show that for high PKA energy, BCA simulation in W provide damage cascades with a significant higher number of FP as compared to the damage cascades obtained by means of MD simulations. This difference has a clear influence on the OKMC results obtained at high temperature, due to the clusterization of vacancies, which turn out almost immobile. However, in the case of He irradiation at 625 keV, the great majority of PKA have an energy lower than 250 eV. As a consequence, it is safe to say that light ion irradiation (which produces low PKA energy) cascades obtained by means of BCA simulations turn out appropriate for OKMC simulations of defect evolution. As an example of ion irradiation, OKMC simulation of pulsed He (625 keV) irradiation in W show almost no difference regardless the origin of the defect cascades, used as input. The only minor difference is that more single vacancies and a slightly higher number of pure vacancy clusters appear when BCA cascades are used. As a result, BCA turn out accurate enough to be used in OKMC simulation for light ion irradiation. In fact, this thesis in many cases is based on BCA cascades to simulate with OKMC He and H irradiation in W.

3.5 Simulations in MMonCa: validation and helium irradiation in tungsten (continuous and pulsed flux)

3.5.1 Validation of the MMonca code for He irradiation in W

In order to validate the MMonCa code for simulating W, a comparison with previously published results obtained with the OKMC code LAKIMOKA [145] were carried out. Becquart *et al.* [66] and Hou *et al.* [146] have simulated with LAKIMOKA the thermal desorption of He-irradiated W at different energies (400 eV and 3 keV) and fluences (up to 12, 13 and 350 ppm). Their results have a good agreement with the experiments published by Soltan *et al.* [112].

To this end, MMonCa has been parameterized for He irradiation in W as LAKIMOKA was. The whole parameterization can be found in Ref. [66], in which is based the parameterization described in Sections 3.2.1 and 3.2.2. For the simulations described in Chapters 4 and 6, parameterization from Ref. [66] was improved with new DFT data for binding energies of He atoms to vacancies and some other considerations described in

Section 3.2. In addition, the same irradiation conditions were set [66,146]. The dimensions of the simulation box were $1001 \text{ (depth)} \times 399 \times 400$ in lattice units ($\lambda = 0.317 \text{ nm}$), with periodic boundary conditions (PBC) applied to the four lateral surfaces. The top and bottom surfaces were desorption surfaces and the He flux was $10^{15} \text{ m}^{-2} \text{ s}^{-1}$, i.e., 16 He/s. The irradiation temperature was 5 K. After the He implantation, an isochronal annealing (steps of 2 K for 60 s) from 1 K was performed. These values are the same in all the results presented in the next Sections. Three sets of simulations were carried out:

- He irradiation at 400 eV. At this low energy, He does not produce any displacement in W, i.e., there is not Frenkel pair production. He ions are introduced at a concentration of 13 ppm, at random initial positions.
- The same, up to 350 ppm.
- He irradiation at 3 keV. At this energy, some Frenkel pairs are produced in W. In addition, 100 ppm of carbon atoms were randomly introduced. C traps vacancies and SIAs and their clusters. Binding energies are: $E^b(\text{C-V}) = 2.01 \text{ eV}$ and $E^b(\text{C-SIA}) = 0.62 \text{ eV}$ [66].

3.5.1.1 *400 eV He irradiation at 13 ppm*

At 400 eV, there is no Frenkel pair production in W. Thus, in this simulation, only He atoms or pure He_n clusters are introduced or formed, respectively. He atoms were randomly introduced in the simulation box. He desorption as a function of temperature, compared with the LAKIMOCA results is presented in Figure 3.15, where a good agreement between both codes can be observed. The number of He atoms has been normalized to the number of He atoms at the beginning of the isochronal annealing, i.e., at the end of the He implantation.

Figure 3.15. Comparison between LAKIMOKA and MMonCa results of He (400 eV, 13 ppm) irradiation in W. The normalized number of He atoms is represented as a function of the temperature (K). LAKIMOKA results are from Ref. [66].

The isochronal annealing starts at 1 K and finishes at 101 K. At such a low temperatures, there is no emission of He atoms from He_n clusters, due to the high binding energies [113]. Thus, only migration of He atoms and He_n clusters takes place, apart from He_n cluster formation. Since the migration energy for He_n clusters increases monotonically with the number of He atoms, He_n cluster migration begins at different temperatures for each cluster size. The larger the cluster size, the higher the temperature needed for the beginning of the migration.

Between 5 and 7 K, the number of He atoms decreases due to desorption of single He atoms. Their migration energy is 0.01 eV, which makes them mobile even at 5 K. Between 7 and 15 K, the number of He atoms remains constant, as there is not desorption at all. All the He atoms have desorbed and the He_2 clusters begin to migrate at 15 K, as their migration energy is 0.03 eV. Again, there is another plateau until ~27 K, when the He_3 clusters begin to migrate. From He_4 , the migration energies increases linearly, 0.01 eV for each additional He atoms in the He_n cluster (see Table 3.4). At 7 K, MMonCa predicts more He desorption than LAKIMOKA (see Figure 3.15). As at this temperature only He atoms can migrate. MMonCa results show a low number of single He atoms, i.e., a lower number of He_n clusters was formed comparing to LAKIMOKA. This must be influenced by the way the capture radii are defined in both MMonCa and LAKIMOKA. Whilst in LAKIMOKA there is a defined capture radius for each He_n cluster size, in MMonCa the capture radius is the overlay of all its constituent He atoms, as previously described. From 9 K, the trend of the results obtained by MMonCa is in good agreement with those

calculated by LAKIMOKA. In the end, the only difference between LAKIMOKA and MMonCa results is the gap at 7 K, which is maintained beyond 7 K.

Figure 3.16 shows the number He_n clusters as a function of the number of He they contain at (a) 5 K, (b) 11 K, (c) 21 K and (d) 41 K. At 5 K, there are almost no He_n clusters, as the great majority of He are in the form of single He atoms. At higher temperatures, there are no single He atoms, all the He belongs to He_n clusters of different size. At 11 K, clusters up to He_5 size are formed. The same trend is observed at 21 and 41 K: the higher the temperature, the larger the He_n clusters. Moreover, the higher the temperature, the lower the number of small He_n clusters, as at 21 K there is not any He_2 cluster, and at 41 K, the smaller cluster is He_5 . As small He_n clusters migrate with the increasing temperature, they desorb at the desorption surfaces or they are trapped by other He_n clusters, forming larger He_n clusters. A perfect agreement between LAKIMOKA and MMonCa is observed in Figure 3.16.

Figure 3.16. Comparison between LAKIMOKA and MMonCa results of He (400 eV, 13 ppm) irradiation in W. The number of clusters as a function of the number of He in them is compared at (a) 5 K, (b) 11 K, (c) 21 K and (d) 41 K. LAKIMOKA results are from Ref. [66].

3.5.1.2 400 eV He irradiation at 350 ppm

Similar studies were carried out, but at 350 ppm instead of at 13 ppm. As previously described, there are only He atoms as no Frenkel pair is produced by He irradiation at 400 eV in W. The results of He desorption as a function of temperature calculated by both LAKIMOKA and MMonCa are shown in Figure 3.17.

Figure 3.17. Comparison between LAKIMOKA and MMonCa results of He (400 eV, 350 ppm) irradiation in W. The normalized number of He atoms is represented as a function of the temperature (K). LAKIMOKA results are from Ref. [66].

The same trend is observed as in the case described for 13 ppm. Since the temperature increases, larger He_n clusters can migrate. Then, they can either desorb from the desorption surfaces or be trapped by other He_n clusters, forming larger He_n clusters. However, some differences can be observed between Figure 3.15 at 13 ppm and Figure 3.17 at 350 ppm:

- The discrepancy between the codes at 7 K for the case of 13 ppm is not observed at 350 ppm. As the initial He concentration is much larger, larger He_n clusters are formed. Thus, the concentration of single He atoms is lower.
- As the He_n clusters are larger, at 101 K only 3.5% of the implanted He has desorbed. On the contrary, at 101 K in the case of a He concentration of 13 ppm, 44.6% of the implanted He was released from the simulation box.

Figure 3.18 shows the comparison between LAKIMOKA and MMonCa results at (a) 5 K, (b) 11 K, (c) 21 K and (d) 41 K. Results calculated with MMonCa are in good agreement with those calculated with LAKIMOKA. Again, the higher the temperature, the higher the number of large He_n clusters and the lower the number of small He_n clusters.

Figure 3.18. Comparison between LAKIMOKA and MMonCa results of He (400 eV, 350 ppm) irradiation in W. The number of clusters as a function of the number of He in them is compared at (a) 5 K, (b) 11 K, (c) 21 K and (d) 41 K. LAKIMOKA results are from Ref. [66].

3.5.1.3 3 keV He irradiation at 12 ppm

Since He irradiation at 3 keV in W produces Frenkel pairs, the damage cascades were calculated with the SRIM code [62], see Sections 2.1 and 3.1. On the one hand, SRIM does not provide the position of SIAs, they have been generated by the methodology described in Section 3.1. On the other hand, SRIM considers W as amorphous. Hou *et al.* [146] produced their damage cascades with other BCA code, the MARLOWE code [58,64], which considers W as amorphous or as a crystal, in the latter case taking into account channelling effects. To get more accuracy with the input parameters of the MARLOWE code, only the results of amorphous W [146] were reproduced in this section. The total number of He atoms, vacancies and SIAs are shown in Figure 3.19.

Figure 3.19. Comparison between LAKIMOKA and MMonCa results of He (3 keV, 12 ppm) irradiation in W. The number of He atoms, vacancies and SIAs is compared as a function of temperature. LAKIMOKA results are from Ref. [146].

A very good agreement is observed in the case of both the number of He atoms and the number of vacancies. A good agreement is also observed in the case of SIAs, with the exception of the lower number of SIAs obtained with the MMonCa code at 7 K. The number of vacancies is the same in both codes which implies that the SIAs have been left the simulation box through the free surfaces.

Figure 3.20. Comparison between LAKIMOKA and MMonCa results of He (3 keV, 12 ppm) irradiation in W. The total number of He atoms, trapped He atoms and free He atoms is compared as a function of temperature. LAKIMOKA results are from Ref. [146].

In Figure 3.20, the number of trapped and free He atoms is plotted. The results calculated by LAKIMOCA and MMonCa codes are in good agreement. However, at low temperatures, MMonCa provides a higher number of trapped He atoms and a lower number of free He atoms. As stated before, it can be attributed to the different methods of calculating the capture radii. In MMonCa, the capture radius is the overlap of the capture radii of the single particles that form the cluster. Thus, the resulting radii are slightly higher on average, producing more He trapping.

With the exception of the capture radii, the same parameterization, irradiation conditions, isochronal annealings, and simulation boxes were used in both codes. As described in previous Sections, irradiations were carried out with different ion energies and fluences. The results of these sections indicate that MMonCa [51] provides accurate results in agreement with those of LAKIMOKA [66,146].

3.5.2 Helium irradiation in tungsten (continuous and pulsed flux)

3.5.2.1 Introduction

Tungsten is considered the material of choice for the first wall and divertor in both inertial confinement fusion (ICF) and magnetic confinement fusion (MCF). In both cases, inertial fusion with direct drive target and magnetic fusion, the most detrimental situations that tungsten components must face are those originated by intense ion pulses [11] (see Chapter 1). Numerous studies [33,37] carried out under different helium irradiation conditions in continuous mode show that exceeding certain threshold value of fluence, around 10^{17} - 10^{18} cm⁻², has fatal consequences for W components. Scanning Electron Microscope (SEM) images reveal that swelling and pore formation take place, which eventually lead to W exfoliation with mass loss. Renk *et al.* [16] clearly showed that the situation is even worse when W is subject to intense He pulses rather than to continuous irradiation. In this situation, the fluence threshold for mass loss is around two orders of magnitude lower ($\sim 10^{15}$ cm⁻²). This has serious implications for fusion reactor W-based components.

The origin of these adverse effects upon He irradiation is unclear. However, it is logical to consider excessive He retention as a possible cause [16]. A detailed study of He retention is not trivial due to the subtleties imposed by the exact temperature profile, ion energy, pulse duration and the presence of impurities, which lead to complicated evolution of defect clusters. In this Section, a study of He (3 keV) irradiation in W in both continuous and pulsed modes, at four different temperatures (700, 1000, 1300 and 1600 K) and two different fluxes (low flux, 2×10^{12} cm⁻² per second and high flux, 2×10^{13} cm⁻² per second), is presented. The results clearly indicate that in fact He retention is significantly higher in the case of pulsed irradiation, provided the temperature is high enough (≥ 700 K)

to enable vacancy migration. Moreover, in pulsed mode, He is retained in a much lower volume, i.e., the damage is much more concentrated and He_nV_m clusters, in which He is mainly retained, contain a lower number of vacancies, i.e., they are highly pressurized.

3.5.2.2 Simulation methods

In order to study the effect of flux mode in the case of He irradiation, object kinetic Monte Carlo (OKMC) simulations with the MMonCa code [51] have been carried out. MMonCa has been parameterized as described in Section 3.5.1. Carbon traps were not considered in this study. Damage cascades of He irradiation in W have been obtained with the SRIM code [62], as described in Section 3.1. The simulation box employed was $310 \times 126 \times 126 \text{ nm}^3$. The irradiation is along the X axis. In Y and Z dimensions, periodic boundary conditions (PBCs) were set. The generated vacancies (Vs) and self-interstitial atoms, i.e., SIAs (Is) may migrate, annihilate or cluster. Clusters of vacancies (V_m) and SIAs (I_m) are also mobile and may annihilate at the surfaces [66]. The implanted He gives rise to mobile interstitial He clusters (He_n) that desorb from the surface or gets trapped at vacancies, SIAs and their clusters (V_m and I_m), forming mixed He_nV_m or He_nI_m , respectively. The aim of the work presented in this Chapter is to compare pulsed irradiation with continuous irradiations.

Figure 3.21. Scheme of (a) continuous and (b) pulsed irradiation during 1 s. The same number of He ions is irradiated in both cases. The temperature of the simulation box is the same in both continuous and pulsed, during the whole second.

For the continuous mode, He ions and the generated FPs were introduced at a constant rate (flux 2×10^{12} or $2 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$), see Figure 3.21(a). Thus, in this case there is a continuous introduction of He ions in the simulation box. Defect evolution is enabled during the irradiation. For the pulsed mode, see Figure 3.21(b), a certain number of He ions (2×10^{12} or $2 \times 10^{13} \text{ cm}^{-2}$ per pulse) were introduced instantaneously along with the generated Frenkel pairs (FPs) and let them evolve for 1 s at a certain temperature until the next He pulse arrives.

The process described above is repeated during 150 s (see Figure 3.22).). In continuous mode, see Figure 3.22(a), a certain number of He ions and Frenkel pairs, i.e., cascades ($x = 2 \times 10^{12} \text{ cm}^{-2}$ in the case of low flux and $x = 2 \times 10^{12} \text{ cm}^{-2}$ in the case of high flux) are introduced every second, homogeneously distributed in time. In pulsed mode, see Figure 3.22(b), the same number (x) of cascades is implanted every second, but instead of homogeneously distributed in time, it is introduced instantaneously at the beginning of every second. In both continuous and pulsed irradiation, the temperature is constant during the whole irradiation, making possible for the defects to migrate during the 150 s of the simulation. After 150 s, in both continuous and pulsed irradiation, the same number of He ions were introduced in the simulation box.

Figure 3.22. Scheme of the whole continuous (a) and pulsed (b) irradiation, during 150 s. In both continuous and pulsed irradiation, the temperature is maintained constant during the 150 s of simulation. X represents the number of He (3 keV) ions introduced every second ($x = 2 \times 10^{12} \text{ cm}^{-2}$ in the case of low flux and $x = 2 \times 10^{12} \text{ cm}^{-2}$ in the case of high flux).

Several temperatures and fluences have been studied in both continuous and pulsed fluxes, in order to observe their influence on He retention. Thus, 16 different simulations have been carried out (see Table 3.10). The study covers a wide range of temperatures: 700, 1000, 1300 and 1600 K.

Table 3.10. Simulation conditions regarding the flux, temperature and irradiation mode that have been used in the study presented in this section.

Flux ($\text{cm}^{-2}\text{s}^{-1}$)	Temperature (K)	Irradiation mode
Low flux (2×10^{12})	700	Continuous and pulsed
Low flux (2×10^{12})	1000	Continuous and pulsed
Low flux (2×10^{12})	1300	Continuous and pulsed
Low flux (2×10^{12})	1600	Continuous and pulsed
High flux (2×10^{13})	700	Continuous and pulsed
High flux (2×10^{13})	1000	Continuous and pulsed
High flux (2×10^{13})	1300	Continuous and pulsed
High flux (2×10^{13})	1600	Continuous and pulsed

3.5.2.3 Results

The vast majority of He atoms are retained in mixed He_nV_m clusters. At the simulated temperatures (700 to 1600 K), there are no pure He_n clusters in the simulation box because they have enough time to reach either the desorption surface or any other cluster. Only in the case of high flux ($2 \times 10^{13} \text{ cm}^{-2}$ per second) at both 700 and 1000 K, a very small number of He atoms are retained in mixed He_nI_m clusters. For this reason, the results plotted in the present Chapter refers to He atoms trapped in mixed He_nV_m clusters, unless otherwise indicated.

Figure 3.23. Number of retained He atoms divided by the number of implanted ions, as a function of the time, at different temperatures in the case of (a) continuous and (b) pulsed irradiation, both of them at low flux ($2 \times 10^{12} \text{ cm}^{-2}$ per second).

Figure 3.23 shows the time evolution of the ratio of retained He to implanted He, as a function of different temperatures at low flux. The retained He fraction increases with the increasing time, i.e. with the increasing fluence, up to values that turn out almost constant at the end of the simulation. Helium retention increases only around 3-4% between 100 and

150 s. The same trend is observed in both continuous and pulsed irradiation: the higher the temperature, the lower the retained He fraction.

Figure 3.24. Number of retained He atoms divided by the number of implanted ions, as a function of the time, at different temperatures in the case of (a) continuous and (b) pulsed irradiation, both of them at high flux ($2 \times 10^{13} \text{ cm}^{-2}$ per second).

Figure 3.24 shows the ratio of retained He to implanted He at high flux. Similar results are obtained comparing to the results obtained for low flux (Figure 3.23). The higher the temperature, the lower the He retention, with the only exception of pulsed irradiation at 700 and 1000 K, see Figure 3.24(b). It can be observed a higher He retention at 700 K than a 1000 K. Comparing the high flux with the low flow, it can be observed that in the case of high flux, the saturation of ratio of retained He to implanted He is reached at lower times of He irradiation (after ~ 30 s). The ratio of retained He to implanted He is higher than in the case of low flux, for every simulation. Thus, the higher the flux, the higher the ratio of retained He to implanted He and the lower the time needed to reach the saturation value.

Figure 3.25. Number of retained He atoms divided by the number of implanted He atoms, as a function of the temperature in the case of (a) low flux ($2 \times 10^{12} \text{ cm}^{-2}$ per second) and (b) high flux ($2 \times 10^{13} \text{ cm}^{-2}$ per second), after 150 s of He irradiation.

The temperature has a clear influence on the number of retained He atoms. A comparison is shown in Figure 3.25. The higher the temperature, the lower the ratio of retained He to implanted He. Regardless the ion flux (low or high), pulsed irradiation leads to higher He retention than continuous irradiation, at all the temperatures, with the only exception of 700 K. Moreover, the higher the temperature, the higher the difference of retained He to implanted He ratio between continuous and pulsed irradiation modes. On the one hand, in the case of low flux, at 700 K this difference is very small (0.36%), but it increases with increasing temperature (10.95%, 41.1% and 39.1 % at 1000, 1300 and 1600 K, respectively). On the other hand, the same trend is observed in the case of high flux. At 700 K the difference is only 0.54% and it increases with increasing temperature: 8.98%, 36.94% and 81.69% at 1000, 1300 and 1600 K, respectively. As stated before, at high flux the difference between continuous and pulsed modes is higher than at low flux.

3.5.2.4 *Discussion*

The higher helium retention in the case of pulsed irradiation can be explained as follows. In the pulsed case, see Figure 3.25(b), all the He ions are instantaneously implanted every pulse, and no more He ions are implanted until the next pulse, 1 s later. On the contrary, in the continuous case, see Figure 3.25(a), the ions arrive distributed uniformly over every second. This implies that in the case of pulsed mode, from the very beginning of the irradiation, all the defects are already introduced in the simulation box. They have a higher probability to find each other and, thus, form clusters. On the contrary, in the case of continuous irradiation, the ions arrive one by one. The very first He ions have lower number of defects available to cluster with. For this reason, higher diffusion is observed (Figure 3.26) and thus, lower He retention is observed. The same effect appears at high flux: as there are more defects, there is a higher probability for He atoms to cluster.

(a) Continuous irradiation (high flux, 1300 K)

(b) Pulsed irradiation (high flux, 1300 K)

He_nV_1	He_nV_3	$\text{He}_n\text{V}_{5-10}$
He_nV_2	He_nV_4	$\text{He}_n\text{V}_{>10}$

Figure 3.26. 3D scheme of He retention in high flux irradiation ($2 \times 10^{13} \text{ cm}^{-2}$ per second) at 1300 K after 150 s in (a) continuous and (b) pulsed mode. The trapped He atoms are sorted by the size of the He_nV_m clusters in which they are retained [141,147].

Regarding of the type of clusters in which He atoms are retained, results show that the vast majority of He atoms are retained in He_nV_m clusters. On the one hand, the migration energy of SIAs (0.013 eV) is much lower than the migration energy of vacancies (1.66 eV) [66], leading to a much lower He retention in He_nI_m clusters as SIAs easily reach the desorption surface. On the other hand, the binding energy of He atoms to SIAs (0.94 eV, [66]) is much lower than the binding energy of He to vacancies (see Table 3.6), which is up to 4.67 eV in the case of a single He atom in a single vacancy (He_1V_1). Thus, He atoms trapped by SIAs are emitted from the clusters in a much higher rate than in the case of He atoms trapped in vacancies.

Figure 3.27. Number of retained He atoms with respect to the total He atoms implanted, retained in (a) He_nV_m and (b) He_nI_m clusters, at 700 and 1000 K, in the case of pulsed irradiation and high flux ($2 \times 10^{13} \text{ cm}^{-2}$ per second).

The only cases in which He is retained in He_nI_m clusters are at pulsed mode and high flux, at 700 and 1000 K (Table 3.10). As can be observed in Figure 3.27, although the great majority of He atoms are retained in He_nV_m clusters, there is a small number of them retained in He_nI_m clusters. Thus, if only He atoms retained in He_nV_m clusters are taken into account, higher He retention occurs at 1000 K. Nevertheless, if He atoms in both He_nV_m and He_nI_m clusters are taken into account (see Figure 3.28), a higher He retention is observed at 700 K. Therefore, as in all the cases of this study, the same trend is observed: the higher the temperature, the lower the He retention.

Figure 3.28. Total number of retained He atoms with respect to the total He atoms implanted, retained in both He_nV_m and He_nI_m clusters, at 700 and 1000 K, in the case of pulsed irradiation and high flux ($2 \times 10^{13} \text{ cm}^{-2}$ per pulse).

The influence of the temperature is clear: the higher the temperature, the lower the He retention. Although He_nV_m clusters are formed, the higher temperature leads to a higher dissociation rate. He atoms are able to be emitted from the He_nV_m clusters and, as the

dissociation is related with the temperature by an Arrhenius law, the higher the temperature, the higher the dissociation probability. A detailed He atoms retention by cluster size is presented in Figure 3.29.

Figure 3.29. Ratio of retained He to implanted He, as a function of time in the case of pulsed irradiation and low flux at (a) 700 K, (b) 1000 K, (c) 1300 K and (d) 1600 K. Trapped He is sorted by the size of the He_nV_m cluster.

Temperature influences not only the number of He atoms trapped but also in the size of He_nV_m clusters in which they are trapped. As can be seen in Figure 3.29(a), the number of He retained in He_nV_1 increases in the first seconds of the simulation. As the irradiation continues, the number of He atoms trapped in larger clusters slightly increases. Nevertheless, with the increasing temperature, the number of He atoms trapped in monovacancies decreases whereas it increases in larger clusters. Moreover, the irradiation time needed for this trend decreases with the increasing temperature. At 1600 K, see Figure 3.29(d), after ~40 s of He irradiation, the great majority of He atoms are retained in clusters with more than 10 vacancies ($\text{He}_n\text{V}_{>10}$). This behaviour can be explained as follows. As the migration energy of vacancies is 1.66 eV, at 700 K due to the low vacancy mobility, vacancy clusters are not formed. For this reason, He atoms are mainly trapped in monovacancies. With the increasing temperature, vacancy mobility becomes appreciable and He_nV_m clusters are generated. As a result, the temperature has a clear influence on

vacancy migration, and thus, on the type of clusters in which He atoms are trapped. The higher the temperature, the larger the number of vacancies in He_nV_m clusters and the lower the irradiation time needed to see the effect.

Figure 3.30. Comparison of the size of He_nV_m clusters in which He atoms are trapped between high and low flux, in the case of pulsed irradiation at 1300 K.

The effect of the flux on the type of He_nV_m clusters in which He atoms are trapped is also analysed in Figure 3.30. In the case of continuous mode there is a higher proportion of He atoms trapped in $\text{He}_n\text{V}_{>10}$ than in the case of pulsed irradiation. Due to the instantaneous He irradiation in the case of pulsed irradiation, vacancy clusters are formed with a lower chance to diffuse and there is less vacancy migration. Thus, He atoms are trapped in a higher variety of He_nV_m clusters. Nevertheless, the difference between low and high flux is very small.

Figure 3.31. Comparison between continuous and pulsed irradiation mode, regarding the size of He_nV_m clusters in which He atoms are trapped. The results show high flux irradiation ($2 \times 10^{13} \text{ cm}^{-2}$ per second) at 1300 K.

Finally, the effect of the irradiation mode (continuous or pulsed) is analysed, regarding the size of He_nV_m clusters in which He atoms are trapped. The case of high flux at 1300 K is taken as example (Figure 3.31). In the continuous mode, almost all the He atoms are trapped in $\text{He}_n\text{V}_{>10}$ clusters from the very beginning of the simulation. The results can be explained as in the comparison between high and low flux described above. As the continuous mode allows a higher diffusion of the defects, including vacancies, they form He_nV_m clusters with more vacancies than in the pulsed mode. Thus, He atoms are retained in $\text{He}_n\text{V}_{>10}$ clusters from the first seconds of simulation.

The higher diffusion in the case of continuous mode can be seen in the scheme for both continuous and pulsed modes after 150 s, in the case of high flux ($2 \times 10^{13} \text{ cm}^{-2}$ per pulse) at 1300 K, shown in Figure 3.32.

Figure 3.32. Lateral section of He retention in high flux irradiation ($2 \times 10^{13} \text{ cm}^{-2}$) at 1300 K after 150 s in (a) continuous and (b) pulsed mode. The trapped He atoms are sorted by the size of the He_nV_m clusters in which they are retained [141,147].

In the case of continuous mode, see Figure 3.32(a), there is a higher diffusion of defects, as they are present at deeper positions compared to the pulsed mode. In the case of pulsed mode, see Figure 3.32(b), all the trapped He is concentrated in a volume up to ~ 40 nm in depth. This leads to a higher defect concentration in the case of pulsed mode. The irradiation mode (continuous or pulsed) has a great influence not only in the total number of trapped He atoms and in the size of the He_nV_m clusters in which they are trapped, as described above, but also on the concentration of defects. In pulsed mode, they are much more concentrated in the region of He implantation. SRIM code calculates that the mean depth of implanted He ions, irradiated at 3 keV in W, is ~ 13.5 nm. Thus, almost no He diffusion is observed in the pulsed mode.

Figure 3.33. Lateral section of He retention in high flux irradiation ($2 \times 10^{13} \text{ cm}^{-2}$) at 1300 K after 1, 2, 5 and 150 s in (a) continuous and (b) pulsed mode. The trapped He atoms are sorted by the size of the He_nV_m clusters in which they are retained [141,147].

Figure 3.33 shows the lateral section of He retention as a function of time. As can be observed, the diffusion of defects in the case of continuous mode is more pronounced at the beginning of the simulation. As the irradiation time increases, the He trapped near the surface increases. In the case of pulsed mode, see Figure 3.33(b), it can be observed that in

the first seconds of He irradiation, all the He is trapped in monovacancies (He_nV_1) near the desorption surface. As the irradiation time increases, more He and defects arrives, creating larger He_nV_m clusters. Moreover, the He trapped in larger He_nV_m clusters is around the implantation depth calculated from SRIM, supporting the idea of immobile defects, i.e., neither at the beginning (during the first seconds) nor at the end (after 150 s of He irradiation) of the simulation defect diffusion is observed.

3.5.2.5 *Conclusions*

3 keV He irradiation in W has been studied by means of OKMC, with the code MMonCa. 16 different simulations have been carried out, to study the influence of (i) the flux of irradiated He (high and low flux), (ii) the temperature (from 700 to 1600 K) and (iii) the mode of irradiation (continuous and pulsed).

The flux of He irradiation (high or low flux) has a direct influence on He retention. The higher the flux, the higher the retained He/implanted He ratio, regardless other parameters. With respect to the size of He_nV_m clusters in which He atoms are trapped, the flux turns out to play a major role.

The temperature has a direct influence on the number of retained He atoms: the higher the temperature, the lower the He retention because the dissociation rate of He_nV_m clusters increases with the increasing temperature. Thus, although He trapping occurs, at high temperatures He atoms cannot remain trapped in He_nV_m clusters and are emitted from them.

The mode of irradiation has a clear influence on (i) the quantity of He atoms trapped, (ii) the size of clusters in which they are trapped and (iii) the defect concentration in depth. Since the irradiation is instantaneous in pulsed mode, from the very beginning of the pulse all the defects are inside W. Thus, they have more chances to cluster with other defects and diffuse less than in the case of continuous mode. This leads to a higher He trapping rate, He atoms are concentrated in He_nV_m clusters with a lower number of vacancies and He_nV_m clusters are concentrated in a smaller volume, near the irradiation surface in pulsed mode compared to continuous mode. This might lead to detrimental effects in W in the case of pulsed irradiation as more He atoms are retained and the He_nV_m clusters might be much more pressurized, as they contain more He atoms in a lower number of vacancies. In addition to all this, He_nV_m clusters are much more concentrated, as all of them remain trapped in a much smaller volume. These results could qualitatively explain the experiments published in Ref. [16], where it was already pointed out the higher deleterious effects observed in He irradiated W in pulsed mode.

To summarize, the mode of irradiation has a high influence on He retention, expecting to be much worse the W response in the case of pulsed irradiation. Thus, the experiments carried out with continuous irradiation should take into account this effect, provided that the plasma facing materials will have to deal with pulsed rather than continuous irradiation.

4 Helium irradiation in tungsten: high and low grain boundary density

After presenting the simulation methods used in this thesis and, in particular the MMonCa code in the previous Chapters, three different studies of helium and hydrogen irradiation in tungsten are presented in the following three Chapters. Chapters 4 and 5 include studies about the role of the grain boundary density tungsten under helium and hydrogen irradiation, respectively. In Chapter 6, the effect of low energy and high flux helium irradiation is studied.

In Chapter 1, it was commented that the grain boundaries play an important role regarding defect evolution in tungsten. In this Chapter, pulsed helium irradiation in both monocrystalline tungsten, i.e., tungsten with no grain boundaries (GBs) and nanocrystalline tungsten (high GB density) is studied.

The experimental conditions reported in Ref. [16] were simulated. Thus, pulsed helium (625 keV) irradiation in monocrystalline and nanocrystalline tungsten was studied. The results shows that, in fact, high grain boundary density has an influence on defect evolution. Therefore, in nanocrystalline tungsten there is a lower Frenkel pair annihilation, the helium-vacancy clusters have lower helium to vacancy ratio and thus, are less pressurized, being this difference larger with the increasing number of helium pulses. Thus, a better response is expected in nanocrystalline tungsten, regarding helium irradiation. The results presented in this Chapter were published in Ref. [54].

4.1 Introduction

Many efforts are being carried out in order to mitigate the effect of He retention in W. Nanostructured W might be able to deal with He retention better than monocrystalline W due to its large grain boundary density. In Ref. [44] it has been reported that grain boundaries act as defect sink for vacancies, SIAs and He atoms, thereby presenting nanostructured W with high grain boundary density is a candidate as material to prove whether it presents superior radiation tolerance than monocrystalline W. At grain boundaries, vacancies and SIAs annihilate [45]. Nanocolumnar W has recently been fabricated with a high grain boundary density [43] and it has been experimentally observed that high grain boundary density has a direct influence in the retention of light species [49]. A point not elucidated yet is whether inter-grain He migration allows for efficient He release or if the distribution and size of defects in the interior of a grain is affected by the high density of grain boundaries. The latter effect is the purpose of the study described in the present Chapter. The influence of high grain boundary density in damage production by pulsed He irradiation in W has been studied, by comparing monocrystalline W (MW) to nanocrystalline W (NW). For this purpose, MMonCa has been parameterized, for He irradiation in W, as described in Sections 3.2.1 and 3.2.2. Two different sets of simulations have been carried out in both MW and NW, in order to reproduce the experimental conditions used by Renk *et al.* [16]. They showed that pulsed He irradiation leads to detrimental effects (pore formation and protrusion, with fluxes up to $2 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$) at fluences as low as 10^{15} cm^{-2} .

4.2 Simulation methods

In order to reproduce the irradiation conditions reported by Renk *et al.* [16], a simulation box of $1300 \text{ (depth)} \times 50 \times 50 \text{ nm}^3$ was set to simulate 625 keV He irradiation. Damage cascades were simulated with binary collision approximation code SRIM [62]. As SRIM provides the final position of both vacancies and incident ions (He ions, in the present study) but not the positions of SIAs, the methodology described in Section 3.1 was used. The damage cascades corresponding to 10^{13} cm^{-2} were introduced in the simulation box during 500 ns, i.e., $2 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$, with a time step between consecutive pulses of 1 s, time enough for point defects to cluster and recombine. In order to get a more accurate simulation to He pulses, during He implantation the temperature changes due to the energy deposition was taken into account. W temperature increases from a base temperature of 773 K up to $\sim 1500 \text{ K}$, followed by a fast cooling back to the base temperature in several tens of μs , as described in Section 3.4.2.

The parameterization for He irradiation in W described in Section 3.2. However, this parameterization was proved to work on a temperature region from 0 to ~900 K. In order to validate the parameterization for the high temperatures considered in the simulations of the present Chapter, the experiments published by Debelle *et al.* [126,148] were simulated.

Figure 4.1. Experimental (Debelle *et al.* [148]) and computational (MMonCa) data comparison in the case of He (60 keV) irradiation at 300 K and subsequent annealing during 1 h at 1473, 1573, 1673, 1773 and 1873 K.

They implanted 60 keV ^3He ions at ~300 K at a fluence of $2 \times 10^{13} \text{ cm}^{-2}$. After the implantation, one sample was kept as reference and five other samples were annealed during 1 h at different temperatures (1473, 1573, 1673, 1773 and 1873 K). After the annealing processes, they measured the released He fraction with respect to that at the end of the implantation. A good comparison between the experimental and computational results is obtained (Figure 4.1). This indicates that the used parameterization is adequate for the range of temperatures of interest, up to 1873 K.

Figure 4.2. Schematic view of (a) monocrystalline and (b) nanocrystalline W simulations. In monocrystalline W, periodic boundary conditions have been set in the four lateral surfaces whereas in nanocrystalline W, the four lateral surfaces are perfect sinks for defects, to reproduce the effect of grain boundaries.

In both MW and NW, the same simulation box has been used, in order to make a comparison taking into account the same volume of W. In both MW and NW, the top surface is considered as a desorption surface whereas atoms reaching the bottom surface were considered to move further deep into the bulk and thus ignored. In the case of MW, periodic boundary conditions (PBCs) were applied to the four lateral surfaces, to reproduce monocrystalline W. On the other hand, in the case of NW the four lateral surfaces were considered as perfect sinks, in order to reproduce the effect of grain boundaries (see Figure 4.2). Only the defects that remain in the interior of the grains were taken into account in the results. The goal was to assess the role of grain boundaries on vacancy cluster formation and pressurization. The behaviour of He and defects at grain boundaries deserves further attention since they may play an important role in the performance of W as a functional material. However, for the total fluences reached in this study we can consider that the sink character of the boundaries does not depend on the fluence. Since the grain boundary surface is very large, it is a good assumption to consider that point defects usually reached a fresh grain boundary. This justifies the fact that the grain boundaries were considered as perfect sinks. Nevertheless, significant interstitial accumulation at the grain boundaries might affect their trapping potential and requires a more sophisticated grain boundary model.

4.3 Results

Regarding He retention, the results for both MW and NW are plotted in Figure 4.3. In the case of MW, all the implanted He atoms are retained in both He_nV_m and He_nI_m clusters, reaching the 100% of He retention. The great majority of He atoms are retained in He_nV_m clusters. After an initial increase in the percentage of retained He in He_nI_m clusters after around 10 pulses, it decreases down to a value of only 4.2% after 490 pulses. In the case of NW, an almost constant value of retained He ($\sim 50\%$) in the interior of the grain is reached after around 100 pulses. The other 50% has reached the grain boundaries and thus, is not considered in the results.

Figure 4.3. Retained He fraction with respect to the implanted He for MW and NW as a function of time (and fluence). The results show the total He retention and the He retained in both He_nV_m and He_nI_m clusters.

Helium depth profiles are shown in Figure 4.4(a). In both MW and NW, most of the He atoms are retained in a small region between 900 and 1200 nm in depth. This region is called “damaged volume”. Both profiles coincide with the as-implanted profile obtained by SRIM, therefore, He atoms are readily retained inside mixed He_nV_m clusters near their initial position in MW and the same behaviour is observed for the He atoms that remain in the interior of the grain in NW, i.e., He atoms that did not reach the grain boundaries.

Another important issue is the number, size and distribution of vacancies. In NW there are more vacancies inside the grain than in MW, as can be observed in Figure 4.4(b). However, the difference is not very large. After 490 pulses, the number of remaining vacancies per implanted ion is around 0.85 in MW and around 1.25 in NW. SRIM provided a value of 38.44 vacancies per He ion. Thus, significant recombination between vacancies and SIAs

($V + I \rightarrow \emptyset$) occurs in both cases, being slightly higher in MW. Figure 4.4(b) shows the profiles of vacancies retained in the grain interior for pure vacancy (V_m) or mixed He_nV_m clusters. The profiles in the case of pure V_m clusters are very similar in MW and NW. In both cases most of them belong to small V_m clusters with less than 10 vacancies (91% and 66%, respectively). Indeed, almost all the vacancies remain isolated, i.e., they are not part of any clusters, and they distribute almost homogeneously all over the implantation volume. In the case of vacancy profiles being part of He_nV_m clusters, their distribution in depth is also similar; in both cases, the mixed He_nV_m clusters are concentrated in the “damaged volume”. The main difference lies in the size of the clusters, which are larger in NW than in MW.

Figure 4.4. Total He concentration (a) and vacancy concentration in pure V_m clusters or mixed He_nV_m clusters (b) as a function of depth in both MW and NW after 490 pulses. Total He concentration profiles are compared with the He initial profile (a), immediately after the implantation as given by SRIM code.

Figure 4.5 the mixed He_nV_m cluster density in the “damaged volume” after 400 pulses is presented in histograms as a function of the number of vacancies (m) forming the cluster. In MW the cluster population is mainly composed of small clusters, whereas in NW

significantly larger clusters are formed. That is, the grain boundaries have a direct influence on the size of mixed He_nV_m clusters.

Figure 4.5. Mixed He_nV_m cluster concentration in the “damaged volume” as a function of their size.

It is very important to know the ratio between the number of He atoms and vacancies forming a mixed He_nV_m cluster because this parameter is related to the pressure inside the clusters. For this reason, the He/V ratio in mixed He_nV_m cluster inside the “damaged volume” has been analysed. In MW, after around 200 pulses, an almost constant number of clusters of low He/V ratio is observed, whereas the density of clusters with $\text{He}/\text{V} > 4$ increases. On the contrary, clusters with $\text{He}/\text{V} > 4$ are virtually absent in NW and the great majority of clusters have a low He/V ratio. The results after 400 pulses are shown in Figure 4.6.

Figure 4.6. Cluster density comparison between MW and NW after 400 pulses, as a function of their He/V ratio.

4.4 Discussion

He implantation at 625 keV leads to a large number of Frenkel pairs (38.44 FP per irradiated He ion), mostly in the “damaged volume”, the region between 900 and 1200 nm in depth direction (a volume of $300 \times 50 \times 50 \text{ nm}^3$). The results show clearly that: (i) the damage is in the form of mixed He_nV_m clusters, (ii) these mixed He_nV_m clusters are concentrated in a small volume, the so called “damaged volume”, and (iii) in the interior of a grain in NW, the He/V ratio is low and thus, low pressure is expected whereas in MW the trend is the opposite, i.e., a large He/V ratio is obtained.

The diffusion of the implanted He atoms is in competition with the more effective trapping at vacancy-type defects, resulting in a negligible diffusion out of the “damaged volume” and the formation of immobile mixed He_nV_m clusters. He dissociation energies from these defects are high (see Table 3.6) suppressing He release at the temperatures employed in the present study. Note that the base temperature is 773 K and that higher temperatures are only reached during very short periods of time of $\sim 2 \mu\text{s}$. As a result, 100% of He atoms are retained in MW. This behaviour was pointed out by Debelle *et al.* in Ref. [149] in the case of He irradiation at 500 keV, which is an energy similar to the He energy of the present study (665 keV). Debelle *et al.* implanted ^3He (500 keV) in polycrystalline tungsten at three different fluences (10^{15} , 10^{16} and 10^{17} cm^{-2}) followed by a thermal annealing at 1473 or at 1773 K, during 70 and 60 minutes, respectively. Contrary to He desorption observed in the experiments of He irradiation at 60 keV [148], in the case of He irradiation at 500 keV they did not observe He desorption, with a relative precision of $\sim 3\%$. Moreover, Gilliam *et al.* [150] observed similar results in their experiments. They implanted ^3He at higher energies (500 keV) but similar fluence (10^{16} cm^{-2}) and they did neither observe any change in He retention after flash annealings at higher temperature (2273 K). The results presented in this Chapter follow the same trend observed in these experiments. In the case of NW, the process is similar to that observed in the simulations of MW, i.e., no desorption from the free surface occurs. However, the close vicinity to grain boundaries (note that grain dimensions are $1300 \times 50 \times 50 \text{ nm}^3$), leads to immobilization of He atoms (50%) in the interior of the grain and the other 50% reaches the grain boundaries. Whether He atoms that reach the grain boundaries remain retained in their interior or can migrate along them is out of the scope of this study, as the analysis is focused of He behaviour in the interior of the grain.

To evaluate the influence of grain size and therefore, the grain boundary density, simulations of 625 keV He irradiation in NW with larger grains ($100 \times 100 \times 1300 \text{ nm}^3$ grain dimensions), i.e., lower grain density were also carried out. The results are shown in

Figure 4.7, where the retained He fraction in both grains of $50 \times 50 \times 1300 \text{ nm}^3$ and $100 \times 100 \times 1300 \text{ nm}^3$ dimensions was calculated. These results reveal a clear trend: the lower the grain boundary density, the higher the He retention in He_nV_m clusters formed in the interior of the grain. Grains with $1300 \times 100 \times 100 \text{ nm}^3$ dimensions retain 20% more He atoms than the grains with $1300 \times 50 \times 50 \text{ nm}^3$ dimensions, which evidences a clear influence of the grain boundary density on the number of He atoms retained in He_nV_m clusters.

Figure 4.7. Retained He fraction as a function of time (and fluence) in NW with two different grain size: $1300 \times 50 \times 50 \text{ nm}^3$ and $1300 \times 100 \times 100 \text{ nm}^3$.

In this study, the temperature of W reaches $\sim 1500 \text{ K}$ just after the He pulse and then drops very rapidly to 773 K (Figure 3.9). Although the migration energy of a single vacancy is high (1.66 eV), this temperature is high enough to enable vacancy migration. However, vacancies turn out to be not very mobile and remain near their initial positions. Neither in MW nor in NW can vacancies reach the free surface. In NW only a small fraction of them reaches the surrounding grain boundaries. The higher number of vacancies in NW comparing to MW is determined by defect annihilation ($\text{V} + \text{I} \rightarrow \emptyset$) not by vacancy mobility. SIAs migrate so fast at the simulation temperatures (see migration energy in Table 3.2), that they can reach the free surface in the case of MW and not only the free surface but also the surrounding grain boundaries in the case of NW. In the latter case, the SIAs reach the grain boundaries before finding a vacancy to annihilate with, leading to a larger number of vacancies in the interior of the grain.

There is almost no He atoms retained in mixed He_nI_m . It can be explained as follows: on the one hand, the binding energies of He atoms to mixed He_nI_m clusters [66] are much lower than the binding energies to mixed He_nV_m (Table 3.6) and thus, more efficient emission from mixed He_nI_m clusters occurs. On the other hand, vacancy mobility is much lower than that of SIAs (Table 3.2), which results in a much larger vacancy population than SIA

population inside W. Thus, the great majority of He atoms are trapped in vacancy clusters (He_nV_m). This effect is more evidenced in the case of NW, where SIAs can leave the simulation box not only through the desorption surface or far inside the W, but also through the grain boundaries. A similar behaviour is described in the simulations carried out by De Backer *et al.* [137,138], in the case of W implanted at ~300 K with 800 keV ^3He atoms and subsequently annealed from 300 to 900 K, at fluences from 10^{17} to $5 \times 10^{16} \text{ cm}^{-2}$.

As a result, in both MW and NW almost all the He atoms are retained in mixed He_nV_m clusters in the “damaged volume”. A better understanding of the size and composition of this He_nV_m clusters will lead to a better understanding of the whole problem, as they control the response of the material to He irradiation.

The cluster density as a function of their He/V ratio in both MW and NW after 400 pulses is shown in Figure 4.6. In NW, it can be observed that the majority of the clusters have low He/V ratio. After the formation of a certain number of immobile mixed He_nV_m clusters, the incoming He ions from later pulses are mainly retained inside them. As there are more vacancies per implanted ion after each pulse (1.25 remaining vacancies per implanted ion), these clusters tend to maintain the He/V ratio or even decrease its value. Thus, it is not expected a significant increase of the pressure inside the grain in NW with the increasing number of pulses. In MW there are 0.85 remaining vacancies per implanted He. The He/V ratio tends to increase with the increasing number of pulses, leading to a lower cluster density with lower He/V ratio and a higher density of clusters with He/V ratio > 4. This indicates that pressure seriously increases with the number of pulses.

The different defect configuration in MW and in NW may lead to a different mechanical behaviour, since the size and He/V ratio of mixed He_nV_m clusters have an influence on it. The total elastic strain energy has been compared for both MW and NW (Figure 4.8), calculated as the sum of the elastic strain energy generated by each single cluster making use of the equation published by Wolfer in Ref. [151]. This equation takes into account not only the pressure inside each He_nV_m cluster (p_i) but also its volume (V_0):

$$E_p(p_i) = \frac{3V_0 p_i^2}{8\mu}, \quad (4.1)$$

where E_p is the elastic strain energy and μ the shear modulus of W. The volume of the mixed He_nV_m clusters has been assumed as the sum of the volume of each vacancy:

$$V_0 = m \cdot V_1, \quad (4.2)$$

where m is the number of vacancies in the He_nV_m cluster and V_1 is the volume of a single vacancy, calculated as:

$$V_1 = \frac{4}{3}\pi \left(\frac{a}{2}\right)^3, \quad (4.3)$$

where a is the lattice parameter of the W ($a = 3.172 \text{ \AA}$). In order to calculate the pressure inside these mixed He_nV_m clusters, it has been calculated by using the Mills-Liebenberg-Bronson (MLB) semiempirical equation of state (EOS) [152]. Although the limits of MLB-EOS are $0.2 < P < 2 \text{ GPa}$ [152], Donnelly [36] used this EOS even at a pressure 50 times higher than the upper limit (up to 100 GPa) and it is widely used nowadays [119,153] for this purpose. The evolution of the total strain energy in MW and in the interior of a grain in NW as a function of the time (and fluence) is shown in Figure 4.8.

Figure 4.8. Total elastic strain energy as a function of time (and fluence). The elastic strain energy corresponding to each He_nV_m cluster was calculated [151]. The figure represents the sum of all of the elastic strain energies in both MW and NW.

The trend is clear: in MW, the elastic strain energy increases while in the interior of a grain in NW, its increase is negligible, as it remains almost constant. Although at the beginning of the irradiation the difference between both materials is not so high, after 400 pulses the elastic strain energy in MW is 122.24 J cm^{-3} and in the interior of a grain in NW it takes a value of 4.03 J cm^{-3} . This result shows that the interior of a grain in NW will be subject to a lower stress than the MW, extending the life service of the material.

Gao *et al.* [154,155] suggest for iron at room temperature that these overpressurized He_nV_m clusters will deform the lattice around them and finally the emission of a SIA will occur to release the pressure inside. This emitted SIA is bond to the He_nV_m clusters and remains in its surroundings, as was observed experimentally in steel by Chen *et al.* [156]. Similar mechanisms are proposed for He in W [117,118,157]. They were not included in the present simulations, as the irradiation with He ions of 625 keV produces huge number of Frenkel pairs. The number of clusters with very high He/V ratio ($\text{He}/\text{V} = 9$), which would lead to the so called “trap mutation” mechanism, is negligible. Thus, “trap mutation” is not

expected to be relevant in the irradiation conditions simulated in the present Chapter. “Trap mutation” is important when irradiating He at low energy, as is the case of the study presented in Chapter 6.

4.5 Conclusions

An OKMC model parameterized with DFT data was used to simulate He irradiation in W up to a fluence of $\sim 10^{16} \text{ cm}^{-2}$ and at relatively high temperature (up to 1500 K). A comparison with experimental data on He desorption has been carried out in order to validate the parameterization at these temperatures. Both computational and experimental results are in good agreement, which leads to conclude that the parameterization is appropriate for applications at these high temperatures.

Simulation of 625 keV He ion irradiation in MW reveal no He desorption at the desorption surface. In MW, 100% He atoms are retained. In NW, $\sim 50\%$ of the He atoms are retained in the interior of the grain of $1300 \times 50 \times 50 \text{ nm}^3$ dimensions, whilst the other 50% reached the grain boundaries. In the case of NW with larger grains, the number of retained He atoms at the grain boundaries decrease: in a grain four times larger ($1300 \times 100 \times 100 \text{ nm}^3$ dimensions), this value drops down to $\sim 30\%$. As a conclusion, the grain boundary density has a huge influence in the trapping mechanism of He atoms.

On the one hand, the number and distribution of pure vacancy clusters (V_m) are similar in both cases. Mixed $\text{He}_n V_m$ clusters turn out concentrated in a small “damaged volume” at around 1000 nm. On the other hand, the size and number of He atoms in the mixed $\text{He}_n V_m$ clusters is different in the interior of a grain in NW and in MW. The trend is clear: in NW, mixed $\text{He}_n V_m$ clusters are larger (they have more vacancies) and their He/V ratio is lower. Therefore, mixed $\text{He}_n V_m$ clusters in the interior of a grain in NW are less pressurized. The grain boundary has a clear influence on the size and type of mixed $\text{He}_n V_m$ clusters in which they are trapped. The pressures built in mixed $\text{He}_n V_m$ clusters in MW are considerably higher than in clusters in the interior of the grain in NW.

The value of the elastic strain energy is lower in the interior of the grain in NW than in MW. Moreover, while in MW a significant increase in the elastic strain energy is observed, in NW it remains almost constant. As a conclusion, it can be said that not only the NW is less pressurized than the MW, but also that as the number of pulses increases, the difference also increases. A better response of NW would then be expected at higher He irradiation fluence.

5 Hydrogen irradiation in tungsten: high and low grain boundary density

Chapter 4 includes the analysis of helium irradiation in both monocrystalline and nanocrystalline tungsten. A similar study in the case of hydrogen irradiation is presented in this Chapter. The relevance of this study stems from the fact that tungsten as a plasma facing material will be exposed to hydrogen irradiation (see Chapter 1). Three different types of tungsten (regarding the grain boundary density) were studied experimentally and by computer simulations. Monocrystalline tungsten (MW) has no grain boundaries at all, coarse-grained tungsten (CGW) presents grains of μm dimensions, i.e., has an intermediate grain boundary density and finally, nanocrystalline tungsten (NW) is formed by grains of tens of nm dimensions, i.e., has a high grain boundary density.

The samples were implanted with hydrogen and carbon ions in different conditions: (i) hydrogen single implantation, (ii) carbon and hydrogen co-implantation and (iii) carbon and hydrogen sequential implantation. OKMC simulations were performed by using the MMonCa code. From the analysis of the results, it can be reported that (i) grain boundaries have a clear influence on the number and distribution of vacancies, being the vacancy concentration larger in NW than in MW, (ii) hydrogen retention is highly influenced by both the grain boundaries themselves and the vacancy concentration, (iii) the size of H_nV_m clusters is slightly influenced by the presence of grain boundaries, as the great majority of H atoms are retained in monovacancies and (iv) it can be inferred, from the comparison between experimental and computational results, that grain boundaries act as preferential paths for hydrogen diffusion.

The study of helium (Chapter 4) and hydrogen (this Chapter) irradiation in nanocrystalline tungsten reveals that a better response to ion irradiation is expected than in monocrystalline tungsten. Helim-vacancy clusters are less pressurized and hydrogen ions can be released from the material along the grain boundaries. For these reason, both studies open a new path to investigate these nanostructured materials for fusion purposes.

The study reported in the present Chapter is under revision in *Acta Materialia* [55].

5.1 Introduction

Light species such as hydrogen [30,31] and helium [32,33] in tungsten tend to nucleate in defects resulting in detrimental effects: cracking, exfoliation or blistering, which are unacceptable for W applications as plasma facing material (PFM). Therefore, there is a need to develop materials based on W, capable to withstand the expected harsh conditions (extreme irradiation and large thermal loads) that will take place in future nuclear fusion reactors.

In the case of direct drive targets in inertial confinement fusion (ICF), as described in Chapter 1, H ions are expected to reach PFMs at energies high enough to produce Frenkel pairs (FPs), i.e., vacancies (Vs) and self-interstitial atoms (SIAs) [29]. According to literature, H mobility in tungsten strongly depends on the presence of vacancies, since H atoms get easily trapped at them with a high binding energy. DFT results, see Refs. [122,123,128,130–133], show a binding energy of a H atom to a vacancy higher than 1 eV (see Figure 3.5). Nanostructured materials have a large density of grain boundaries (GBs) which, depending on the irradiation conditions, have a clear influence on the distribution of both FPs and light species such as H [49]. Refs. [158–160] indicate that SIAs migrate towards GBs, whilst vacancies remain in the interior of the grains. The temperature may play an important role regarding FP annihilation at the GBs, as vacancies start to diffuse at higher temperature than SIAs [46–48]. H behaviour at GBs is still unclear. On the one hand, some authors showed that H atoms experience enhanced diffusion along GBs with a migration energy lower than in the bulk [161,162]. Thus, GBs might act as preferential diffusion path for H atoms [163]. On the other hand, some other works report that the migration energy along the GBs is higher than in the bulk [164]. Therefore, the physical mechanisms for neither FPs nor H atoms at GBs are well understood.

Another important point about H trapping at GBs is whether H atoms get trapped at vacancies formed in the GBs or in their vicinity or, on the contrary, at GBs themselves. The fact that the formation energy of vacancies in the GB region [161,162] is lower than that in the bulk [66] may facilitate the trapping of H atoms in vacancies formed at the GBs. Thus, the role of vacancies (and in turn, temperature) in the case of the observed H concentration enhancement at the GB region is not clear [164,165].

In this Chapter, it is presented a study of H behaviour in three kinds of materials with different GB densities: nanostructured tungsten (NW) with a large GB density, coarse-grained tungsten (CGW) with a lower GB density and monocrystalline tungsten (MW), with no GBs at all. The goal is to contribute to a better understanding of the role of GBs on

the H behaviour in W at a temperature of 300 K. For this purpose, experimental measurements were compared to the theoretical results (see Figure 5.1) calculated with the MMonCa code [51], the object kinetic Monte Carlo (OKMC) simulator described in Section 3.3.

Figure 5.1. Scheme of H irradiation in nanocrystalline tungsten, as carried out in the experiments (a) and the simulations with the MMonCa code (b).

Three different irradiation scenarios were studied both experimentally (in CGW and NW) and by means of OKMC simulations (in MW and NW): (i) H single implantation (NW-H, CGW-H, and MW), (ii) C and H co-implantation (NW-Co-CH, CGW-Co-CH and MW-Co-CH) and (iii) sequential C and H implantation (NW-Seq-CH, CGW-Seq-CH and MW-Seq-CH). The simulation conditions were selected to mimic the experiments. However, in the case of CGW, huge simulation times would be needed. For this reason, monocrystalline W

(i.e., no GBs at all present in W) was simulated instead of real CGW. The comparison between MW and NW helps in the understanding the role of GBs. H and V distributions as well as the type and size for H_nV_m clusters are analysed in detail in order to assess the influence of the GB density on them.

5.2 Experiments

Pure α -phase, nanocrystalline W coatings preferentially oriented along the α -(110) direction, with a thickness of $\sim 1.2 \mu\text{m}$ and a root mean square (rmw) roughness lower than 3 nm were deposited by DC magnetron sputtering from a pure (99.95%) W commercial target at a normal incidence angle on a single-side polished Si (100) substrate. The deposition setup consists of a high vacuum chamber with a base pressure in the 10^{-6} Pa range, equipped with a 5 cm diameter magnetron designed and manufactured by Nano4Energy SL [166]. Deposition took place in the presence of a pure argon (Ar) atmosphere (99.9999%) at room temperature. The Ar pressure was 8×10^{-1} Pa, the plasma power was 45 W and the target-substrate distance was 8 cm. The coatings are constituted of columns that grow perpendicular to the substrate, presenting an inverted pyramidal shape (compatible with the zone T in the morphology diagram of Thornton [167]) having a diameter of ~ 100 nm at the coating surface. A more detailed description of the morphological and microstructural properties of the coatings is found in Ref. [43].

In order to study the influence of the sample microstructure on H behaviour, two types of W samples were selected: the first type is the previously mentioned home-made nanostructured W (see Figure 5.2) and the second type is commercial CGW with a grain size in the μm range. A first set of samples was implanted with H (NW-H and CGW-H). With a view to study the influence of irradiation induced damage and microstructure on the H behaviour, a second set of samples was sequentially implanted first with C and then with H (NW-Seq-CH and CGW-Seq-CH cases). For the purpose of assessing the influence of the synergistic effect on the radiation-induced damage and on H retention, a third set of samples was simultaneously implanted with C and H (NW-Co-CH and CGW-Co-CH cases). All implantations were performed at room temperature. In order to mimic the expected H isotope energies in future HiPER-type power plants, the implantation energies were selected to be 170 and 665 keV for H and C, respectively [168]. The implantation fluence for both H and C was $5 \times 10^{16} \text{ cm}^{-2}$. Irradiation conditions are summarized in Table 5.1. The implantations were performed at the Helmholtz-Zentrum Dresden-Rossendorf (HZDR), in Germany. Prior to implantation and in order to achieve a higher depth resolution when carrying out Resonant Nuclear Reaction Analysis (RNRA) experiments, the CGW samples were mechanically polished by using napless synthetic cloth. For the

first rough polishing step at 0.5 μm , colloidal alumina was used. The second polishing was done by using a 0.03 μm colloidal alumina. The CGW samples were heated neither before nor after polishing. The NW samples did not need any treatment before implantation because their rms was lower than 3 nm.

Figure 5.2. Nanocolumnar W, deposited by DC magnetron sputtering [43].

The H depth profiles were characterized by RNRA experiments, using the $\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ nuclear reaction [169] with a N^{2+} beam impinging onto the sample surface at normal incidence. This reaction has a sharp resonance at 6.385 MeV. The beam energy was varied in the range from 6.425 to 11.033 MeV. The 4.43 MeV γ -rays were detected by a $10 \times 10 \text{ cm}^2$ BGO detector mounted immediately outside the vacuum chamber at about 1.5 cm behind the sample. Some special precautions were taken in order to carry out reliable depth profiling measurements and to avoid ion beam-induced H diffusion [170]. The beam spot and the current were selected to be $2 \times 2 \text{ mm}^2$ and $\sim 10 \text{ nA}$, respectively. In addition, the beam spot position was changed every two measurements. As described in Ref. [171], in order to ensure that the selected experimental configuration does not lead to ion beam-induced diffusion, several spectra were sequentially measured on the sample point up to a dose 10 times higher than that used in these experiments. No ion beam-induced H diffusion was detected in any case. More details about RNRA characterization are given in Ref. [49].

5.3 Simulation methods

OKMC simulations were performed with the MMonCa code [51], parameterized as described in Chapter 3.2. Note that pure H clusters (H_n) cannot be formed due to the large repulsive energy between H atoms, as has extensively been reported [124,125]. Thus, the

clusters that can be formed are pure vacancy clusters (V_m), pure SIA clusters (I_m) and mixed $\text{He}_n V_m$ and $\text{He}_n I_m$ clusters.

The goal was to simulate high and low GB density samples to compare with the experiments carried out with CGW and NW samples. A simulation box of $1000 \text{ (depth)} \times 10 \times 10 \text{ nm}^3$ with periodic boundary conditions (PBCs) in the four lateral surfaces was used. In this case, GBs were completely ignored. Instead of simulating a polycrystalline material with grain sizes of the order of microns (as the CGW samples used for experiments), in this way, a monocrystalline material (MW) is simulated. This is computationally affordable unlike the simulation of CGW, which requires simulation boxes of the order of the grain size, i.e., of the order of μm^3 , at least 100 times larger than the boxes necessary to simulate MW. In the case of nanostructured tungsten (NW), a simulation box of $1000 \text{ (depth)} \times 50 \times 50 \text{ nm}^3$ was used (see Figure 5.3).

Figure 5.3. Schematic view of (a) monocrystalline and (b) nanocrystalline W simulation boxes. In monocrystalline W, periodic boundary conditions were set in the four lateral surfaces. This is a limit case of low GB density, as no GBs are simulated at all. In the case of nanocrystalline W, the four lateral surfaces are perfect sinks for defects, to reproduce the effect of GBs.

In order to reproduce the GBs, the four lateral surfaces were considered as perfect sinks, i.e., all the defects (vacancies, SIAs and H atoms) that reach GBs were removed out of the simulation. This approximation turned out as sufficiently accurate to study GB behaviour in the case of helium irradiation, as described in Chapter 4. Therefore, only defects present in

the interior of the grain were taken into account, not those that reach GBs. In both MW and NW, the top surfaces were considered as desorption surfaces, whereas atoms reaching the bottom surfaces were considered to move further deep into the bulk and thus ignored. The temperature in all the simulations was 300 K, as the experiments were carried out at this temperature [49]. In order to mimic the experimental procedure as much as possible, an annealing of 10 days at 300 K was also simulated after C and/or H irradiation during 5 h, in every simulated case (both MW and NW in the three different irradiation scenarios). Thus, the period of time between the irradiation in the experimental facility and the analysis of the samples was also taken into account. The irradiation conditions in experiments and simulations are presented in Table 5.1.

Table 5.1. Irradiation conditions in experiments (CGW and NW) and simulations (MW and NW).

Sample code	Type of W	Type of study	H irradiation		C irradiation		Comment
			Energy (keV)	Fluence (cm ⁻²)	Energy (keV)	Fluence (cm ⁻²)	
MW-H	Monocrystalline	Computational	170	5×10^{16}	-	-	-
CGW-H	Coarse-grained	Experimental	170	5×10^{16}	-	-	-
NW-H	Nanocrystalline	Computational and experimental	170	5×10^{16}	-	-	-
MW-Co-CH	Monocrystalline	Computational	170	5×10^{16}	665	5×10^{16}	C and H simultaneous implantation
CGW-Co-CH	Coarse-grained	Experimental	170	5×10^{16}	665	5×10^{16}	C and H simultaneous implantation
NW-Co-CH	Nanocrystalline	Computational and experimental	170	5×10^{16}	665	5×10^{16}	C and H simultaneous implantation
MW-Seq-CH	Monocrystalline	Computational	170	5×10^{16}	665	5×10^{16}	H implanted after C implantation
CGW-Seq-CH	Coarse-grained	Experimental	170	5×10^{16}	665	5×10^{16}	H implanted after C implantation
NW-Seq-CH	Nanocrystalline	Computational and experimental	170	5×10^{16}	665	5×10^{16}	H implanted after C implantation

Damage cascades produced by H (170 keV) or C (665 keV) irradiation were calculated with the SRIM code [62], following the methodology described in Section 3.1 to obtain the positions of SIAs. Damage cascades were introduced in the simulation box at a flux of $2.78 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ during 5 h, reaching a fluence of $5 \times 10^{16} \text{ cm}^{-2}$, for both H and C irradiation. On the one hand, in the case of H irradiation, the final positions of H ions, vacancies and SIAs were introduced in the simulation box. On the other hand, for

simplicity, in C irradiation only FPs created by C (665 keV) irradiation were introduced, i.e., vacancies and SIAs, but not C ions. This approximation is justified by the fact that C atoms do not trap H atoms in W. Ou *et al.* [172] have recently described that C, in interstitial position, is not capable of capturing H atoms efficiently because of Coulomb repulsion between negatively charged C and H atoms in W. They reported that the binding energy between C and H is repulsive ($E^b = -0.42$ eV). In case C atoms are in substitutional positions, i.e., bound to a vacancy, they are able to trap H atoms, as stated by Ou *et al.* [172] and Heinola *et al.* [173]. However, substitutional C can only occur significantly if either C atoms or vacancies can migrate. Due to the large migration energy at 300 K of C ($E^m = 1.69$ eV [174]) and V ($E^m = 1.66$ eV [66]), both can be considered immobile. In addition, the negligible fraction of C atoms that reach an existing vacancy upon thermalization is not completely ruled out, because in the simulations the vacancy acts as a trap for H, similarly as substitutional C atoms, due to the binding energies of C-V complexes, very similar to those of single vacancies [172–174]. However, Ahlgren *et al.* [175] published that impurities play a significant role as they decrease Frenkel pair annihilation by trapping SIAs. In the case of NW this effect is not expected to happen, as SIAs preferentially reach the grain boundaries rather than the C atoms (grain dimensions $1000 \times 50 \times 50$ nm³). In the case of MW, SIA trapping at 300 K is not important, since the binding energy of C atoms to SIAs is low ($E^b = 0.33$ eV [66], $E^b = 0.43$ eV [132]) making C atoms to not effectively trap SIAs [132].

A concern regarding the chosen small simulation boxes in MW is related to the lateral straggling of the incoming H and C ions (236 and 220 nm, respectively), which is much larger than the lateral dimensions of the simulation boxes (10×10 nm²). MMonCa introduces the defect positions taking into account PBC and this could have an effect on the cluster formation. Simulation of H (170 keV) irradiation during 1800 s in four different simulation boxes were carried out. Results of H retention and V concentration, shown in Figure 5.4(a) and Figure 5.4(c) respectively, reveal that there is not a high influence on the size of the simulation box. In order to simulate a larger box ($1000 \times 100 \times 100$ nm³), shorter simulations were carried out. Results shown in Figure 5.4(b) and Figure 5.4(d) reveal a similar trend regarding H and V concentration in depth in all the simulation boxes. Moreover, the formation of vacancy clusters could have an effect on H retention. However, as it can be seen in Figure 5.8, more than 90% of H atoms are retained in monovacancies in MW-H. Thus, simulation boxes as small as $1000 \times 10 \times 10$ nm³ can be used for H (170 keV) irradiation.

Figure 5.4. Comparison of defect concentration after H (170 keV) irradiation, obtained with simulation boxes of different sizes. Results of (a) H and (c) V concentration after 1800 s of H irradiation and of (b) H and (d) V concentration after 720 s of H irradiation are shown.

The same simulations, but in case of C (665 keV) irradiation were carried out, to assess the accuracy of small simulation boxes in the case of MW-Co-CH and MW-Seq-CH.

Figure 5.5. Comparison of vacancy concentration after C (665 eV) irradiation during 1800 s, by using simulation boxes of different sizes.

As can be seen in Figure 5.5, similar results were obtained in all the simulation boxes, regarding vacancy concentration. As in the case of H irradiation, more than 90% of H

atoms are retained in monovacancies in MW-Co-CH and MW-Seq-CH (see Figure 5.4). Thus, simulation boxes as small as $1000 \times 10 \times 10 \text{ nm}^3$ can be used for C (665 keV) irradiation.

5.4 Results

Figure 5.6 shows the implantation profiles of vacancies generated by H (170 keV) and C (665 keV) ions in W, (mean implantation range ~ 550 and ~ 400 nm, respectively) obtained with the SRIM code.

Figure 5.6. (a) Vacancy concentration as a function of depth per C or H ion as calculated with the SRIM code. Also H concentration is shown. Vacancy concentration calculated with OKMC (MMonCa code) as a function of the depth, in the case of H irradiation (b) or C and H irradiation (c), both simultaneously or sequentially

irradiated. (b) and (c) show the final vacancy concentration just after 5 h of C and/or H irradiation in MW and NW calculated with OKMC (MMonCa code).

Carbon ions are responsible for the great majority of vacancies. The calculated number of FPs produced per incoming ion is on average 363 for C and 2.3 for H. The vacancy profiles calculated with OKMC show that the vacancy concentration is systematically much higher in NW (high GB density) than in MW (no GBs at all), i.e., the GB density dramatically affect the resulting vacancy concentration. In MW, most vacancies annihilate with SIAs, whereas in NW a much higher fraction (around 9 times higher) of vacancies survives after the irradiation due to the efficient role of GBs as sinks for (highly mobile) SIAs, as shown in Table 5.2.

Table 5.2. Remaining vacancies after at the end of the 10 days annealing, with respect to the total generated vacancies due to ion (C and/or H) irradiation.

Simulation code	Remaining vacancies (%)
MW-H	0.9
NW-H	9.3
MW-Co-CH	0.1
NW-Co-CH	0.8
MW-Seq-CH	0.1
NW-Seq-CH	0.9

Regarding H concentration, the attention is focused on the region between 150 and 1000 nm, where the radiation-induced damage is mainly generated. In this thesis, this region is called “damaged volume”. Although a surface effect on H desorption from the surface has been reported [176], the high H concentration near the irradiation surface observed in the experiments (Figure 5.7) is mainly related to surface contamination [49]. For this reason, the surface effect on H retention was not simulated. In this study, all the simulation results refer to H and defects present in the interior of the grain, and not at the GBs. The H profile calculated with MMonCa resembles the H profile predicted by SRIM for the high GB density material (NW) but not for the GB-free material (MW), see Figure 5.6. Thus, H atoms are trapped near their implantation positions, obtaining a very good agreement between simulations and experiments in all NW cases (see Figure 5.7).

In the case of MW-H irradiation, since only 2.3 vacancies per H ion are generated, there is a very high diffusion of H atoms, leading to only 7.6% retention after the irradiation and the subsequent 10 days annealing, see Figure 5.7(a). Since there are no GBs at all, the annihilation between vacancies and SIAs leads to a low vacancy concentration and thus, small trapping sites for H atoms. As a result, the simulated H profile (MW-H) is almost constant in the “damaged volume”, since H atoms diffuse all along the depth direction. In

the case of experimental results in CGW-H, a higher H retention between 300 and 800 nm appears, as shown in Figure 5.7(a). In this case, the GBs present in the sample might lead to a lower annihilation rate between vacancies and SIAs, as some of the SIAs will reach the GBs before finding a vacancy to annihilate with. Thus, there should be a higher vacancy concentration and a higher H retention.

Figure 5.7. H concentration as a function of depth in CGW (experiments) or MW (simulations), and NW (both experiments and simulations), depending on the irradiation conditions: H single implantation for CGW or MW (a) and for NW (b), C and H co-implanted for CGW or MW (c) and NW (d) and C and H sequential implantation for CGW or MW (e) and NW (f). The simulation results are calculated after the annealing of 10 days at 300 K. The region between 0 and 150 nm (in blue) has been taken into account neither in the results nor in the discussion because it is highly influenced by surface contamination [49].

On the contrary, in the case of NW-H (both simulations and experiments), there is a higher H retention, see Figure 5.7(b). As GB density increases, the annihilation between vacancies and SIAs decreases, leading to a higher vacancy concentration in the interior of the grain. H atoms are retained between 600 and 800 nm in depth, which corresponds to the H implantation range calculated with the SRIM code, see Figure 5.6. H atoms are trapped near their implantation positions, implying that there is low H diffusion.

Carbon and hydrogen simultaneous irradiation leads to different results, which can be observed in Figure 5.7(c) and (d). In the NW-Co-CH case, the simulated H profile is in good agreement with the experimental one. In addition, the total H retention is almost the same in the simulations (46.5%) as in the experiments (42.0%). Comparing the MW-Co-CH case (simulations) with the CGW-Co-CH (experiments), it can be observed that there is a higher H retention between 150 and 540 nm and a lower He retention between 540 and 1000 nm in MW-Co-CH than in CGW-Co-CH, see Figure 5.7(c) and Table 5.3. In MW-Co-CH, the main H retention peak appears at ~400 nm, corresponding to the C irradiation-induced vacancies. This result stems from ignoring the GBs in MW-Co-CH. Since H atoms cannot reach any GB, their only way to diffuse is along the irradiation direction (X direction). In their migration to the irradiation surface, H atoms reach a highly vacancy populated region at ~400 nm, which leads to a high trapping rate of H atoms in those vacancies. This explains the differences in the H profile between 150-540 nm. A possible explanation for the experimentally measured H retention at depths >800nm would be that H is trapped in other defects apart from vacancies, for instance dislocations [177] to which H atoms can migrate thanks to the low vacancy population as compared to the experimental NW-Co-CH.

Table 5.3. Total H retained fraction between 150 and 1000 nm, at 300 K, measured from experiments or calculated by MMonCa just after the irradiation or after the subsequent annealing during 10 days at 300 K.

Sample code	Exp. H retention (%)	MMonCa H retention (%) just after C and/or H irradiation	MMonCa H retention (%) after 10 days annealing
MW-H	-	11.6	7.6
CGW-H	17.0	-	-
NW-H	31.0	33.0	32.4
MW-Co-CH	-	57.4 (150-540 nm)	58.1 (150-540 nm)
CGW-Co-CH	25.0 (150-540 nm)	-	-
NW-Co-CH	42.0	46.5	46.2
MW-Seq-CH	-	94.7	94.3
CGW-Seq-CH	42.0	-	-
NW-Seq-CH	48.0	53.2	53.0

In the NW-Seq-CH case, see Figure 5.7(f), the simulated H profile is in good agreement with the experimental one, as in the previous case, showing a H retention peak at ~650 nm

in depth in both experiments and simulations. In addition, the total retained fraction observed experimentally corresponds with that obtained from the simulations (42.0% and 53.2%, respectively). In the case of MW-Seq-CH (simulations), a much higher H retention is observed when comparing to CGW-Seq-CH (experiments), see Table 5.3. Again, there is a much higher H retention in the case of MW-Seq-CH, as the simulations ignore the GBs, and H atoms can only diffuse along the X direction. When H atoms reach the highly vacancy populated region at ~400 nm, they are trapped in the vacancies.

It is worth mentioning that an effect of the type of C and H irradiation (sequentially or simultaneously irradiated) can be observed regarding the type of W. On the one hand, there is no difference in the H retention profile between NW-Co-CH and NW-Seq-CH. On the other hand, a difference between MW-Co-CH and MW-Seq-CH and also between CGW-Co-CH and CGW-Seq-CH can be observed. In the case of C and H simultaneously irradiated, there is a lower H trapping in the vacancies created by C irradiation, compare Figure 5.7(c) and (e). This leads to a higher H diffusion.

Figure 5.8. Retained H (%) in monovacancies, i.e. ($H_n V_1$) with respect to the total retained H, after 10 days of annealing at 300 K.

Concerning the type and size of clusters at which H atoms are trapped, all the simulations show the same trend: more than 90% of H atoms are retained in monovacancies with different H content (see Figure 5.8). The migration energy for a single vacancy is so high that vacancies turn out immobile at 300 K, as previously reported both by experiments and by DFT calculations. Thus, the formation of vacancy clusters is prevented either in MW or in NW, regardless the type of irradiation (single H irradiation, C and H simultaneously irradiated or C and H sequentially irradiated).

5.5 Discussion

The OKMC parameterization for hydrogen in tungsten described in Section 3.2.3 reproduces a variety of irradiation conditions at 300 K. Furthermore, the discrepancies in the case of experimental low grain boundary W (CGW) and high grain boundary density (NW) results can be explained by the simulation results of MW (no grain boundaries).

Hydrogen atoms get trapped at vacancies forming mixed H_nV_m clusters. As described in Section 5.3, H atoms cannot form pure H clusters (H_n). Thus, the process of “self-trapping” described for He in W [157], i.e., the emission of a W atom from its lattice position creating a vacancy in which He atoms get trapped, is not possible in this case. In addition, the H-SIA trapping mechanism at 300 K is inefficient due to its low binding energy (0.33 eV). Therefore, the retention of H is determined by the density and distribution of surviving vacancies (those that did not annihilate with SIAs). The initial cascades calculated with the SRIM code shown in Figure 5.6(a) correspond to the FP profile assuming no annihilation. If annihilation is considered, the vacancy profiles clearly differ from the ones calculated by SRIM, as shown in Figure 5.6(b) and (c). At 300 K, vacancies are immobile, $E^m(V)=1.66$ eV, unlikely highly mobile SIAs, $E^m(I)=0.013$ eV, which are able to annihilate at free surfaces, at grain boundaries (lateral surfaces in the case of NW simulations) and with vacancies. In all the NW cases, the maximum H retention in both experiments and simulations is observed between 600 and 700 nm, which corresponds to the H range as calculated by SRIM, see Figure 5.6(a). Contrary to this, in MW simulations higher vacancy annihilation rate occurs (~ 9 times higher than in NW in all the simulations, see Table 5.2). The resulting vacancy profile completely differs with respect to that predicted by SRIM, resulting in an almost constant vacancy concentration all along the “damaged volume”. This can be observed in the case of single H irradiation comparing Figure 5.7(a) to (b), MW-H and NW-H, respectively. Due to this low vacancy concentration for MW-H samples, the H atoms are able to migrate along bulk W and get trapped at vacancies far away from their initial positions. Since GBs are completely ignored in MW simulations, the vacancy concentration reduction is considerably larger than in the experimental CGW-H results, the latter corresponding to samples with low GB density, but not null.

As previously mentioned, nanostructured materials (high GB density) are considered as “self-healing” materials under certain circumstances [46], due to the enhanced annihilation of FPs at GBs, as reported for Cu [178,179], Cu-Nb interfaces [180] and W [181]. Indeed, the effect is rather general in metals [47,48]. The interaction of vacancies and SIAs at GBs can be explained by a three-step process, depending on the temperature of the metal, as described in Refs. [48,182]. Firstly, SIAs migrate due to their high mobility and get trapped

at GBs. At low temperature, the process ends at this stage, resulting in a higher vacancy density in nanostructured materials as compared to monocrystalline ones [159,183]. Secondly, at intermediate temperatures, SIAs that have been retained at GBs are emitted, migrating inside grains and annihilating more vacancies. Thirdly, at high temperature, vacancies become mobile and migrate, finding GBs at which they annihilate. The whole “self-healing” process can explain the experimental results of Chimi *et al.* [184] in nanostructured and polycrystalline Au. They reported that, on the one hand, the defect accumulation in nanocrystalline Au at ~15 K is larger than in polycrystalline Au (at 15 K, only the first step of the process might have taken place). On the other hand, at 300 K, defect accumulation becomes much smaller in nanocrystalline Au than in polycrystalline Au, showing the “self-healing” behaviour of nanocrystalline metals when the temperature is high enough for vacancies to migrate (at 300 K, the third step of the process is supposed to have occurred). In the case of W analysed in this Chapter, both the experiments and the simulations were carried out at 300 K. Nevertheless, at 300 K only the first step is expected to occur in W, contrary to what happens in Au, as both the formation ($E^f(V)_W \approx 3.23$ eV, $E^f(V)_{Au} \approx 0.94$ eV) and migration ($E^m(V)_W \approx 1.66$ eV, $E^m(V)_{Au} \approx 0.71$ eV) energies are much higher for W than for Au [66,185–187]. Therefore, the needed temperature for each of the previously described steps to happen is higher for W than for Au. Thus, the simple model used in the simulations presented in this Chapter, which considers GBs as perfect sinks, turns out good enough to reproduce the first step, responsible for the higher vacancy density in NW than in CGW, observed experimentally [49].

From the comparison between the experimental and computational results in the case of NW, H behaviour in GBs can be deduced. The simulated H profiles only include H atoms in the interior of the grain. Since simulations and experiments agree regarding both the total H fraction and the H profile, a major conclusion is that H atoms that reach the GBs can migrate along them towards the surface, and there desorb. This argument is also evidenced by the comparison between simulations in MW and in NW (see Figure 5.7). Since in MW H atoms can only diffuse along X direction, they get trapped at the abundant vacancies volume generated by C irradiation, at ~400 nm. On the contrary, in NW simulations, H retention at ~400 nm is not observed. Thus, it can be deduced that H atoms do not migrate along X direction, what implies that they reach GBs before reaching the high concentration vacancy volume. Otherwise, in the NW experiments, higher H retention would be observed at ~400 nm. The fact that H atoms can migrate along GBs is in good agreement with data reported by Zhou *et al.* [161] about the influence of symmetric GBs on H atoms in W. Their DFT calculations gave a H migration barrier of 0.13 eV along the GBs, i.e., 0.07 eV lower than the value (0.2 eV) in bulk W. The diffusion barrier for H atoms becomes lower when they approach the GB, suggesting that H atoms cannot easily escape out of the

GB [161]. Similar results have been published by González *et al.* [162] in a non-coherent interface formed by two W(110) and W(112) surfaces. Thus, DFT results in different types of interfaces and, in addition, MD studies [163] support the idea that H atoms get trapped at GB regions, diffusing along them. Nevertheless, other works carried out at higher temperatures ($T > 300$ K) show that H is retained at GBs. Yu *et al.* [165] observed H retention at GBs in W at temperatures ranging from 600 to 1200 K whilst Piaggi *et al.* [164] obtained similar results between 1200 and 2000 K. However, at such high temperatures, more physical processes might take place apart from those described at 300 K in the present Chapter. For instance, vacancy formation in the vicinity of GBs. The value of formation energy of a vacancy from a GB in W has been published in Refs. [161,162]. This value ($E^f(V)_{GB} = 1.6$ eV) is much lower than the formation energy of a vacancy in bulk tungsten ($E^f(V)_{Bulk} = 3.23$ eV). This means that at temperatures higher than 300 K (~ 650 K), vacancies might be formed at GBs, being able to efficiently trap H atoms. In Ref. [49], it was pointed out that GBs might act as trapping sites of H atoms, showing a clear trend, namely, the higher the GB density, the higher the retained H fraction. However, the comparison between experimental and OKMC results in the case of NW clarifies that, although this is so, the trend is not related to H trapping at GBs themselves, but to the effect that GBs have on FP annihilation at 300 K, resulting in a higher vacancy concentration and consequently, a higher H retention.

With regard to carbon irradiation, the experimental and OKMC results show a much lower influence on H retention in the case of NW, compared to CGW (experiments) or MW (simulations), as can be seen in Figure 5.7. In addition, a less pronounced H retention enhancement is observed in NW comparing to CGW (experiments) or MW (simulations), when W samples are irradiated with C both simultaneously or sequentially or they are only irradiated with H ions. As commented before, this also supports the idea of the GBs acting as diffusion paths for H atoms. The presence of a higher GB density in NW leads to a higher probability of H atoms to be released along GBs, being less affected by the presence of the higher vacancy concentrations induced by C irradiation. On the contrary, in CGW cases, H atoms must cross the high vacancy density region in their way to the surface, which leads to a larger H retention in these samples than in NW. Moreover, comparing MW-Co-CH and MW-Seq-CH (see Figure 5.7), a clear influence of the irradiation procedure itself, either simultaneous or sequential C and H implantation, can be observed. In MW-Co-CH, as C and H ions arrive at the same time, the first H atoms can diffuse along X direction, before the huge vacancy concentration at ~ 400 nm is formed all along the simulation. On the contrary, in MW-Seq-CH, the huge vacancy concentration at ~ 400 nm is already formed from the very beginning of H ion irradiation, leading to an enhanced H trapping in this volume.

Figure 5.9. Retained H fraction with respect of the total H retained in monovacancies, as a function of the H atoms in the monovacancy, from H_1V_1 to $H_{10}V_1$, in all the cases simulated: single H irradiation in MW (a) and NW (b), C and H simultaneously irradiated in MW (c) and NW (d), and C and H sequentially irradiated in MW (e) and NW (f) in both just after the ion irradiation and after the subsequent annealing during 10 days at 300 K.

An interesting outcome of the simulations is the determination of the type and size of H_nV_m clusters. Simulations reveal that the presence of some H_nV_m clusters with more than one vacancy ($m>1$) only occurs when a vacancy is created in the vicinity of a pre-existing one, as vacancies do not migrate at 300 K. This implies that in all the simulations independently of the density of GBs or irradiation conditions, more than 90% of H atoms are retained in H_nV_1 clusters, i.e., in monovacancies (see Figure 5.8). Figure 5.9 shows the results of H

trapped in monovacancies (%), as a function of the number of H in the monovacancy, just after the H and/or C implantation and after the subsequent annealing of 10 days at 300 K. As described in Section 3.2.3, DFT calculations showed that up to 10 H atoms can be trapped in a single vacancy, with a binding energy that decreases as the H content of the vacancy increases. All the NW simulations, regardless the type of C and/or H irradiation, show that no more than 5 H atoms are trapped by a monovacancy after the annealing of 10 days at 300 K. This corresponds to a binding energy for H_5V_1 ($H \rightarrow H_4V_1$) of 0.87 eV. The binding energy for the three next H atoms, i.e., H_6V_1 , H_7V_1 and H_8V_1 , are 0.52, 0.5 and 0.46 eV, respectively. Thus, at 300 K the temperature is high enough to enable slow H emission. On the other hand, the 5th H atom cannot be emitted at 300 K.

Figure 5.10. H concentration as a function of depth arranged by cluster type (H_nV_1). In the case of single H irradiation in both MW-H just after H irradiation (a) and after an annealing of 10 days at 300 K (c) and NW-H, also in the case of being plotted just after H irradiation (b) and after an annealing of 10 days at 300 K (d).

In the case of MW, different results were obtained. On the one hand, just after the irradiation, H atoms are trapped at clusters such as H_5V_1 , H_6V_1 , H_7V_1 and H_8V_1 . On the other hand, after the annealing of 10 days at 300 K, H atoms trapped in H_6V_1 , H_7V_1 and H_8V_1 are emitted, leading to dominant formation of H_5V_1 clusters. This can be explained as

follows. Just after the C and/or H irradiation, H atoms are trapped in H_6V_1 , H_7V_1 and H_8V_1 . However, they are unstable at 300 K and H atoms are constantly being emitted from these clusters and trapped in cluster nearby. After the 10 days annealing at 300 K, there is time enough to observe all the emissions of these clusters, the diffusion of the emitted H atoms and the subsequent trapping by other clusters or, in a very small number, the desorption at the irradiation surface. This effect is clearly shown in Figure 5.10(a) and (c), Figure 5.11(a) and (c) and Figure 5.12(a) and (c).

Figure 5.11. H concentration as a function of depth arranged by cluster type (H_nV_1). In the case of C and H simultaneously implanted in both MW-Co-CH just after H irradiation (a) and after an annealing of 10 days at 300 K (c) and NW-Co-CH, also in the case of being plotted just after H irradiation (b) and after an annealing of 10 days at 300 K (d).

Another issue regarding the size of H_nV_1 clusters in which H is trapped, is that in NW, the lower the number of H atoms in the monovacancy, the closer they are to the desorption surface, as can be seen in Figure 5.10(b) and (d), Figure 5.11(b) and (d) and Figure 5.12(b) and (d). Since H mean implantation range is ~ 650 nm in depth, the monovacancies with more H atoms are around this value. Thus, the GB not only affects the H transport by means of enhanced diffusivity along them, but also GBs play a role in the resulting H content of vacancies, being lower in the case of NW than in the case of MW. From these

results, it can be stated that, although DFT calculations show that H_nV_1 clusters are stable up to $n = 10$, the binding energy of H atoms in H_nV_1 clusters with $n > 5$ is so low that, at 300 K, these clusters efficiently emit H atoms, resulting in clusters with a maximum of 5 H atoms per monovacancy.

Figure 5.12. H concentration as a function of depth arranged by cluster type (H_nV_1). In the case of C and H sequentially implanted in both MW-Seq-CH just after H irradiation (a) and after an annealing of 10 days at 300 K (c) and NW-Seq-CH, also in the case of being plotted just after H irradiation (b) and after an annealing of 10 days at 300 K (d).

Hodille *et al.* [188] reported that H atoms should be retained in three different types of traps, with binding energies of 0.83, 1.0 and 1.5 eV between 300 and 700 K. This is in good agreement with the results presented in this Chapter, as the simulations reveal that the main trapping of H atoms is in monovacancies, from H_5V_1 to H_1V_1 . The values of the traps proposed by Hodille *et al.* [188] can be assimilated to those used in the simulations presented in this Chapter, as can be seen in the comparison shown in Table 5.4.

Table 5.4. Comparison between DFT binding energy (eV) of the clusters formed in this work and the trapping energy proposed by Hodille *et al.* [188].

Cluster	DFT binding energy eV, this work	Trapping energy in eV [188]
HV ($H \rightarrow V$)	1.20	1.5
H ₂ V ($H \rightarrow HV$)	1.19	1.5
H ₃ V ($H \rightarrow H_2V$)	1.07	1.0
H ₄ V ($H \rightarrow H_3V$)	0.95	1.0
H ₅ V ($H \rightarrow H_4V$)	0.87	0.83

Furthermore, the fact that a H atom can be trapped and detrapped from a monovacancy is in good agreement with the model proposed by von Toussaint *et al.* [189].

5.6 Conclusions

Experiments were performed to study H behaviour at 300 K in single H irradiation, simultaneous and sequential C and H implantation. In order to gain a better understanding of the experimental results, all the conditions were simulated with an OKMC code (MMonCa), parameterized by DFT data. An overall good agreement between experimental and computational results was obtained in the case of NW. On the contrary, in the case of CGW, different results were obtained, as for computational reasons, monocrystalline W (MW) was simulated rather than CGW, i.e., no GBs at all were considered in this case. Although the comparison between simulations (MW) and experiments (CGW) are not in good agreement, some information of these simulations can be extracted.

The first conclusion is that the larger the GB density, the higher the chance for fast SIAs to reach a GB before annihilating vacancies which, on the contrary, cannot move to reach any GB at 300 K. This leads to a higher vacancy density in NW than in MW and, thus, a higher H retention in the interior of the grain. A second consequence of the vacancy immobility is that the great majority of H is retained in single vacancies in both MW and NW. Moreover, if there is time enough for the unstable H_nV_1 clusters to emit all the H atoms at binding energies lower than 0.87 eV (in the case of this work, an annealing of 10 days at 300 K, to simulate the time between the experimental irradiation and the analysis of the samples), all the H atoms are retained in clusters with a number of 5 H (H_5V_1) atoms or lower. Thus, there is not a high influence of the GBs neither on the size of H_nV_m clusters nor on the number of H atoms in monovacancies.

There is a very good agreement between experiments and simulations in the case of NW samples. Both the total H concentration and its distribution in depth measured in the

experiments are well-reproduced by the theoretical results. For this reason, it can be concluded that in the experiments, all the H atoms should be retained in the interior of the grains and thus, GBs may act as preferential paths for H atoms to diffuse in W at 300 K.

The comparison of the results presented in this Chapter with previous publications suggests a strong dependence of the irradiation temperature on the potential “self-healing” behaviour of nanostructured W. This result indicates that “self-healing” in W would happen at temperatures at which the mobility of vacancies is activated. This fact, together with the fact that GBs favour H release, point out that nanostructured W may be a candidate for this kind of applications, as it exhibits higher radiation resistance than the traditionally suggested CGW. Nevertheless, there is still an open question when considering this kind of application, which is related to the thermal stability of nanostructured W. This is a very important point, not properly investigated so far.

6 Helium irradiation in tungsten: fuzz formation

As described in Chapter 1, tungsten is a candidate for plasma facing material for the divertor region in future magnetic fusion reactors. Under the expected He irradiation conditions, low ion energy, high flux and high temperature, it has been experimentally found that a highly underdense nanostructured morphology (fuzz) is formed in W. However, it has been demonstrated that fuzz is only formed in a temperature window ranging from 900 to 2000 K [38,190,191].

In this Chapter, object kinetic Monte Carlo (OKMC) simulations of He (60 eV) irradiation at a flux of $5 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$ and temperatures from 700 to 2500 K are presented. Simulations were carried out with the MMonCa code (see Section 3.3). MMonca has been parameterized as described in Section 3.2. Furthermore, trap mutation mechanism was included (see Section 6.2), which reveals decisive at this irradiation conditions, as He ions at 60 eV do not generate Frenkel pairs in W by direct collision. In order to simulate these irradiation conditions and the fuzz growth, a new physical process has been implemented in MMonCa, to account for the generation of highly He pressurized volume and the associated surface expansion.

From the simulations, it can be observed that on the one hand, at low temperatures ($<900 \text{ K}$), fuzz does not grow because almost all He is trapped in very small He-vacancy clusters, unable to grow. On the other hand, at high temperatures ($>2000 \text{ K}$) He-vacancy clusters are unstable, preventing the formation of clusters. On the contrary, in the intermediate temperature range (from 900 to 2000 K), fuzz grows due to the formation of large He_nV_m clusters.

The previous Chapters found application mainly for inertial confinement fusion. This Chapter extends the scope of this thesis to the irradiation conditions that will take place in magnetic confinement fusion. This broadens the uses of W as plasma facing material and the capabilities of the MMonCa code to a broad range of irradiation conditions and physical processes relevant for the study of fusion materials. The results described in this Chapter are being written in a manuscript, to be sent for its publication in a scientific journal [56].

6.1 Introduction

As commented in Chapter 1, sections of the divertor in future magnetic confinement fusion (MCF) devices will reach high temperatures (≥ 1000 K) while exposed to large particle fluxes ($> 10^{23} \text{ m}^{-2} \text{ s}^{-1}$) of low-energy H and He ions [39,40]. Experimental studies of W irradiated under these conditions report on the formation of voids and underdense W nanostructures (fuzz), which has also been observed in other materials such as molybdenum [38]. Experiments in a linear divertor-plasma simulator [39] and with a magnetron sputtering device [41] provided similar results. Baldwin *et al.* [39] studied the kinetics of fuzz growth and found that it scales with the square root of time, $t^{1/2}$, at the temperatures they studied: 1120 and 1320 K. At 1120 K the ion energy threshold for nanostructure formation was determined to be around 35 eV [192] and the growth rate to increase with the increasing flux [193].

The role of defects in these processes was also reported [194]. A clear influence of temperature was observed, revealing a limited temperature window for fuzz growth between, approximately, 900-2000 K [38,190,191]. Some theoretical studies have been carried out in order to explain the growth rate dependence with $t^{1/2}$. Modeling performed in Refs. [68,195] showed that the growth rate is driven by the balance of two processes: formation of He bubbles and their rupture at the surface. Along these lines, a four-step process has been proposed by Ito *et al.* [67,195] at 2000 K: (i) He ions penetrate the W surface; (ii) He diffusion and agglomeration even at interstitial sites occurs; (iii) He bubbles grow at both vacancy and the interstices and (iv) based on hybrid Molecular Dynamics-kinetic Monte Carlo simulations, they explained how He bubbles burst, forming fuzzy nanostructures. Moreover, the behaviour of small He clusters when forming near the W surface has been extensively studied [190,196–200]. Nevertheless, no quantitative studies were found in the literature addressing why fuzz formation occurs only in this limited temperature window.

In this Chapter, it is reported an object kinetic Monte Carlo (OKMC) simulation study of low energy He irradiation (60 eV) of W. Simulating a broad range of temperatures, from 700 to 2500 K, it has been determined a fuzz growth temperature window, in agreement with published experiments [38,190,191]. More precisely, at low temperatures (700K), the great majority of He atoms are retained in monovacancies (He_nV_1 clusters), which remain stable. At intermediate temperatures (900-2000 K), He atoms are retained inside larger He_nV_m clusters, which grow to trigger the formation of fuzz-like structures. At high temperatures (2500 K), He atoms and vacancies are emitted from small He_nV_m clusters

($n < 40$, $m < 10$), preventing the formation of larger He_nV_m clusters and the growth of fuzz nanostructures.

6.2 Simulation methods

The simulations have been performed using MMonCa [51]. It has been parameterized as described in Section 3.2, with the exception of the migration of pure He clusters (He_n). They are assumed immobile and cannot emit He atoms. Although small clusters can migrate [201,202], the assumption is justified because cluster diffusion slows down with the cluster size and is strongly suppressed by impurities and interstices [67,195,203]. In addition, trap mutation reactions would trap the pure He_n clusters [157,204]. Trap mutation consists of the growth of He_n (in the case of pure He atoms in interstitial positions is also named self-trapping [157]) and He_nV_m clusters by trapping He. When the number of He atoms reaches a certain value, the pressure is high enough to emit a surrounding W atom to decrease the pressure, creating a vacancy and a SIA ($\text{He}_n \rightarrow \text{He}_n\text{V}_1 + \text{I}$ in the case of pure He atoms, $\text{He}_n\text{V}_m \rightarrow \text{He}_n\text{V}_{m+1} + \text{I}$ in the case of mixed He_nV_m clusters). Trap mutation in MMonCa depends on the energies involved in the process. The balance between the energy needed to create a vacancy, $E^f(\text{V}) = 3.23$ eV, and a SIA, $E^f(\text{I}) = 9.96$ eV, and the energy released by the system creating a mixed He_nV_m cluster defines the reaction of trap mutation. In the case of pure He_n clusters, the activation energy for the trap mutation can be seen in Figure 6.1.

Figure 6.1. Activation energy for trap mutation ($\text{He}_n \rightarrow \text{He}_n\text{V} + \text{I}$) in the case of pure He_n clusters.

It is a process similar to migration and emission, i.e., it follows an Arrhenius law. This means that the higher the temperature, the lower the number of He atoms needed to activate the trap mutation process. As the irradiation energy of He atoms is low (60 eV), they are implanted near the irradiation surface. It has been reported that trap mutation reactions are

enhanced near surface [205–207], which reinforces the assumption of no He_n migration. Thus, trap mutation process is important in the irradiation conditions simulated in this Chapter.

Figure 6.2. Simulation box dimensions for simulating fuzz growth. The simulation box is divided into small boxes, called “mesh elements”. The “mesh element” can be made of tungsten or of vacuum. As tungsten increases or decreases spatially, mesh elements change from vacuum to tungsten or vice versa, respectively.

Thin boxes of $20\text{ (X, depth)} \times 4\text{ (Y)} \times 40\text{ (Z)}\text{ nm}^3$ of tungsten were used to carry out pseudo-3D simulations (see Figure 6.2). Larger boxes, needed to reproduce a real 3D simulation, were very computationally demanding and turned out impractical. Thus, fuzz can only grow in X and Z directions (free surfaces were set), but not in Y direction, where periodic boundary conditions (PBC) were set. The top surface (normal to the X -axis) was considered as a desorption surface, whereas atoms reaching the bottom surface were considered to move further deep into the bulk and thus ignored. The simulation box is composed of small cells of $0.5 \times 0.5 \times 0.5\text{ nm}^3$, either of W or of vacuum, named “mesh elements”. In fact, the simulation box made of W $20\text{ (X, depth)} \times 4\text{ (Y)} \times 40\text{ (Z)}\text{ nm}^3$ is surrounded by “mesh elements” of vacuum, in order to change into “mesh elements” of W , as fuzz grows, see Figure 6.3(a). Thus, the simulation box of W was surrounded by 30 nm of vacuum “mesh elements” in both sides along Z direction, and 200 nm above the irradiation surface.

Figure 6.3. Simulation of fuzz growth and bubble bursting in MMonCa. The simulation box and the surrounding vacuum are divided into “mesh elements”, which can be either W or vacuum.

The process of fuzz growth and bubble bursting, as modeled in MMonCa, is described in the scheme shown in Figure 6.3. On the one hand, if the number of retained He atoms is equal or larger than the volume of a “mesh element”, assuming 0.033 nm^3 as the volume of a single He atoms, the closest “mesh element” to this He atoms changes from vacuum to W, see Figure 6.3(b) and (c), simulating thus the fuzz growth due to He accumulation. On the other hand, if a He_nV_m cluster has grown so close to the surface that it is at a distance lower than 0.2 nm , the “mesh elements” with a volume equal to the He atoms retained in the cluster changes from W to vacuum and the He_nV_m cluster disappears from the simulation, reproducing the bursting of He bubbles at the surfaces, see Figure 6.3(d) and (e). Because of the pseudo-3D simulation, these two processes can take place in the surfaces perpendicular to X and Z directions. In the Y direction it cannot occur, as PBCs were set.

Figure 6.4. He is implanted at depth positions as calculated by SRIM, from the “mesh elements” made of W, which define the irradiation surface.

This approach to fuzz growth is similar to that presented in Ref. [68]. Nevertheless, with the current methodology presented in this Chapter, fuzz can grow not only normal to the irradiation surfaces but also along the Z direction. Furthermore, in the code used in Ref. [68] no reactions of He detrapping from He_nV_m clusters were possible. The initial positions of He ions were calculated with the SRIM code [62]. Any FPs were produced by He irradiation in W, due to the low energy of He ions (60 eV). It is worth mentioning that MMonCa implants He ions at the positions from the irradiation surface calculated by the SRIM code, taking as W surface the “mesh elements” made of W closest to the He irradiation, in X direction (see Figure 6.4). The flux of He ions was $5 \times 10^{22} \text{ m}^{-2} \text{ s}^{-1}$, up to a fluence of $1.5 \times 10^{23} \text{ m}^{-2}$, i.e., He ions are irradiated during 3 s. The reflection yield provided by SRIM was taking into account. Fuzz was considered to be the W region that grows above the initial surface layer (see Figure 6.5).

Figure 6.5. Fuzz is considered as the region that grows from the initial irradiation surface.

He irradiation times of up to 3 s, at impacting energies of 60 eV, were simulated at eight different temperatures: low temperature (700 K), intermediate temperatures (900, 1120, 1320, 1500, 1700 and 1900 K) and high temperature (2500 K). Although attempts to simulate 2100 and 2300 K were made, the large number of reactions activated at these temperatures and the high growing rate of fuzz would imply the use of huge simulation boxes, which lead to computational times impractically long. For the same reasons, in the case of 1700 and 1900 K only results up to 1.25 and 0.25 s, respectively, were obtained. Nevertheless, the temperatures reported in this Chapter constitute a representative set to study the temperature influence on fuzz formation.

6.3 Results and discussion

A schematic view of the results after 3 s irradiation at 700, 900, 1120, 1320, 1500 and 2500 K can be seen in Figure 6.6. At low temperature (700 K), the whole simulation box (20 nm deep) turns out populated by He_nV_m clusters. However, there is no fuzz growth, as the irradiation surface remains in the same position as initially.

Figure 6.6. Schematic representation of fuzz growth at 700, 900, 1120, 1320, 1500 and 2500 K after 3 s of He (60 eV) irradiation.

At intermediate temperature, fuzz growth due to the accumulation of He atoms in He_nV_m clusters is observed. At 900 K, fuzz slightly grows normal to the irradiation surface. Between 1120 and 1500 K, there is a significant fuzz growth in both X and Z directions. Figure 6.6 shows qualitatively that the higher the temperature, the more pronounced the fuzz growth. Finally, at high temperature (2500 K), neither fuzz growth nor He retention takes place. These results are qualitatively in very good agreement with the temperature window for fuzz growth (900-2000 K) reported by experiments [38,191,208]. The mean diameter of He_nV_m clusters has been calculated, giving as a result 0.36 and 0.44 nm at 700 and 900 K, respectively. These results are in very good agreement with experimental results, which gave a value of He nano-bubbles mean diameter between 0.36 and 0.62 nm, at similar irradiation conditions [209,210].

Figure 6.7. Fuzz height as a function of time (and fluence) at the simulated temperatures. Fuzz height obtained from experimental data at both 1120 and 1320 K [39] are also plotted.

The fuzz height for different temperatures as a function of time (i.e., fluence) is presented in Figure 6.7. At low temperature (700 K), the absence of fuzz growth previously described is observed all along the 3 s of He irradiation. At 900 K fuzz slightly grows, reaching 14.5 nm after 3 s of He irradiation. Between 1120 and 1500 K, fuzz grows faster, as it heights up to 56 and 94 nm, respectively, after 3 s. Also the fuzz growth for 1700 and 1900 K is plotted. Although no longer simulations were carried out, it can be observed that fuzz grows very fast, mainly at 1900 K. At high temperature (2500 K), no fuzz growth occurs at all. Figure 6.7 also shows the fuzz growth obtained from experimental data at 1120 and 1320 K [39]. It grows with the square root of time.

Figure 6.8. Fuzz only grows after an incubation fluence, as can be observed at 1120, 1320 and 1500 K.

As can be observed in Figure 6.7, for short He irradiation times, fuzz growth is far from the experimental results. Recent experimental results reported in Ref. [42] indicate that fuzz growth following the square root dependence only starts after accumulating an incubation fluence. Although the experiments were carried out at different irradiation conditions (He ion energy, flux and temperature), the incubation fluence is qualitatively comparable to the simulation results presented in this Chapter. As fuzz grows due to the accumulation of He atoms inside vacancies in He_nV_m clusters, it cannot grow from the very beginning of He irradiation. Furthermore, the simulation results reveal that the higher the temperature, the lower the incubation fluence, as can be observed in Figure 6.8.

Figure 6.9. Retained He fraction as a function of time (and fluence) for the simulated temperatures: 700, 900, 1120, 1320, 1500, 1700, 1900 and 2500 K.

In order to analyse if the retained He fraction is the main responsible of fuzz growth, the fraction of retained He with respect to the implanted He, as a function of time (and fluence), is plotted in Figure 6.9. As can be observed, He retention alone cannot explain fuzz growth. Up to irradiation times of 2.5 s, the He retained fraction at 700 K is higher than at 900, 1120, 1320 and 1500 K, even though at 700 K fuzz growth does not occur

whilst at the other temperatures, it does. An analysis of the He population in different types of clusters evidences that at low temperatures (900 K), the incoming He ions are trapped at first in pure He_n clusters. Once the size of He_n clusters reaches 9 He atoms (He_9), they emit a SIA, creating a vacancy and becoming stable He_9V_1 . This is the trap mutation process described in Section 6.2. Indeed, 95.9% of He atoms are retained in He_9V_1 at 700 K (see Figure 6.10). This indicates that there is almost no coalescence of clusters. The absence of large He_nV_m clusters prevents the formation of fuzz.

Figure 6.10. He retention ration at different temperatures, sorted by the size of He_nV_m clusters in which they are trapped.

At 900 K, a similar process is observed regarding trap mutation: only He_9 clusters are able to emit a SIA and create a vacancy, to become He_9V_1 clusters. However, the crucial difference is that at this temperature, He atoms are emitted from He_nV_m clusters, as the temperature is high enough (see Table 3.6). On the one hand, this leads to a lower He retention, as previously trapped He atoms in He_9V_1 clusters are emitted and some of them reach the desorption surface. On the other hand, some of the emitted He atoms are trapped in the vicinity of the emitting He_9V_1 clusters, as He ions are constantly irradiated and migrating through the W. This leads to the formation of new He_9V_1 clusters. As these clusters are formed next to the emitting He_9V_1 clusters, the coalescence among them is favoured, resulting in the formation of large He_nV_m clusters, which promote fuzz growth.

At higher temperatures (1120, 1320 and 1500 K), He retention decreases until irradiation times of 1 s (Figure 6.9). Beyond this time, He retention increases in a similar way for the three temperatures. At these temperatures, fuzz growth occurs not only normal to the irradiation surface, but also along the Z direction. Therefore, more volume of W is available for the trapping of He atoms, increasing the retained He fraction. The processes governing the temperature dependence of fuzz growth are: (i) trap mutation and (ii) H emission from He_nV_m clusters, with the subsequent coalescence and formation of larger He_nV_m clusters.

On the one hand, the number of He atoms needed to enable trap mutation decreases with the increasing temperature. For instance, at 1500 K even He_4 clusters are able to emit a SIA and create a vacancy to become a He_4V_1 , similar to results reported in Ref. [207,211]. This fact strongly promotes trap mutation and therefore, He trapping. On the other hand, the emission of He atoms from He_nV_m clusters increases with temperature, favouring cluster coalescence. The higher concentration of He atoms in large clusters at these temperatures (Figure 6.10) leads to efficient fuzz growth. A different regime in the retention is observed at 1900 K. Although only short simulations were carried out, a much higher He retention rate can be observed. The same process as the previously described occurs at this temperature, but much more accelerated due to the higher temperature.

Finally, at high temperature (2500 K), He emission from the formed He_nV_m clusters dominates, suppressing further cluster formation or growth, and thus, fuzz formation. In fact, almost no He is retained at 2500 K (Figure 6.10). In this case, the emitted He atoms cannot be trapped, but they migrate until they have reached the surface and desorb.

Figure 6.11. Vacancy concentration in the fuzz region as a function of fuzz height after He irradiation during 3 s at intermediate temperatures (900, 1120, 1320 and 1500 K), at which fuzz growth takes place.

Figure 6.11 shows the vacancy concentration in the fuzz region at intermediate temperatures (900, 1120, 1320 and 1500 K). At 900 K, the vacancy concentration reaches the highest value, $\sim 6.8 \text{ nm}^{-3}$, i.e., 10.8% of the W atoms are removed from their lattice positions, forming the corresponding vacancies. The vacancy concentration reaches successive peaks, which tend to be lower with the increasing fuzz height. This result indicates that, as fuzz height increases, the incoming He ions interact mainly with the He_nV_m clusters formed closest to the irradiation surface. Regarding the effect of temperature on vacancy concentration, the profile peaks become less pronounced with the increasing temperature.

Figure 6.12. Mean vacancy concentration, calculated as the total number of vacancies divided by the total W-fuzz volume, for 900, 1120, 1320 and 1500 K.

For a better comparison among temperatures, the mean vacancy concentration has been calculated, in the W-fuzz region (Figure 6.12). As a result, it can be observed that the higher the temperature, the lower the mean vacancy concentration.

6.4 Conclusions

In this Chapter is presented an OKMC study on the effect of temperature on fuzz growth in He-irradiated W, simulating He (60 eV) irradiation in W at different temperatures, ranging from 700 to 2500 K. A new feature of the MMonCa code has been developed for these simulations. Also trap mutation mechanism has been included in the parameterization of He irradiation in W. As the irradiation of He ions at 60 eV in W does not promote any FP generation, trap mutation reveals as a key mechanism in He trapping.

In the simulations, fuzz growth is observed in the temperature range from 900 to 1900 K, in agreement with experimental observations. Thanks to the simulations, it has been identified that the fuzz growth is driven by the formation of large He_nV_m clusters, which are only formed between 900 and 1900 K. Two main mechanisms lead to this temperature dependence: (i) emission of SIAs (trap mutation) and (ii) coalescence of small He_nV_m clusters due to emission of He atoms and formation of new He_nV_m clusters in their vicinity.

At low temperatures (700 K), fuzz growth is prevented by the stability of small He_9V_1 clusters, leading to no He emission. In contrast, at high temperatures (2500 K) fuzz does not grow due to the high He emission from He_nV_m clusters, leading to their dissolution and thus, avoiding He retention.

It can be concluded that fuzz growth is not only influenced by He retention, but by the size of He_nV_m clusters in which He atoms are retained. Regarding the temporal evolution of fuzz growth, an incubation fluence was observed, qualitatively similar to recent experiments.

7 Conclusions and future work

7.1 Conclusions

This thesis presents a multiscale methodology, mainly based on object kinetic Monte Carlo, for application studies of helium and hydrogen-irradiated tungsten. The thesis covers several irradiation conditions that tungsten, as a plasma facing material, will have to face in both inertial fusion and magnetic fusion confinement approaches.

OKMC simulations were carried out with the MMonCa code. As a first step, MMonCa was validated by comparing the obtained results with those from another OKMC code (LAKIMOKA). A complete OKMC parameterization has been developed for helium and hydrogen in tungsten. In addition to the parameterization for helium and hydrogen, different physical processes have been implemented in the MMonCa code. Furthermore, a methodology for using binary collision approximation SRIM code to generate damage cascades in tungsten has been developed. The obtained cascades by means of this methodology have been compared with cascades obtained by means of molecular dynamics. Different helium or hydrogen irradiation conditions have been carried out to study the response of different types of tungsten: pulsed or continuous irradiation modes in nanocrystalline or monocrystalline material at high and low energy and flux. MMonCa simulations were validated with experimental results and, at the same time, used as fundamental tool to analyse experimental results.

The major conclusions of this thesis can be summarised as follows:

- i. The developed computational methodology based on OKMC and applied to tungsten for fusion energy applications turns out a powerful tool for the analysis of experiments, as it clarifies the underlying physical processes that otherwise are very difficult to understand.
- ii. The ion flux plays a major role in the response of tungsten ion irradiation.
- iii. Nanostructured tungsten is expected to have a superior behaviour with regards to helium or hydrogen irradiation. On the one hand, in the interior of a grain of nanometric size, helium-vacancy clusters are less pressurized than in monocrystalline tungsten. Moreover, this trend increases with the increasing helium irradiation. On the other hand, nanocrystalline tungsten has a clear effect on both

Frenkel pairs and hydrogen behaviour in tungsten. Furthermore, grain boundaries act as preferential paths for hydrogen diffusion.

- iv. The influence of temperature on fuzz formation is highly influenced by the process of helium trapping, as it is thermally activated. Thanks to the emission of helium atoms trapped in helium-vacancy clusters, the temperature window for fuzz formation (900 – 2000 K) observed experimentally can be explained.

7.2 Future work

The work presented in this thesis can be used as the basis for further research, as described next:

1. Study of continuous and pulsed irradiation modes at different irradiation conditions, as it has been demonstrated that the irradiation mode has a clear influence on helium retention in tungsten. It would help in the developing of new materials capable to withstand the irradiation conditions that will take place in both inertial and magnetic confinement fusion.
2. Since high grain boundary density has been demonstrated to have an influence on helium retention, more sophisticated grain boundary models can be developed to study not only in the interior of the grain, but also the grain boundaries themselves. Furthermore, as the pressure of in He-V clusters has an influence on the tungsten response to helium irradiation, the study of the thermomechanical response due to the defect micro-structure generated by ion irradiation will have much relevance for practical applications.
3. Based on the parameterization for hydrogen irradiation in tungsten presented in this thesis, the behaviour of hydrogen on tungsten irradiation surface can be modelled, as hydrogen desorption is important (and complex) to understand hydrogen interaction with tungsten. Moreover, the parameterization can be expanded to higher temperatures, by a detailed analysis of large hydrogen-vacancy clusters, similarly to what has been studied in this thesis in the case of helium irradiation.
4. The model of fuzz formation can be improved to simulate larger time and spatial scales. This way, the incubation fluence needed for the fuzz to start growing will be better understood and more accurate comparison with experiments will be achieved.
5. Based on the parameterization of both hydrogen and helium, a new parameterization including helium and hydrogen interactions can be developed. The concomitant

effects related to the simultaneous presence of both species have been recognized in experiments. DFT studies of these interactions are already appearing in the literature and will make possible this challenge.

Generally speaking, by using a similar methodology that the one described in this thesis, other materials apart from tungsten, irradiated with other ions than helium or hydrogen can be studied. This methodology opens new paths of research in the general field of materials subjected to ion irradiation.

Publications, conferences and other works

Stays abroad

- Department of Physics of the University of Helsinki, Helsinki, Finland.

Duration: September 1, 2014 – December 15, 2014

Supervisor: Kai Nordlund, Professor in Computational Materials Physics

Achievements: Study of the temperature dependence of underdense nanostructure formation in tungsten under helium irradiation with the MMonCa code. The stay resulted in the writing of a paper, to be sent to a scientific journal.

Publications

- MMonCa: An Object Kinetic Monte Carlo simulator for damage irradiation evolution and defect diffusion, I. Martin-Bragado, A. Rivera, **G. Valles**, J. L. Gomez-Selles, M. J. Caturla, Computer Physics Communications 184 (2013) 2703-2710.

Described in Sections 3.3 and 3.5.1.

- Effect of ion flux on helium retention in helium-irradiated tungsten, A. Rivera, **G. Valles**, M. J. Caturla, I. Martin-Bragado, Nuclear Instruments and Methods in Physics Research B 303 (2013) 81-83. (Described in Section 3.5.2).

Described in Section 3.5.2.

- A multiscale approach to defect evolution in tungsten under helium irradiation, **G. Valles**, A. L. Casalilla, C. Gonzalez, I. Martin-Bragado, A. Prada, R. Iglesias, J. M. Perlado, A. Rivera, Nuclear Instruments and Methods in Physics Research B 352 (2015) 100-103.

Described in Section 3.5.1.

- The influence of high grain boundary density on helium retention in tungsten, **G. Valles**, C. Gonzalez, I. Martin-Bragado, R. Iglesias, J. M. Perlado, A. Rivera, *Journal of Nuclear Materials* 457 (2015) 80-87.

Described in Chapter 4.

- Influence of grain boundaries on the radiation-induced defects and hydrogen in nanostructured and coarse-grained tungsten, **G. Valles**, M. Panizo-Laiz, C. Gonzalez, I. Martin-Bragado, R. Gonzalez-Arrabal, N. Gordillo, R. Iglesias, C. L. Guerrero, J. M. Perlado, A. Rivera, *Acta Materialia* (under review).

Described in Chapter 5.

- Temperature dependence of underdense nanostructure formation in tungsten under helium irradiation, **G. Valles**, I. Martin-Bragado, K. Nordlund, A. Lasa, C. Björkas, E. Safi, J. M. Perlado, A. Rivera. In preparation.

Described in Chapter 6.

Conferences and Workshops

- Computer Simulation of Radiation Effects in Solids (COSIRES 2012), Santa Fe, New Mexico (USA), June 24 – 29, 2012

Effects of ion flux on helium retention in helium-irradiated tungsten. A. Rivera, **G. Valles**, M. J. Caturla, I. Martin-Bragado. Poster presentation.

MMonCa: A flexible and powerful new Kinetic Monte Carlo Simulator. I. Martin-Bragado, A. Rivera, **G. Valles**, M. J. Caturla. Oral presentation.

- Trends in Nanotechnology International Conference (TNT 2012), Madrid (Spain), September 10 – 14, 2012
- IEA Fusion Modeling Workshop, Alicante (Spain), May 16 – 18, 2013
- 16th International Conference on Emerging Nuclear Energy Systems (ICENES 2013), ETSII-UPM, Madrid (Spain), May 26 – 30, 2013

- 11th Symposium of the Fusion Nuclear Technology (ISFNT-11), Barcelona (Spain), September 16 – 20, 2013

Defect evolution in tungsten under helium irradiation: OKMC simulations. **G. Valles**, I. Martin-Bragado, R. Gonzalez-Arrabal, N. Gordillo, M. J. Caturla, J. M. Perlado, A. Rivera. Poster presentation.

- International Workshop on the Mechanical Behavior of Nanoscale Multilayers, Getafe (Spain), October 1 – 4, 2013

An object kinetic Monte Carlo approach to helium interaction with grain boundaries in tungsten. A. Rivera, **G. Valles**, R. Gonzalez-Arrabal, J. M. Perlado, I. Martin-Bragado. Oral presentation.

- NanoSpain2014 Conference, Madrid (Spain), March 11 – 14, 2014

An Object Kinetic Monte Carlo comparison of helium retention in nanocrystalline tungsten and monocrystalline tungsten. **G. Valles**, I. Martin-Bragado, C. Gonzalez, O. Peña-Rodriguez, R. Gonzalez-Arrabal, J. M. Perlado, A. Rivera. Poster presentation.

- European Materials Research Society Spring Meeting (E-MRS 2014), Lille (France), May 26 – 30, 2014

An object kinetic Monte Carlo study of the influence of grain boundary density in He retention in tungsten. **G. Valles**, I. Martin-Bragado, O. Peña-Rodriguez, J. M. Perlado, A. Rivera. Poster presentation.

- Computer Simulation of Radiation Effects in Solids (COSIRES 2014), Alicante (Spain), June 8 – 13, 2014

An object kinetic Monte Carlo study of the influence of grain boundary density in He retention in tungsten. **G. Valles**, C. González, I. Martin-Bragado, I. Romero, O. Peña-Rodriguez, A. L. Cazalilla, R. Gonzalez-Arrabal, J. M. Perlado, A. Rivera. Poster presentation

- SPIE Optics + Optoelectronics, Prag (Czech Republic), April 13 – 16, 2015

Role of tungsten nanostructure on pulsed helium irradiation-induced defects. **G. Valles**, C. González, I. Martin-Bragado, R. Iglesias, J. M. Perlado, A. Rivera. Oral presentation.

- 15th International Conference on Plasma-Facing Materials and Components for Fusion Applications (PFMC-2015), Aix-en-Provence (France), May 18 – 22, 2015

Temperature dependence of the hydrogen content in nanostructured W films.

M. Panizo-Laiz, **G. Valles**, N. Gordillo, A. Rivera, F. Munnik, I. Martin-Bragado, E. Tejado, J. M. Perlado, R. Gonzalez-Arrabal. Poster presentation.

- Inertial Fusion Sciences & Aplicaciones (IFSA-2015), Seattle (USA), September 20 – 25, 2015

Capabilities of nanostructured tungsten for plasma facing material. R. Gonzalez-Arrabal, N. Gordillo, A. Rivera, M. Panizo-Laiz, **G. Valles**, C. Gonzalez, C. Guerrero, G. Balabanian, I. Martin-Bragado, E. M. Bringa, R. Iglesias, E. Tejado, J. Y. Pastor, J. Molina, M. J. Inestrosa-Izurietta, J. Moreno, F. Munnik, J. M. Perlado. Oral presentation.

- Nano Security & Defense International Conference, Madrid (Spain), September 22 – 25, 2015

- Advances in Materials & Processing Technologies Conference (APMT-2015), Leganés, Madrid (Spain), December 14 – 17, 2015

Defect evolution in irradiated nano- and poly-crystalline tungsten under realistic nuclear fusion irradiation conditions: the valuable role of object kinetic Monte Carlo methods. A. Rivera, **G. Valles**, I. Martin-Bragado. Oral presentation.

- Industriales Research Meeting (IRM16), ETSII-UPM, Madrid (Spain), April 20, 2015

Hydrogen irradiation in tungsten for nuclear fusion reactors: an OKMC study.

G. Valles, I. Martin-Bragado, C. Gonzalez, J. M. Perlado, A. Rivera. Poster presentation.

- Computer Simulation of Radiation Effects in Solids (COSIRES 2016), Loughborough (UK), June 19 – 24, 2016

Coarse-grained and nanostructured tungsten under ion irradiation for nuclear fusion feasibility studies: An object kinetic Monte Carlo description. **G. Valles**, I. Martin-Bragado, M. Panizo-Laiz, N. Gordillo, J. M. Perlado, K. Nordlund, C. Björkas, A. Lasa, E. Safi, R. Gonzalez-Arrabal, A. Rivera. Oral presentation

- 43th Conference on Plasma Physics, European Physical Society (EPS 2016), Leuven (Belgium), July 4 - 8, 2016

Study of the role of grain boundaries on radiation-induced damage and on H behaviour in tungsten: An experimental and theoretical approach. M. Panizo-Laiz, **G. Valles**, A Rivera, N. Gordillo, C. Guerrero, F. Munnik, C. Gonzalez, I. Martin-Bragado, J. M. Perlado, R. Gonzalez-Arrabal, Poster presentation.

- 26th IAEA Fusion Energy Conference, Kyoto (Japan), October 17 - 22, 2016

Multiscale Modeling of Materials: Light Species Dynamics in nano-W and EOS of Hydrogen. J. M. Perlado, C. Gonzalez, C. Guerrero, **G Valles**, N. Gordillo, R Iglesias, I. Martin-Bragado, M. Panizo-Laiz, A. Prada, R. Gonzalez-Arrabal, A. Rivera. Poster presentation.

Courses

- Materiales avanzados bajo irradiación y su desarrollo en fusión y fisión nuclear. El papel de la ICTS Techno-Fusión, UPM, La Granja de San Ildefonso (Spain), July 6 – 7, 2011
- Simulación computacional de sistemas de Fusión Nuclear: integración de modelos en TECHNOFUSIÓN, UPM, La Granja de San Ildefonso (Spain), July 11 – 12, 2012
- Application of Electronics in Plasma Physics, Erasmus Intensive Programme APPEPLA 2012, Rethymno, Crete (Greece), July 16 – 27, 2012
- Curso de programación aplicada sobre C/C++, ETSII-UPM, Madrid (Spain), September 25 – October 9, 2012
- Short Course on Materials, Technologies and Applications in Nuclear Fusion, ETSIC-UPM, Madrid (Spain), April 7 – 9, 2014

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