4.1 Final publishable summary report

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Executive Summary

The RadInterfaces project studies a novel class of nanostructured multilammelar compounds considered to have practical application in the nuclear industry. The aim of the project is to develop a software suite capable of studying these compounds over a vast range of time and length scales from individual atomic interactions to a complete characterization of the mechanical response of the material over the reactor lifetime. These compounds present the very promising property of being self-repairing under the damage sustained by materials under heavy and continual irradiation, and thus present a possibly ground breaking application of nanoscience and functional material design to the nuclear industry. A common goal for materials in nuclear reactors, be they containment vessels or fuel cladding materials, is to exhibit the highest radiation tolerance possible. The emergence of new concepts using nanoscience in the design of bulk structural materials shows promise for providing the breakthroughs needed for future nuclear energy systems. In particular, the design and control of nanostructures and complex defect structures can create self-healing materials for radiation-induced defects and impurities that can yield radiation impervious materials. This concept has the potential to make radiation damage much less critical in design considerations, provided that complete defect absorption and self-healing can be achieved. The realization of this concept presents enormous scientific and technical challenges in the design and fabrication of bulk alloys using concepts developed for manipulating materials at the nanoscale. In reality, this entails expanding emerging capabilities for the synthesis of nanostructured materials at low dimensions (thin films and three-dimensional assemblies of precipitate phases) to true bulk alloys with the requisite thermo-mechanical properties required for reactor operation. In a nuclear reactor the structural materials and the fuel components can undergo significant radiation damage. Most commonly radiation damage occurs via the impingement of neutrons into the material. The neutrons interact with a single atom, the primary knocked-on atom (PKA), leading to a cascade of collisions with other atoms. After the very fast dissipation of the thermal energy spike, the radiation induced damage takes the form of point defects, vacancies and self-interstitials and clusters thereof, within the material. Over time these point defects agglomerate and interact with the existing microstructure, leading to weakening effects such as void swelling and irradiation creep.

Additionally, hydrogen and helium gas can be produced via neutron capture reactions. These gases are insolubile in the metals and alloys used in the nuclear industry, and thus tend to aggregate at voids, dislocation and grain boundaries, further weakening the mechanical properties.

A class of materials have recently been developed which exhibit a tremendous ability to repair the damage associated with the initial cascade from a PKA. The materials are constructed from nanoscale thick layers of immiscible metals deposited in alternating layers via, e.g. physical vapour deposition. The interfaces between the metallic layers serve as almost limitless sinks for the as yet still mobile point defects. Additionally the point defects that are absorbed into the interface interact over a much larger length scale. The point defects themselves, the vacancies and interstitials, are each the anti-defect of the other and annihilate when they come into contact, leaving behind pristine, that is

"repaired", crystal. So that this increased interaction scale leads to increased annihiliation.

In order to utilize the full potential of nanoscience in designing materials for nuclear systems, it is necessary to develop a full physical and chemical understanding of defect production, diffusion, and trapping under extreme conditions of temperature and radiation fluences. Theory, modeling and simulation tools can provide detailed understanding and predictive capability for nanostructured structural and functional materials for the nuclear energy systems. In order to create these materials, novel synthesis techniques spanning the full range from nanoscale to the bulk will be required along with analytical tools to characterize defect structures at the atomistic level.

Summary description of project context and objectives

Context

The RadInterfaces project aims to provide tools to study the irradiation related properties of Nanoscale Metallic Multilayer Composites (NMMC) using a true multiscale approach - from individual atoms interactions to the a complete characterization of mechanical response of the material over the reactor lifetime. These materials present the very promising property of being self-repairing under the the damage sustained by materials under heavy and continual irradiation, and thus present a possibly ground breaking application of nanoscience and functional material design to the nuclear industry.

A common goal for materials in nuclear reactors, be they containment vessels or fuel cladding materials, is to exhibit the highest radiation tolerance possible. The emergence of new concepts using nanoscience in the design of bulk structural materials shows promise for providing the breakthroughs needed for future nuclear energy systems. In particular, the design and control of nanostructures and complex defect structures can create self-healing materials for radiation-induced defects and impurities that can yield radiation impervious materials. This concept has the potential to make radiation damage much less critical in design considerations, provided that complete defect absorption and self-healing can be achieved. The realization of this concept presents enormous scientific and technical challenges in the design and fabrication of bulk alloys using concepts developed for manipulating materials at the nanoscale. In reality, this entails expanding emerging capabilities for the synthesis of nanostructured materials at low dimensions (thin films and three-dimensional assemblies of precipitate phases) to true bulk alloys with the requisite thermo-mechanical properties required for reactor operation.

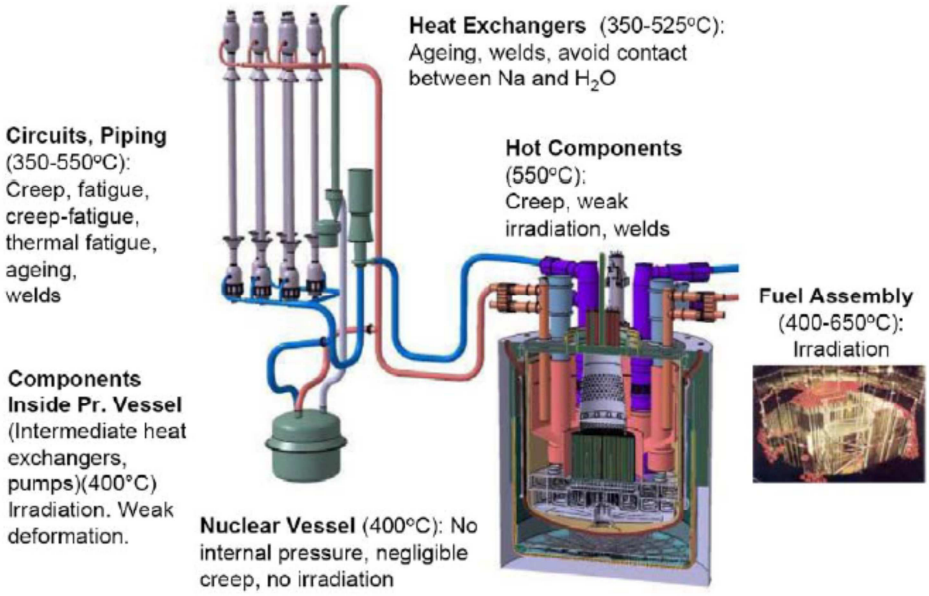


Figure 1: Service conditions envisaged for the different main components of a future SFR design

Both the fuel components and structural materials within nuclear reactors can sustain substantial radiation damage. Regardless of the type of reactor, this damage initially appears in the form of local intrinsic point defects within the material – vacancies and interstitials.

- The point defects agglomerate, interact with the underlying microstructure and lead to undesirable effects such as void swelling and irradiation creep.
- Vacancies provide a pathway for solutes to segregate to grain boundaries and dislocations leading to chemical inhomogeneities that translate into phase transformations and/or property variations in these materials, rendering them unsuitable for the desired application.
- Additional radation damage can occur by the creation and accumulation of gases produced via transmutation reactions.

Most harmful effects of irradiation on the material properties and thermo mechanical behavior — e.g. void swelling, irradiation creep, radiation-induced hardening and embrittlement — can be traced back to the formation of point defect clusters and gas bubbles.

In order to utilize the full potential of nanoscience in designing materials for nuclear systems, it is necessary to develop a full physical and chemical understanding of defect production, diffusion, and trapping under extreme conditions of temperature and radiation fluences. Theory, modeling and simulation tools can provide detailed understanding and predictive capability for nanostructured structural and functional materials for the nuclear energy systems. In order to create these materials, novel synthesis techniques spanning the full range from nanoscale to the bulk will be required along with analytical tools to characterize defect structures at the atomistic level.

The nanoscaled metallic multilayer compounds (NMMCs), which are the subject materials of this study, have a high interface to volume ratio. The atomic structures of these interfaces are substantially different from those of bulk materials and have a substantial effect on the materials properties and radiation response. Recently, an extremely promising heterophase interface design approach was proposed, where interfaces could be structured so as to act as efficient and essentially endless sinks for irradiation-induced vacancy-interstitial (Frenkel) pairs, leading to their enhanced recombination, and, in so doing, restoring part of the material to its undamaged state. The combination of such interfaces with a multilaminate material design concept was shown to produce nanostructured materials exhibiting ultra-high strengths and enhanced radiation damage tolerance. This concept was recently illustrated using a model copper (Cu)-niobium (Nb) nanolayered system, a Scanning Electron Microscopy (SEM) micrograph of which is shown in Figure 1. The flow strengths of these composites are on the order of 2.5 GPa for layer thicknesses of around 2 nm, and the best radiation damage tolerance is also observed at similar thicknesses.

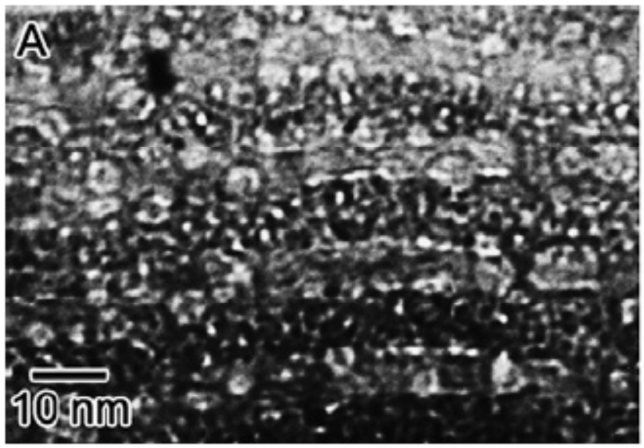


Figure 2: He Bubbles in a Cu-Nb nanolaminate. In the Nb layers the bubbles do not exceed 2nm while the bubble size in the Cu layers is limited by the layer thickness.

Published results point out clearly that NMMCs are the most promising systems for new advanced materials with enhanced radiation damage resistance. Currently, some of the most critical limitations to design NMMCs with optimum tailored properties are the lack of predictive modelling tools for (1) radiation-induced damage and (2) the mechanical behaviour of undamaged and damaged NMMCs. Indeed, even in the simpler non-irradiated FCC/FCC systems, for which transmission electron microscopy (TEM) has shown that the main deformation mechanism is by the channelling of dislocations, the most refined models are not able to accurately predict the effect of individual layer thicknesses on the mechanical response of NMMCs.

Conventional molecular dynamics simulations can be used to demonstrate the mechanisms of radiation damage in some multilayer systems, but these are necessarily limited by both length and time-scales, and therefore cannot directly conclude on its macroscale efficiency. Larger time scale phenomena (i.e. diffusion, interface roughening) need be considered.

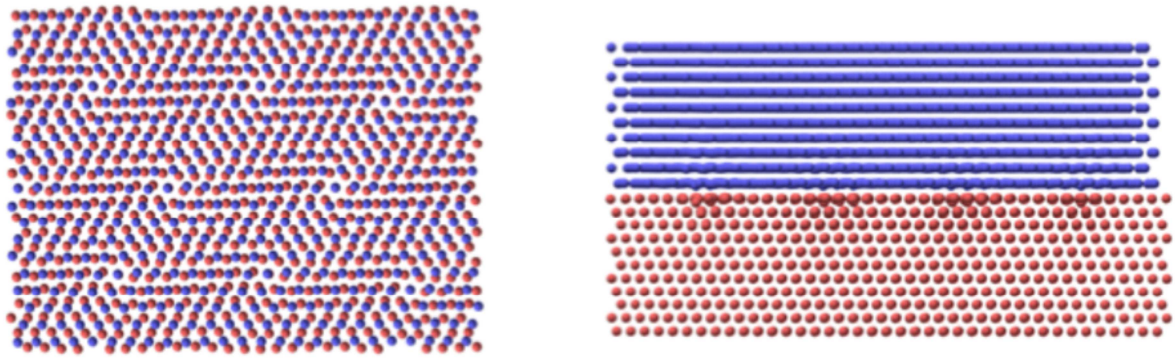


Figure 3. DFT simulation of the local structure of the Cu-Nb interface in top (left) and side (right) views (Cu = blue, Nb = red).

Regarding morphological stability, interfaces under irradiation are perturbed by repeated collision cascades and by fluctuations in defect fluxes arriving from the neighboring crystalline material. These perturbations may cause local mixing, roughening, or amorphization. Counteracting these effects are thermodynamically-driven de-mixing of substitutional impurities at interfaces formed by immiscible materials, smoothing by interfacial diffusion driven by capillary forces, and devitrification by processes such as solid phase epitaxial growth. Moreover, high fluxes of point defects diffusing towards interfaces can bias the transport of species such as alloying elements, impurities, and implanted elements (especially He) to or away from interfaces, depending on how the species couple to the diffusing point defects. These phenomena cause significant variations in the composition of interfacial material as a function of irradiation, leading to detrimental effects such as embrittlement due to radiation-induced segregation. In spite of the past work demonstrating segregation and precipitation at interfaces under irradiation environments, the knowledge base to design interface structures that are morphologically and chemically stable under irradiation is still lacking.

Finally, irradiation is known to dramatically enhance material creep due to the super-saturation of point defects (vacancies and interstitials) produced by ion collision cascades. Under the influence of external stresses, interstitials diffuse preferentially to dislocations oriented favorably with respect to the external stress axes, causing them to climb. Some interfaces can reduce the rate of creep under irradiation by absorbing point defects as well as dislocations before they can contribute to creep. Depending on their transport properties, shear resistance, and ability to nucleate and transmit dislocations, however, interfaces can also lead to enhanced Coble creep, interface sliding, and dislocation multiplication. These effects are described below in Figure 3.

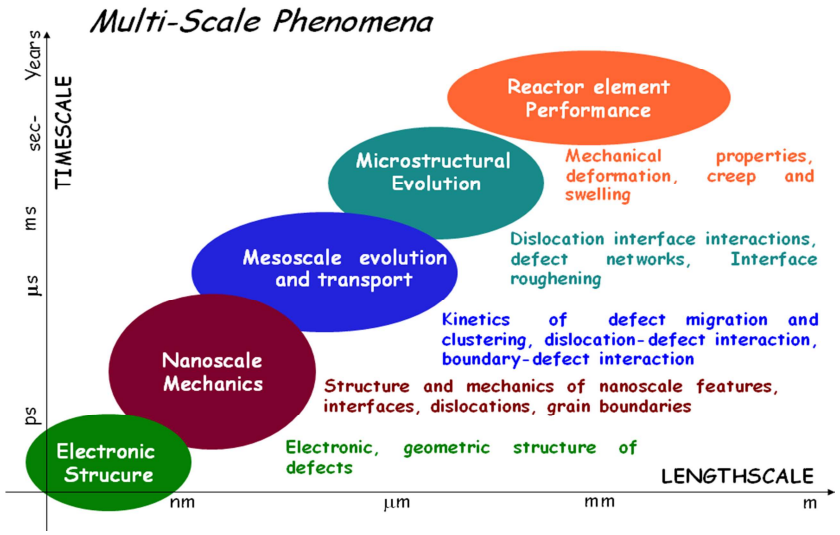


Figure 4: A description of physical effects expected for NMMCs under irradiation

The preliminary design concept discussed above provides the basis for the hypotheses which will drive the research approach proposed here, namely:

(1) The atomic structure of an interface controls the absorption, emission, storage and annihilation of defects at the interface.

(2) The interactions of misfit dislocations with others of the same type and with disconnections are the most favorable sites for point defect absorption and delocalization.

(3) Multilayer based composite materials with well-designed interfaces can be tailored to have overall properties which constitute a good compromise between high strength, good ductility and improved resistance to radiation damage.

Objectives

The overall objective of the proposed project is to **develop a multiscale predictive modelling framework able to identify suitable strategies for optimising the properties of existing NMMC systems and for identifying new compounds with improved radiation damage resistance and mechanical properties, thus providing a suitable guideline to correlated experimental approaches**.

The framework being developed combines density functional theory to characterise the interface structure at the electronic level, molecular dynamics and atomistic techniques, kinetic Monte Carlo, rate theory and dislocation dynamics to study defect interactions at the atomistic and defect level, and continuum (mesoscopic) approaches to study morphological stabilities of interfaces at the scale of the global NMMC system.

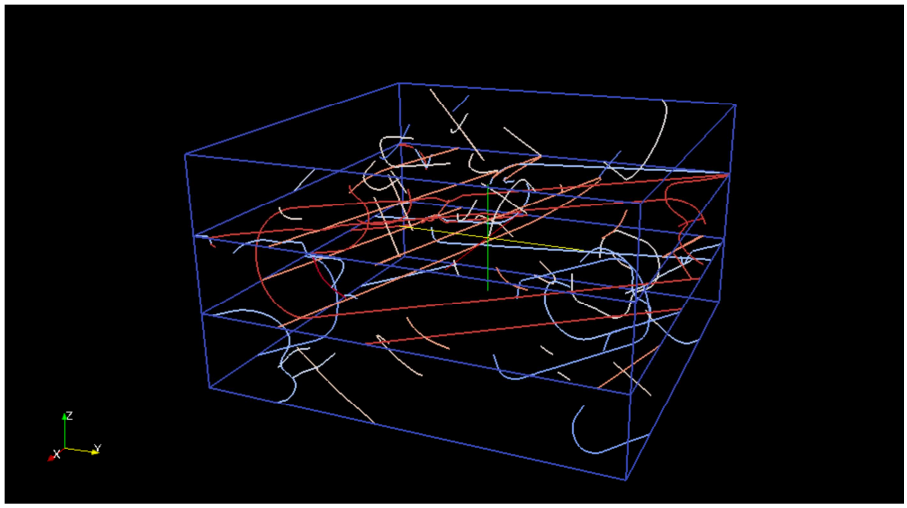


Figure 5: Dislocation dynamics in a multilayer compound under external loading.

Interfaces can be designed to produce materials with ultra-high strengths and enhanced radiation damage tolerance via the tailoring of length scales to take advantage of the atomic structure of their interfaces. However, the advantages for radiation tolerance cannot be quantified until the relevant length scales, such as the layer thickness, are significantly reduced. This is due to the fact that the enhanced radiation damage tolerance of nanolayered composites is the result of the shortening of diffusion distances to the nearest sinks. In layered composites of a few nanometers, diffusion distances to sinks are short enough, due to the large interface area in the material, to enable rapid removal of the point defects before they can gather to form relatively stable aggregates. However, it must also be ensured that the geometry of the structured material is stable under extreme irradiation conditions. It should be possible to tailor the atomic structure and energetics of interfaces to provide the most effective sites for point defect trapping and removal, a proof-of-concept shown already in Cu-Nb nanolayers. Based on the observations above, the development of a multiscale predictive modeling approach for the processing and design of new crystalline multiphase materials with improved resistance to radiation damage requires:

(1) an understanding of the process of radiation damage;

(2) a quantification of the effects of radiation damage on the material behaviour;

(3) the development of methods for analysing the mechanics of both point and line defects in irradiated materials.

(3) exploring the case of systems different from the novel BCC/FCC ones with the Kurdjimov Sachs orientation, which have shown to provide exceptional resistance to radiation damage. Interestingly, other orientations in the BCC/hexagonal close-packed (HCP) systems such as those proposed by Burgers, Potter, Pitsch Schraeder and Rong-Dunlop could be also potential candidates for a new class of NMMC systems.

Description of main S & T results/foregrounds

The RadInterfaces project is broadly split into seven work packages. These cover the entire modelling length and time scales and the experimental studies. The modelling work packages are:

- (micro scale) ab-initio and interatomic potential development, interface modelling and characterization;
- (meso scale) cascade damage and accumulation in single crystals and several multilayers;
- (macro scale) mechanical properties of the entire material in the presence of long-term radiation damage.

The experimental work package covers the creation of suitable CuNb, CuW and NbZr samples via

three techniques: physical vapaour deposition, electrochemical depotision and mechanical alloying.

The main objectives that have been achieved in the RadInterfaces project are:
1. The creation of an accelerated object kinetic Monte Carlo code, MMonCa, that takes account of the microstructure of the multilayer compound and the defect types. This tool is developed in C++ and is intergrated with the TCL scripting language, with the aim of being multi-material, powerful, flexible and intuitive.
2. The development of a spatially-resolved stochastic cluster dynamics method: a new technique which is extremely fast and can follow the interaction and diffusion of populations of a very large variety of cluster types. The spatial resolution means that interfaces and other structural microstructural feature within the material can be modelled.
3. Interatomic potentials have been developed for the Cu/Nb/He and Cu/W/He systems, based on ab-initio simulations.
4. A discrete dislocation dynamics code has been developed which include the multilamellar structure. The interactions between the dislocations and the interfaces between the layers are explicitly taken into account.
5. A consitutive law for the interaction between interfaces and radiation-induced vacancies (self-interstitials are generally quickly abosrbed into interfaces) is in the process of being developed allowing the contrinuum simulations of the machanical response of the ompounds over long times via finite element analysis.
6. Multilayer compound samples of CuNb, CuW and NbZr have been synthesized via PVD, ECD and MA. TEM and Xray characterization has been undertaken.

The main S&T results/foregrounds can be summarized into three major building blocks:

1. *Atomistic Simulation and Developing Potentials for New Systems.*
2. *Processing and Synthesizing of Nanolaminates and nanocomposites and Testing them and different scales.*
3. *Multiscale Modeling and Integration into Design Software of High Radiation Resistance Materials*

Atomistic Simulation and Developing Potentials for New Systems

The main achievements of 1st building block are within four sub-areas of the atomistic work package:

Formation of point defects at semicoherent interface using density functional theory (DFT)

Ab-initio simulations (DFT) as well as molecular dynamics (MD) simulations of selected interfaces were carried out for Cu, Nb, CuNb and CuW. The main achievement here is the realization that existing CuNb MD potentials do not reproduce vacancy and interstitial structures as predicted by first-principles studies. Instead of the de-localized vacancy- and interstitial structures these are in-fact compact as shown in the lower panels of Figure 1. This realization changes the conclusions in many high impact publications. Moreover, the literature CuNb potentials have been, and continue to be, extensively used but should now be revised. The work is under review with *Scientific reports*. [1]

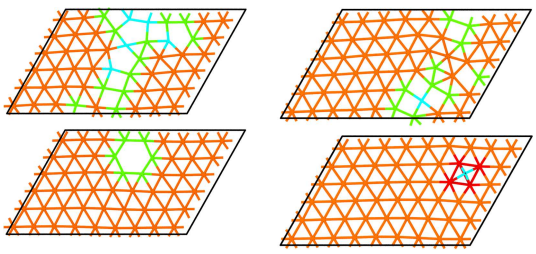


Figure 6. (left) Cu vacancy and (right) Cu interstitial at the Cu/Nb Kurdjumov-Sachs orientation interface. The upper panels result from MD simulations using literature potentials and the lower panels show the corresponding ab-initio results.

Software to generate periodic semicoherent interfaces

Semicoherent interfaces have a complex structure that requires great care in the setup process for atomistic simulations and without scripting the setup task becomes almost impossible. A general script package has been developed within the ASE (atomistic simulation environment) python framework. [2]

CuW embedded atom method type potential suitable for radiation damage studies

“Interatomic potentials” deal with the first of all bridges linking the different scales in the Radinterfaces project. The systems investigated are Cu, W, He, CuW, WHe. The potentials were developed using state-of-the-art methods and are now being tested in, for example, deposition simulations that indeed compares favorably with experiment. See Figure 2 where Cu is deposited on W and vice versa. [3]

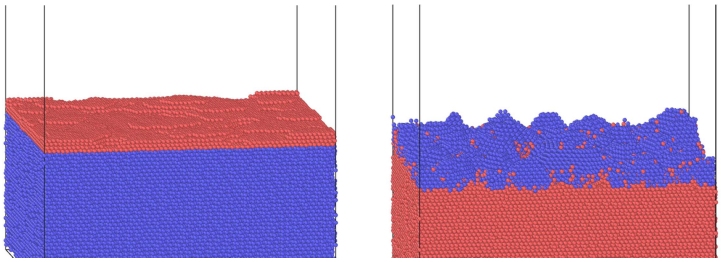


Figure 7. (left) Cu deposited on a W substrate and (right) W deposited on a Cu substrate. The fact that Cu grows smoothly on W and W grows in a rough manner on Cu is what is observed experimentally.

Diffusion barriers

The study of vacancy and He atom migration mechanisms in metallic matrices is crucial in the quest of understanding aging and degradation mechanisms in materials subjected to harsh environments where irradiation is one component. Here the elemental systems Cu, W and Nb were studied with He. The diffusion barriers obtained find immediate application in the modelling of kMC events, as expected from a multiscale approach .[4-8]

[1] "Formation of point defects at semicoherent interface using DFT, E. Metsanurk, A. Tamm, A. Caro, A. Aabloo, M. Klintenberg. Scientific Reports., Submitted/under review.
[2] ”Software to generate periodic semicoherent interfaces for atomistic calculation”, E. Metsanurk, A. Tamm, A, Aabloo, M. Klintenberg. Comput. Phys. Comm. Manuscript in preparation.
[3] "Copper-tungsten embedded atom method type potential suitable for radiation damage studies", Artur Tamm, E. Metsanurk, A. Caro, A. Aabloo, M. Klintenberg. Phys. Rev. B. To be submitted.
[4] ”Migration of helium clusters in Cu/Nb: An MD study”, A. Tamm, E. Metsanurk, A. Aabloo, M. Klintenberg. J. Nucl. Matr. Manuscript in preparation.
[5] ”Helium bubble clustering in copper from first principles”, C González, D Fernández-Pello, M A Cerdeira, S L Palacios and R Iglesias. Modelling Simul. Mater. Sci. Eng. 22 035019 doi:10.1088/0965-0393/22/3/035019.
[6] ”The influence of high grain boundary density on helium retention in tungsten”, G. Valles, , C. González, I. Martin-Bragado, R. Iglesias, J.M. Perlado, A. Rivera. J. Nucl. Matr. In press.
[7] “Electronic origin of He cluster trapping inside a monovacancy in BCC transition metals”, R. Iglesias et al. J. Appl. Phys. Submitted.
[8] “Migration mechanisms of helium in copper and tungsten”, C. González and R. Iglesias. J. Mater. Sci. 49, 8127 (2014)

Processing and Synthesizing of Nanolaminates and nanocomposites and Testing them and different scales

The experimental activity performed within Radinterfaces project can be approximately divided into materials processing and characterization issues. Nanolaminates and nanocomposites have been fabricated by physical vapor deposition, electrochemical deposition and mechanical processing by ball milling. Structural, microstructural and mechanical properties characterization has been mostly performed by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, atomic force microscopy and nanoindentation tests.

A measure of the intensity of experimental efforts and of the determination with which the research units at Czech Technical University, at the Madrid Institute of Advanced Studies and at the University of Cagliari have worked, occasionally involving other units or collaborating with friends and colleagues not belonging to Radinterfaces consortium, can be given by a few representative numbers. Regarding the fabrication of samples, the research unit at Czech Technical University has produced approximately 40 samples by physical vapor deposition, at a rate of about 1 sample per working day. At the University of Cagliari, about 250 successful electrochemical depositions have been performed. The total number of electrochemical depositions, including the ones utilized to systematically explore the electrochemical response of the chemical environment in contact with materials, amount to about 1000. Carried out in collaboration with colleagues at the University of Sassari (Italy), the mechanical processing by ball milling was performed by using 5 laboratory ball mills for about 16000 h.

Concerning the characterization of structural, microstructural and mechanical properties, the use of quantitative X-ray diffraction amounts to a total of approximately 12000 h. Scanning and transmission electron microscopies were utilized for a total of 180 h and 230 h respectively, mostly at the Czech Technical University and at the Madrid Institute of Advanced Studies. The preparation of samples for the characterization of the mechanical behavior required approximately 1100 h of focused ion beam machining, whereas about 5000 h were dedicated to nanoindentation measurements, mostly at the Madrid Institute of Advanced Studies.

Four different irradiation tests have been arranged, although only one was initially indicated in the Radinterfaces project proposal. The irradiation test organized by the Georgia Tech Lorraine CNRS research unit at the JANNuS multi-ion beam irradiation platform (France), and managed in collaboration with the Madrid Institute of Advanced Studies represented the central event of the project, allowing irradiation at room and high temperature and the simultaneous implantation of Cu and He ions at the desired fluence and energy levels. However, additional irradiation tests have been arranged elsewhere due to the initiative and collaboration of other research units.

In particular, He ion implantation experiments have been carried out at the ETH in Zurich consequent to the involvement of colleagues at the Paul Scherrer Institute (Switzerland) by the research unit at the University of Oviedo (Spain). The research unit at the University of Burgos (Spain) managed the organization of long-term gamma irradiation experiments at the gamma irradiation facilities located at the University of Burgos and the University of Sevilla (Spain). The research unit at the Czech Technical University also performed laser beam irradiation tests at the facilities located at the Czech Technical University in Prague and the international SACLA irradiation facility in Japan.

Collaboration has been obtained from colleagues at the Los Alamos National Laboratory (New Mexico, USA) to produce nanolaminates by accumulative roll bonding, from colleagues at the Polytechnic University of Marche in Ancona (Italy) to carry out high-pressure torsion tests on ball milled powders after consolidation by cold pressing, and from colleagues at the Paul Scherrer Institute for the He irradiation tests performed at ETH in Zurich.

Overall, the experimental activity involved a huge amount of work, also due to the choice of dealing with refractory metals such as Nb, W and Zr. It is not surprising that it also had to deal with considerable challenges. At least four of them deserve a particular mention in the light of their crucial importance for the success of the project.

The development of a suitable experimental procedure to perform the electrochemical depositions represents the most difficult challenge. This challenge immediately stems from the choice of synthesizing binary systems containing refractory metals. Due to their remarkably high affinity to O, and then the remarkable propensity to oxidation, refractory metals cannot be deposited from aqueous solutions. In the presence of water, they would be indeed oxidized irreversibly. For this reason, refractory metals are produced by electrolysis using molten salts as solvent phase. However, molten salts cannot be applied to the present case due to the high temperatures involved in the electrolytic process, which would prevent the obtainment of nanometer-sized structures. Therefore, it has been necessary to develop a completely new approach based on the use of ionic liquids as the solvent phase. In the absence of a specific literature, this obliged the research unit at the University of Cagliari to work under ab initio conditions, i.e. to perform a suitably designed experimental activity aimed at investigating the whole electrochemistry of the complex saline solutions formed by the ionic liquid solvent phase, by the electrolyte enhancing electrical conductivity, by the solute metals and counter-ions, by the polarized substrate, and by the inert gas possibly dissolved.

The second challenge to mention is also related to the fabrication of samples. The preparation by ball milling of binary nanocomposites with selected microstructure represents indeed one of the long-standing problems in the field of the mechanical activation of solids. In particular, it is worth noting that the statistical character of the mechanical processing by ball milling, and its approximately random occurrence on the powder particle level, does not allow a strict control of the kinetics of phase transformation and microstructural evolution. More specifically, the powder charge consists of fractions of powder that have undergone a different number of collision events, and therefore exhibit in principle different sets of physical and chemical properties. The design of a microstructure requires therefore the accurate control of the processing dynamics and the knowledge of the relationship between processing and microstructural evolution rates. From this point of view, further complication arises from the very different mechanical properties of the selected metals. In particular, being the refractory metals significantly harder than Cu, plastic deformation mostly involves ductile Cu. It follows that the processing of refractory metals is depressed. To overcome these difficulties, it has been necessary to develop a suitable conceptual framework enabling a mathematical description of the kinetics of the mechanical treatment, and to identify empirical relationship between microstructure of metals and processing rate.

The third challenge is connected again with the nature of the selected systems. The high affinity of refractory metals to O, and the consequent propensity to participate in oxidation processes, required the development of specific experimental protocols to suitably manage O contamination. The formation of metal oxides can indeed rapidly modify the mechanical performances of the selected materials, and determine a significant increase of hardness and brittleness. The necessity of studying the mechanical behavior of the selected systems at relatively high temperatures further complicates this task. In addition, it is worth noting that high temperatures also affect thermal drift and tip-sample reactions during nanoinentation tests, requiring special attention and accuracy in the design and management of the experiments.

Finally, the fourth challenge is intrinsically related to one of the objectives of Radinterfaces project, namely the evaluation of irradiation damage. In fact, measuring the effects of irradiation on the structure and microstructure of the fabricated materials becomes particularly difficult for samples that have been subjected to high temperatures. Thermal effects can indeed eliminate, at least partially, irradiation effects, facilitating the migration of structural defects and contributing to their annihilation.

Despite the above-mentioned challenging issues, the experimental activity produced a wealth of interesting results, which deserved publication in international peer reviewed journals with good reputation in their fields. In particular, nine papers have been already published at present, and others are likely to be submitted or published in the next future. The nine publications are:

1. S. Lotfian, J. M. Molina-Aldareguía, K. E. Yazzie, J. LLorca, N. Chawla, Phil. Mag. Lett. 92, 362 (2012);

2. M. A. Monclús, S. J. Zheng, J. R. Mayeur, I. J. Beyerlein, N. A. Mara, T. Polcar, J. LLorca, J. M. Molina-Aldareguía, APL Materials 1, 052103 (2013);
3. J. Chalupský, T. Burian, V. Hájková, L. Juha, T. Polcar, J. Gaudin, M. Nagasono, R. Sobierajski, M. Yabashi, J. Krzywinski, Opt. Express 21, 26363 (2013);
4. M. A. Monclús, M. Karlik, M. Callisti, E. Frutos, T. Polcar, J. LLorca, J. M. Molina-Aldareguía, Thin Solid Films (2014), in press;
5. S. Garroni, S. Enzo, F. Delogu, Scripta Mater. 83, 49 (2014);
6. S. Garroni, S. Soru, S. Enzo, F. Delogu, Scripta Mater. 88, 9 (2014);
7. A. Vacca, M. Mascia, L. Mais, S. Rizzardini, F. Delogu, S. Palmas, Electrocatalysis 5, 16 (2014);
8. L. Mais, M. Mascia, A. Vacca, S. Palmas, F. Delogu, Chem. Eng. Trans. 41, 97 (2014);
9. M. Mascia, A. Vacca, L. Mais, S. Palmas, E. Musu, F. Delogu, Thin Solid Films, (2014), in press.

These publications discuss a number of new experimental findings that are destined to attract the interest of specialized readers. Publication (2) in the list deserves a special mention because of the outstanding result obtained in the very short term. It has been indeed the most cited APL Materials paper for a few months after publication. This is a clear demonstration of the remarkable interest attracted by the subjects investigated and developed within Radinterfaces project.

Listing all the different results obtained from the experimental activity in the three years of project is out of the scope of the present summary. However, it is suitable to mention in some detail at least the main achievements of the experimental work. The selected achievements are described below:

- Nanostructured composites by electrochemical deposition in ionic liquids
  The systematic variation of the different experimental parameters governing the deposition process allowed to identify nearly optimal conditions for the reduction of metal ions to the corresponding metallic phase. In particular, experimental investigation was performed by using cyclic voltammetry to point out the different reduction and oxidation stages. The study of voltammetric curves as a function of the different parameters indicated in relatively short time acceptable conditions for the deposition of pure Nb in a particular ionic liquid, the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide starting from experimental evidences regarding the electrochemical deposition of Ta. Scanning electron microscopy showed that the deposition process is strongly affected by the total population of nucleation sites on the substrate surface, and by the relatively high nucleation rate intrinsic to the chemical system. The deposition takes place via a sequence of stages that begin with the formation of nanometer-sized islands of metallic phase. As the time elapses, new islands form on the substrate surface while old ones progressively grow. The growth is quite disordered, and gives rise to irregular dendritic agglomerates due to the nucleation of metallic phase also at the surface of the existing islands. At the end of the process, when the whole substrate surface is covered, the deposit exhibit an irregular morphology reminding to the classical example of cauliflowers on a field. However, it is possible to identify pure metals within the aggregates. In particular, the metals form irregular discontinuous layers of size ranging between 30 and 120 nm. The layer thickness can be controlled by suitably adjusting the experimental conditions.
  When a pair of metal is deposited in the single bath mode, nanocomposite are formed. Chemical mapping reveals that the nanocomposite typically exhibits a bi-continuous percolating structure in which the two immiscible metals keep chemically separated, forming an almost continuous interface with irregular shape. The characteristic lengths of the bi-continuous structures can be tuned by modifying the experimental conditions.

It is worth noting that specific continuous micro-reactors have been designed and fabricated to operate under optimal flux conditions.

- Kinetics of the microstructural refinement induced by mechanical processing

A mathematical description of the kinetics of microstructural refinement as a function of the total number of collisions has been developed. In particular, extending previous studies, the rate of microstructural evolution of pure phases and mixtures has been related to the frequency of collisions and their total number by the average volume of powder effectively processed at each collision. This permitted a statistical treatment of the transformations induced by the mechanical processing by ball milling. Once defined the populations of powder subjected to a different number of collisions, any given property was described in terms of average over the properties of each population. Under suitable assumptions, this permitted to relate in principle the rate of microstructural evolution to the property of interest.
To suitably predict the materials behavior, and therefore enable a semi-quantitative description of the system mechanochemistry, a systematic investigation on 21 different chemical system has been carried out. Although most of the necessary experimental evidences came from past work, a few novel systems have been investigated to support the conceptual framework gradually emerging from the study. Following this strategy, a new correlation between the rate of microstructural evolution and the properties of individual metals in mixture has gradually emerged from the body of experimental evidences. In particular, the rate of microstructural refinement and the final average grain size of the processed metals have been found to critically depend on the difference in the Vickers hardness of the two metals in binary mixture. The larger the difference in hardness, the slower the microstructural evolution. In addition, it has been also found that the rate at which Cu, the most ductile element, is processed increases as the hardness of the other metal in mixture increases. It follows that the microstructural evolution process is also affected by chemical composition.

Despite long-lasting research in the field, it is the first time that a clear correlation emerges. This result can be ascribed to the systematic approach, without which a full understanding of the quantities playing a role becomes quite difficult, and the identification of the empirical correlation almost impossible.

- High-temperature mechanical properties of nanoscale multilayers
  The fabrication of nanolaminates with the desired microstructure enabled the study of their mechanical properties as a function of the characteristic lengths and a comparison between the different systems. Physical vapor deposition assured the successful production of samples including interfaces exhibiting the Kurdjumov-Sachs (111)/(110) topology in the case of Cu-Nb and Cu-W systems. In the case of Zr-Nb, predominant interfaces exhibit a (110)/(110) topology. Multilayers obtained by physical vapor deposition were subsequently shaped in the form of micropillars by focused ion beam machining. Then, they were submitted to nanoindentation tests at temperatures roughly between 25 and 400 °C. The results indicate that hardness decreases as the temperature increases for all the investigated systems. In general, the nanolaminates exhibit a relatively high hardness, which can be mostly ascribed to the ordered character of the smooth interfaces separating the chemical domains. The layer thickness definitely affects the mechanical behavior. Plastic deformation takes place relatively easily when the layer thickness is relatively large. As it decreases to 5 nm, the system becomes progressively harder, due to confinement effects and to the consequent increased barrier to the nucleation of dislocations mediating the deformation.
  Irradiation effects are evident. The Cu-Nb samples subjected to irradiation exhibit a significant decrease of hardness. This can be ascribed to the irradiation induced nucleation and growth of voids and bubbles, which negatively affect the mechanical performances. Quite interestingly, the interfacial regions keep relatively free of bubbles and defects. This suggests self-healing effects can play a significant role. Additional experimental evidences are needed to support this conclusion.
  In the case of Zr-Nb, heating surprisingly induces a hardening effect. In the light of accurate investigations carried out, it seems that the observed hardening can be related to the formation of oxides due to O contamination. Although low, O contamination is then able to significantly modify the mechanical response of the selected system.

It is the first time that the mechanical behavior of nanolaminates is studied with this degree of accuracy. The indications obtained have been useful in part to validate the numerical modeling, in part to guide its development.

- Influence of processing method on the mechanical behavior of nanoscale multilayers
  The involvement of colleagues working at the Los Alamos National Laboratory on accumulative roll bonding allowed obtaining Cu-Nb samples with microstructure similar to the one of those obtained by physical vapor deposition. Although the interface topology is completely different, with (112)/(112) predominant interfaces, the Cu-Nb samples produced by severe mechanical deformation exhibit layer thickness close to 5, 15, and 30 nm. This enabled, for the very first time, a comparison between the mechanical properties of Cu-Nb nanolaminates obtained by different methods. Therefore, it has been possible to gain information on the role played by the processing method in the determination of mechanical properties.
  The numerical evidences obtained clearly point out that the samples produced by accumulative roll bonding exhibit a hardness lower than those produced by physical vapor deposition. This is quite surprising in the light of the relatively high content of dislocations that must be expected in the case of materials produced by severe mechanical deformation, and the consequent hardening. However, in the present case, a key role in hardening is played by interfaces. In particular, the highly crystalline character of the interfaces present in samples produced by physical vapor deposition make them significantly harder than others. In particular, it seems reasonable to invoke a definite interface anisotropy effect.
  Mesoscopic models are able to suitably predict, or reproduce, the observed experimental behavior. However, for both samples produced by accumulative roll bonding and physical vapor deposition, it is possible to identify a critical thickness below which the model no longer describes the experimental behavior. This critical thickness amounts to about 5 nm for samples produced by physical vapor deposition and to about 18 nm for samples obtained by accumulative roll bonding. Below 5 nm, the samples produced by physical vapor deposition exhibit a hardening that can be related to interface topology. The study of the materials response at different temperature indicates that an optimal thickness can be identified assuring the highest hardness at any given temperature.

It is also worth mentioning that the results obtained from experimental activity have been used to inspire numerical modeling. In particular, the research unit at the University of Burgos has been asked to perform molecular dynamics simulations aimed at estimating the self-healing behavior of disordered interfaces originating from random orientation of adjacent crystalline grains.

Multiscale Modeling and Integration into Design Software of High Radiation Resistance Materials

Within the RadInterfaces project, this section aimed to create a multiscale software package capable of simulating phenomena occurring across orders of magnitude of space and time. The second major objective was to combine and adapt the software developed in this process into a single, accessible tool for use in an educational context as well as research purposes.

A series of software packages have been developed and integrated, which enable the simulation of the physical phenomena governing the irradiation and mechanical response of NMMCs across many orders of magnitude in time and length scale. Starting at the atomic level, molecular dynamics simulations have been used to study the formation and evolution of irradiation defects shortly after irradiation cascades occur, as well as the activation energies of numerous defect behaviours such as migration and combination. This information is used at in spatially resolved cluster dynamics (SRSCD) simulations, which simulate the evolution of the defect state in an irradiated material for small volumes over long (days, years) timescales. This code relies on stochastic techniques commonly

used in kinetic Monte Carlo to avoid solving a large number of rate equations and therefore can simulate much longer timescales. The caveat in such an approach is the necessity of the transition energies between defect states from molecular dynamics. SRSCD can be used to determine the irradiation defect state at any point over a long time range, but an additional tool is required to translate the defect state into a change in mechanical properties and behaviour of an NMMC.

A discrete dislocation dynamics (DDD) tool was created, which can use input defect states provided by SRSCD to simulate the mechanical response of an irradiated material. Molecular dynamics simulations were used once again to develop a series of behaviour and defect strength rules for dislocation-defect interaction in the DDD code. With these rules and a defect state provided by SRSCD, the irradiation hardening can be calculated from which embrittlement can be directly estimated. Dislocation dynamics simulations also played another important role in the analysis of NMMC materials. The role of interfaces and of dislocations deposited on interfaces strongly influence mechanical response as well as the movement of defects along the interfaces. To study these phenomena, a series of simulations in Cu/Nb were performed to quantify the mechanical response assuming limiting cases of an undeformable (hard) interface which preserved interfacial dislocation cores, and freely deforming (shearable) interface which completely removes deposited dislocation cores. Deposited interfacial dislocation stress field were compared to an identical configuration analysed in molecular dynamics, and it was seen that the interface behaviour lies between the models but is biased towards a shearable interface. This interface characteristic was directly passed to higher scale simulations …….

Presentation of SRSCD code

In an infinite, isotropic medium, the evolution of the defect populations can be modeled by tracking individual defect locations and behaviors, or by using a mean field approximation. The use of a mean field approximation allows the simulation to ignore individual defect behavior, thus reducing the computation time, but assumes spatial homogeneity of defects. Spatially resolved stochastic cluster dynamics (SRSCD) has been developed in this work as a compromise between the two approaches, allowing arbitrary complex systems to be simulated over large volume and time scales.

A physically representative prediction of defect evolution in a heterogeneous microstructure, e.g. polycrystals, nano-structured materials, and nano-laminates, can only be accessed through a spatially resolved method. Indeed, the behavior of defects in the neighborhood of grain boundaries, dislocations, and hetero-interfaces is known to be different from the bulk. While traditional approaches use averaging arguments to treat the impact of grain boundaries and dislocations in homogeneous models, in nano-structured materials this approximation can no longer be made. In addition, defect populations resulting from cascade implantation have been shown to depend on the spatial resolution of the initial cascade state. It is therefore necessary to develop a method that can simulate both large timescales and the spatially resolved structures of nano-structured materials.

Parameterizing SRSCD: using input data from molecular dynamics and ab-initio calculations

In SRSCD, several main reactions are allowed to take place, with rates given by traditional rate theory. The reactions that have been allowed in the work performed here are:

- Clustering of two defects to form one larger defect
- Annihilation of two opposite defects (vacancies and self-interstitials
- Diffusion of defects between volume elements
- Dissociation of point defects from large clusters
- Trapping of defects at dislocation sinks, impurities (carbon), and grain boundaries

The rates for these reactions are typically dependent on the diffusivity of the various defects involved, and the binding energy of point defects to larger clusters. A model such as SRSCD, which allows many defect types, must therefore have a value of diffusivity and binding energy for each point defect type to each cluster type that is allowed to exist within the simulation. In iron, extensive atomistic and ab-initio studies have been performed which can be used to parameterize the majority of needed values.

The scope of a given simulation that can be carried out is typically limited by the confidence that exists in the literature about the various parameters for defect binding and migration in the material being simulated. Therefore, high quality atomistic and ab-initio simulations are required for studies of complex systems such as helium-hydrogen-vacancy-interstitial combinations in metals such as Cu and Nb.

Multiscale Methodology

The multiscale nature of SRSCD is immediately clear: all reaction rates are characterized by energy barriers, provided by ab initio and atomistic calculations. SRSCD simulates the defect interactions and the evolution of the defect state over time and length scales orders of magnitude greater than ab initio and atomistic calculations. However, the evolution of mechanical properties cannot be directly inferred from the defect state – it must be transitioned to a higher scale model such a dislocation dynamics, where the influence of the direct interaction between irradiation induced defects and dislocations can be quantified in terms of mechanical strength and hardening.

Presentation of the DDD code

The Parallel Discrete Dislocation Dynamics (DDD) code is a parallel software written in Fortran 90 that aims at simulating the motion and interactions of a large ensemble of dislocations for single or multi-layered 3D materials on which loading conditions are applied.

The dislocation dynamics code is capable of simulation irradiation hardening using irradiation defect states provided by spatially resolved stochastic cluster dynamics. Using an atomistics informed dislocation-defect behaviour model, the multiscale modeling software is capable of predicting irradiation hardening in bulk and NMMC materials.

A dislocation is a linear defect in a material. Due to its nature, it corresponds to a discontinuity in the lattice structure and hence induces and strain and stress fields. When subjecting to stress, dislocations in a material can glide and interact with each other. The origin of the stress acting on a dislocation comes from two contributions: (1) internal stress generated by the dislocations present in the material and (2) external stress coming from the applied loading conditions.

Due to the non-linear behavior of the dislocation motion and interaction processes, the simulation is performed through an iterative process. At each time step, the motion of all the dislocations is computed and the interactions are performed if applicable. Once the dislocation lines are updated, the mechanical state associated to the newly computed dislocation configuration is evaluated and the code can proceed to the next step. The code will perform as many steps as required in order to complete the simulation run.

Flow chart

This section presents the general flow chart of the DDD code. Except for the parallelization procedures that will be presented in Section Parallelization, the main operations performed by the code are shown here.

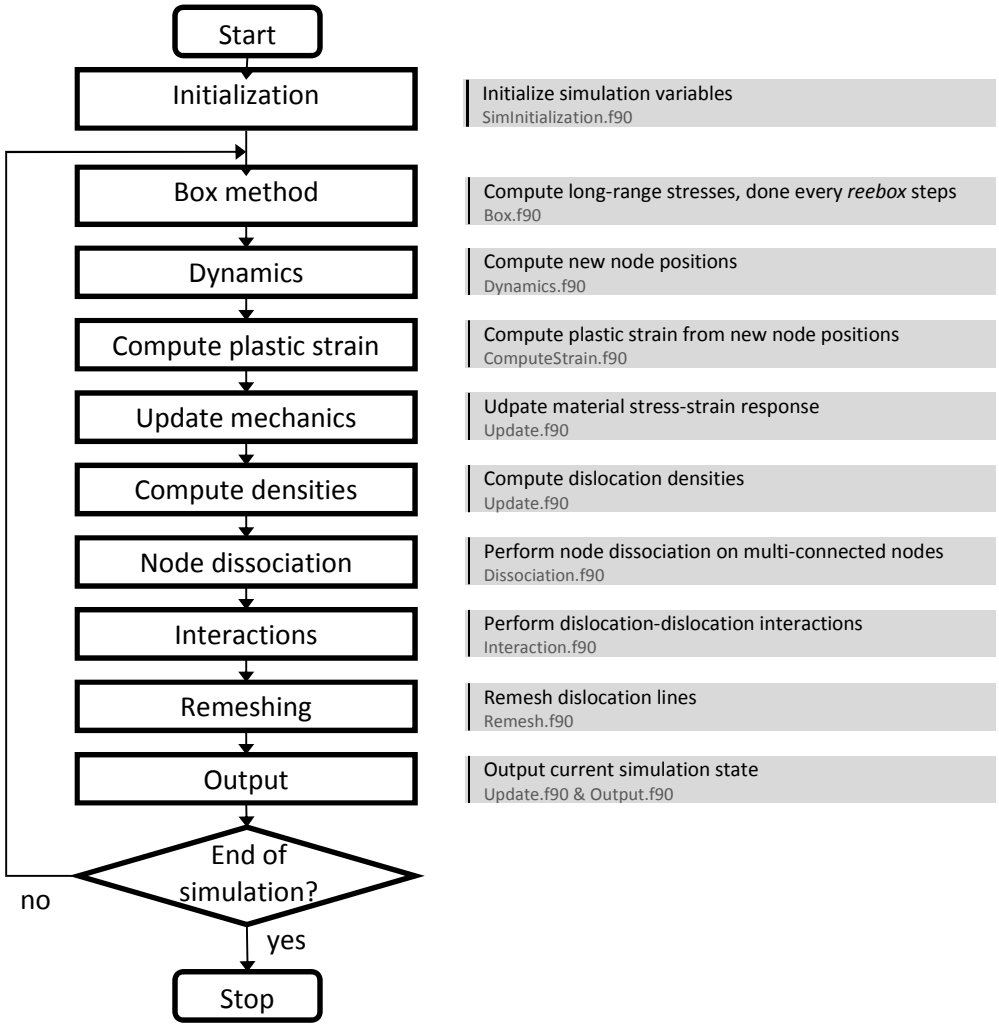


Figure 8: General flowchart of the DDD code

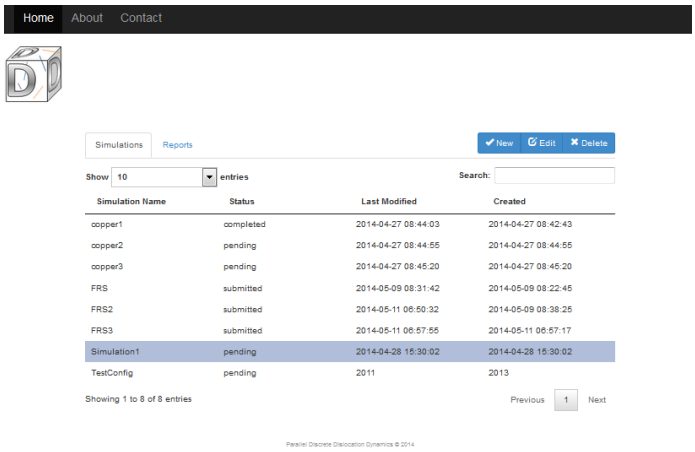
User interface

To simplify the usage of the code, a dedicated graphical user interface has been developed. The objective of this interface is to provide any user that is not necessarily familiar with DDD simulations the ability to easily and quickly run simulations. With such an interface, the aim of the present DDD code is to become a simulation tool that can reach out the entire mechanical and materials science community, and that can be used for educational purposes.

The user interface is a web-based application that can easily be deployed on any computer, and that allows the users to run DDD simulations locally on their computer or remotely on distant

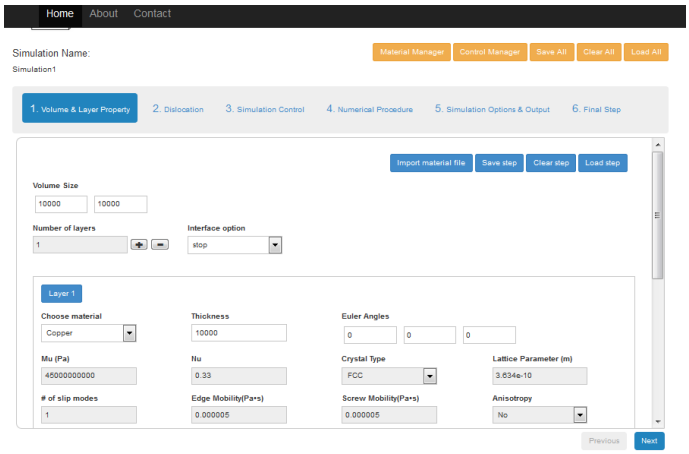
servers/clusters. When using this interface, all the simulations input parameters presented in Section 1.3 are directly selected through the interface. All simulations parameters of DDD simulations launched through the interface are saved within the application database, and can be reused for future simulations. Also, main simulations results (eg. stress-strain curves, etc…) are stored in the database, and can be accessed during and after simulations runs. Additionally, the interface provides a material manager in which essential material parameters are pre-loaded for common materials (eg. Copper, aluminum, magnesium, etc…), and through which users can define their own materials.

Main features of the interface:



Main screen:

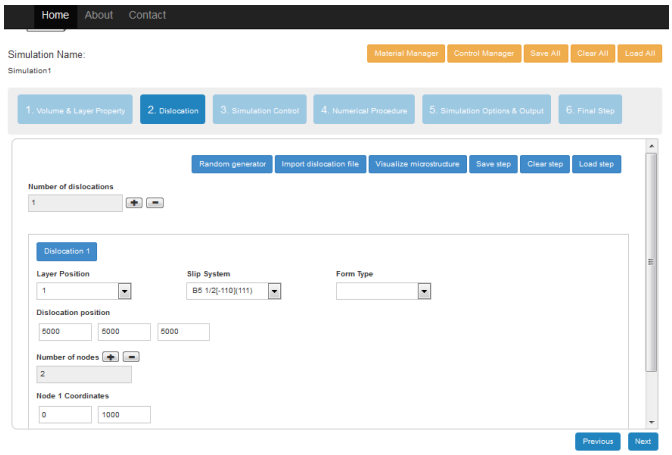
The main screen lists all the simulations created through the user interface and indicate their status.
Pending simulations that have been created but not launched can be edited.
Simulation reports of completed simulations can be displayed (see Results/outputs display).



Simulation setup page:

Simulation parameters are directly selected through drop-down lists and input fields. Helpboxes give a description of each input field. Simulations parameters are divided into different categories and listed under their corresponding tabs:

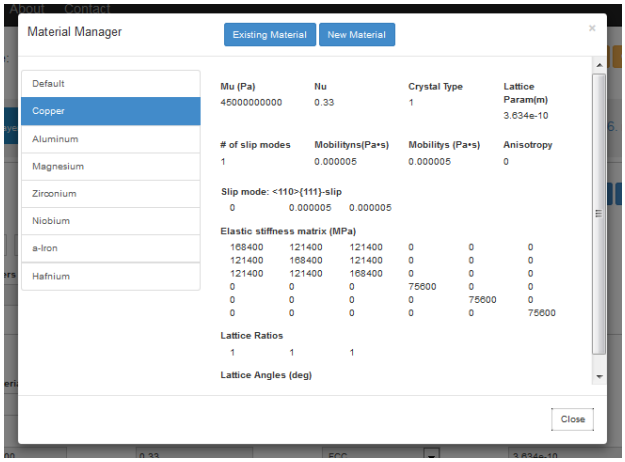
1. Volume and layer properties
2. Dislocation microstructure
3. Simulation control
4. Numerical procedure
5. Simulation options and outputs
6. Simulation launching options



Dislocation microstructure:

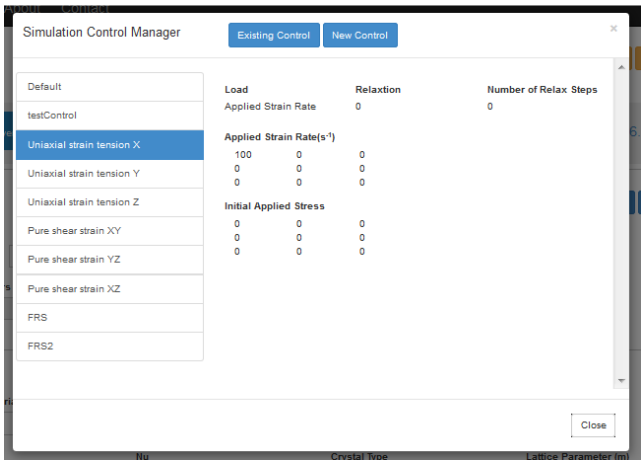
The dislocation lines defining the initial simulated microstructure can be created manually, imported from an existing *interaction_geom_input.txt* file (see Section 1.3.2), or generated according to prescribed options (eg. number of dislocation lines, densities, character, etc…).

The initial microstructure can be directly displayed in 3D through the interface.



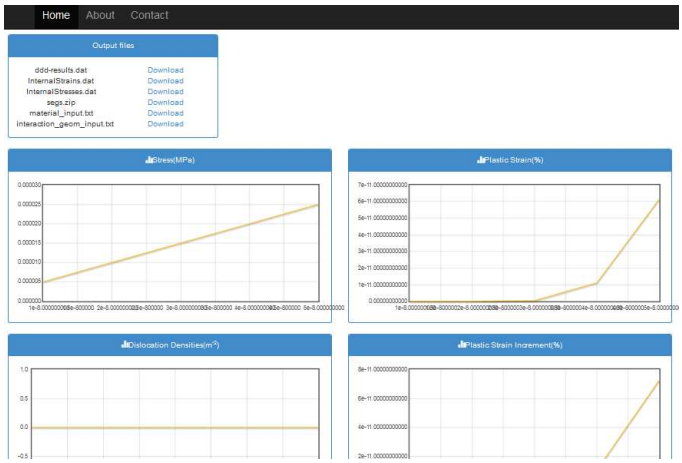
Crystal and Material manager:

The crystal and material manager is a database that provides necessary parameters for common materials, and allows the users to fully define their own material systems: crystal structure, slip systems, material parameters, etc…



Simulation control manager:

The simulation control manager provides basic simulation loading conditions (e.g. uniaxial tension/compression, pure shear, relaxation, etc…) and allows the user to define their own simulations conditions.



Results/outputs display:

Main results of DDD simulations (eg. stress/strain response, dislocation densities, etc…) can be directly visualized through the interface. Other outputs such as dislocations microstructure evolution or internal stress/strain distributions can be directly downloaded from the interface to be opened through visualization software (eg. ParaView).

Scientific advances resulting from this software package have been published in the following publications:

Dunn, A. Y., Capolungo, L., Martinez, E., & Cherkaoui, M. (2013). Spatially resolved stochastic cluster dynamics for radiation damage evolution in nanostructured metals. *Journal of Nuclear Materials*, *443*(1), 128-139.

Dunn, A. Y., McPhie, M. G., Capolungo, L., Martinez, E., & Cherkaoui, M. (2013). A rate theory study of helium bubble formation and retention in Cu–Nb nanocomposites. *Journal of Nuclear Materials*, *435*(1), 141-152.

Dunn, A., Agudo-Merida, L., Martin-Bragado, I., McPhie, M., Cherkaoui, M., & Capolungo, L. (2014). A novel method for computing effective diffusivity: Application to helium implanted α-Fe thin films. *Journal of Nuclear Materials*, *448*(1), 195-205.

Sobie, C., McPhie, M. G., Capolungo, L., & Cherkaoui, M. (2014). The effect of interfaces on the mechanical behaviour of multilayered metallic laminates. *Modelling and Simulation in Materials Science and Engineering*, *22*(4), 045007.

Sobie, C., Bertin, N., & Capolungo, L.. Analysis of Irradiation Hardening Models using Dislocation Dynamics. *Metallurgical and Materials Transactions A*, Submitted September 2014.

Potential impact and main dissemination activities and exploitation results

The experimental findings obtained during the three years of work within Radinterfaces project can be expected to have a significant impact on the different areas of investigation involved. The fact that the results have been published in well reputed, in a few cases outstanding, international peer-reviewed journals represents itself an indirect measure of their potential impact on scientific community. A more direct measure of the interest attracted by the subject of study and by the experimental results obtained is given by the outstanding citation report on one of the published papers, ***namely M. A. Monclús, S. J. Zheng, J. R. Mayeur, I. J. Beyerlein, N. A. Mara, T. Polcar, J. LLorca, J. M. Molina-Aldareguía, APL Materials 1, 052103 (2013). For a few months, it has been indeed one of the five most cited APL Materials papers.***

It can be reasonably expected that the scientific evidences regarding the mechanical properties of nanolaminate samples produced by physical vapor deposition will also attract similar interest, probably fostering further progress in the field.

From a technological point of view, the achievement of the capability of depositing nanocomposites of refractory metals by electrochemical methods can be considered a significant breakthrough. A new technology has been set up, providing a new synthetic route to composite materials. It is a valid alternative to molten salts technology, and is in principle extremely versatile due to the possibility of varying almost without limit the chemical system. At the same time, it also represents a definite alternative to aqueous solutions. Therefore, it could give rise to a completely new sector of application for electrochemistry, which is one of the most widespread methodologies in industry. It follows that the new methodology set up can have a disrupting impact on the existing industrial technology.

The software developed here as not only enabled a fundamental investigation into the irradiation and mechanical properties of NMMC materials, but has also resulted in a user-friendly multiscale tool which has already been incorporated into a graduate level mechanical engineering curriculum (ME6202 at the Georgia Institute of Technology). This software package will also be distributed as an open source teaching resource suitable for upper year undergraduate students and graduate students.

Address of project public website and relevant contact details

These new NMMC concepts are expected to have considerable impact in the nuclear industry. As a result, the consortium members were able to develop software for fast modelling of the mechanical response of NMMCs. Further information can be found at http://www.radinterfaces.eu.