CuNb metallic interfaces as a future material with Helium trapping ability in emerging nuclear systems

Santiago Cuesta-López[1,2*], V. Yeguas[2], Roberto Serrano-López[1]

[1] ICCRAM, International research Center in Critical Raw Materials and Advanced Industrial Technologies. University of Burgos, 09001, Burgos, Spain.

[2] Advanced Materials and Nuclear Technology unit. University of Burgos, 09001, Burgos, Spain.

*Contact, e-mail: scuesta@ubu.es

Abstract

A challenging goal for nanoscience is to contribute to the design and control of radiation impervious materials for its use in emerging nuclear reactors. A very well known problem in nuclear materials science is related with Helium diffusion and void filling, which finally can evolve to a material embrittlement. Especially interesting is the role of the interfaces generated in Nanoscale Metallic Multilayer Composites (NMMCs) like Cu-Nb, that exhibit enhanced radiation damage resistance, since they could be structured to act as efficient sinks for irradiation-induced vacancy-interstitial pairs, leading to their recombination and in so doing, restoring part of the material to its undamaged state. It has been also postulated that this kind of immiscible alloys interfaces, may be efficient in the process of trapping and avoiding diffusion of He atoms. Molecular dynamics simulations allowed us to get a deeper insight into the structural, dynamic and energetic factors that govern He trapping ability of the hetero-interface Cu-Nb. Moreover, the simulations here reported enable a fruitful discussion about the helium aggregation and bubble formation within the interface at particular attraction centers arising from undercoordination sites close to the intersection points of the misfit dislocations. The obtained results have been useful to identify and characterize the process of the helium adsorption and damage over the material performance, what is required to efficiently design and monitor future nuclear materials based on immiscible alloys.

Introduction

Next incoming generation of nuclear reactors is expected to require a new class of materials based in radically different approaches relying on nanoscale strategies in order to mitigate severe damage and to ensure long term safe operation under extreme conditions of neutron irradiation and helium production. 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.

Radiation damage arising from neutron induced cascades of atomic displacements at the level of the crystal structure, and helium bubble formation resulting from neutron capture reactions in materials such as ferritic–martensitic and austenitic steels is known to lead to severe embrittlement and cracking, which results on a major challenge for the next generation of nuclear plants [1-3]. For instance, magnetic confined fusion reactors like DEMO, will share a primordial objective in defining materials that will be capable of reliable performance under severe burning plasma conditions, which will require the development of grade materials with suitable microstructure and mechanical properties. Key elements, like the divertor, will have to face intense neutron, helium and hydrogen isotopes irradiations [4-5]. In the case of first-wall/blanket structural materials He will be produced in ferritic/martensitic steels at concentrations approaching 1800 appm at end-of-life doses of 170 dpa [6].

Recently, an extremely promising heterophase interface design approach was proposed, where interfaces could be structured so as to act as efficient 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 [7]

In the last years, research results point out that Nanoscale Metallic Multilayer Composites (NMMCs) exhibit enhanced radiation damage resistance. For instance, in the case of Cu-Nb system, it has been shown that, due to the particularly dense concentration of misfit dislocations on the interface, point defects delocalize into kink-jog dislocation pairs which interact over a much longer range than the compact form of these point-defects in the bulk, enhancing the annihilation of displacement damage [8]. Furthermore, NMMCs show promising properties in the sequestration and arrest of He bubble growth [9], positioning them as one of the most promising candidates for future nuclear systems.

Currently, some of the most critical limitations to design NMMCs with optimum tailored properties are the lack of predictive modelling tools for understanding the mechanisms underlying the radiation-induced damage resistance, the He diffusion and trapping, as well as the mechanical behaviour of undamaged and damaged NMMCs. Helium is essentially insoluble in metals and tends to aggregate at internal defects such as vacancy clusters, voids, dislocations, grain boundaries, lath boundaries and particle–matrix interfaces, degrading the creep-rupture and fracture properties, thus, in order to achieve an optimal design of helium-resistant interfaces, it is essential to develop a detailed picture of He transport and fate in NMMCs.

One of the most useful computational tools that can be used to analyze and understand the

detailed mechanisms at the level of the atomic structure of an interface that enable a nanocomposite to be stable under high concentration of helium in a material under irradiation is Molecular Dynamics (MD) [10-13]. MD is a simulation technique that models the interaction between atoms or molecules. Using some rules expressed by an empiric 'interatomic potential', a MD process can follow the trajectory and evaluate the energetic values of each individual element of the system. It is also capable of simulate the evolution of computational probes formed by millions of atoms along time.

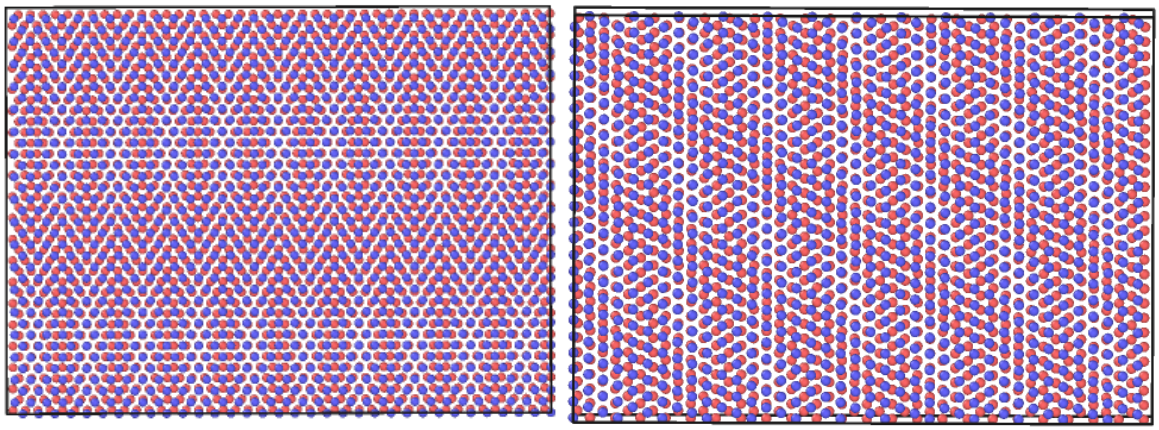
In this work we communicate new insights on the He trapping ability of model Cu-Nb interfaces by means of Molecular Dynamics simulations. A new possible stable interface structure of lower energy than previous successfully predicted [14] is reported. Such an interface structure shows potential ability for He trapping at minimum energy patches of undercoordination, or misfit dislocation intersections (MDI) between the adjoining crystals. Our study suggests a clear He adsorption saturation limit at the Cu-Nb interface highly dependent on the interface atomic geometry. This factor can be of possible use to define up-scaling design parameters making CuNb NMMCs as materials applicable in future nuclear engineering designs.

Results

CuNb Interface stability and lowest energy structure

CuNb interface structure is still over controversy, since it can present either a disordered structure, or an ordered interface structure, which is supposed to be the origin of the exhibited self-healing mechanism against radiation damage [8]. To date, experimental and modelling studies on Cu/Nb interfaces have carried on Kurdjumov-Sachs (KS) or Nishiyama-Wasserman (NW) orientation relationships (see Figure 1) being the KS structures the most studied.

Figure 1. Main interfaces structures considered in our study for CuNb multilayers. (Left) CuNb Nishiyama-Wassermann. (Right) KS1 CuNb created by simply joining Cu and Nb in the KS OR.

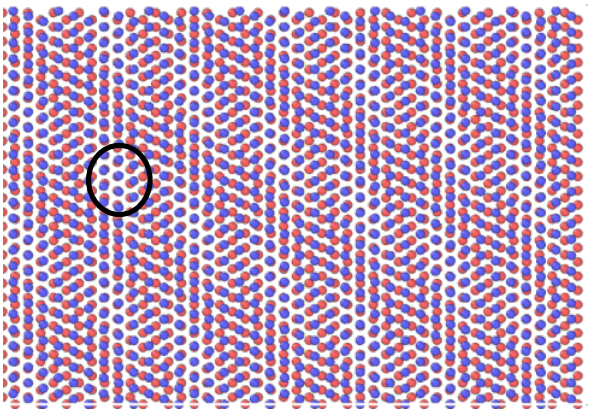


Kurdjumov-Sachs (KS) interface [15-16], follows the traditionally observed KS orientation relation (OR): {111}fcc // {110}bcc, with ⟨110⟩fcc // ⟨111⟩bcc at the interface. The other type of interface also forms in the KS OR, but differs in the orientation of the habit plane, {112}fcc //

{112}bcc, while retaining ⟨110⟩fcc ∥ ⟨111⟩bcc at the interface, for convenience sake termed {112} interface. This interface was recently found in severely plastic deformed (SPD) fcc-bcc composites. One important difference between these two interfaces is that in the KS interfaces, point defects are strongly delocalized (with core size of defects approximately 3 nm in diameter) while in the {112} interface, point defects absorbed remain compact. Thus in KS2, as predicted and detailed by Demkowicz *et al* [8,14] the atomic layer of Cu immediately adjacent to Nb is homogeneously strained and rotated with respect to a perfect Cu {111} plane, reducing its areal density by aprox. 0.5%. Furthermore, a derivation of KS called KSmin has been also reported [8] resulting on a slightly lower interfacial energy. KSmin has 5% vacancies in the Cu layer adjacent to the interface compared to KS1.

Importantly, the atomic configuration proposed for the KS interface between Cu and Nb is characterized by misfit dislocation intersections (MDI) between the adjoining crystals. These MDIs appear in the proximity of locations where an interface Cu and Nb atom are positioned nearly 'on top' of each other. They are also called patches of undercoordination (see Figure 2) and it is believed that they are the major responsible of the capability to acts as defect sinks [17].

Figure 2. Visualization of the KS1 interface configuration looking normal to the interface plane reveals the presence of patches of undercoordination. These patches are identified by circled regions in and occur in the proximity of locations where an interface Cu and Nb atom are positioned nearly 'on top' of each other.

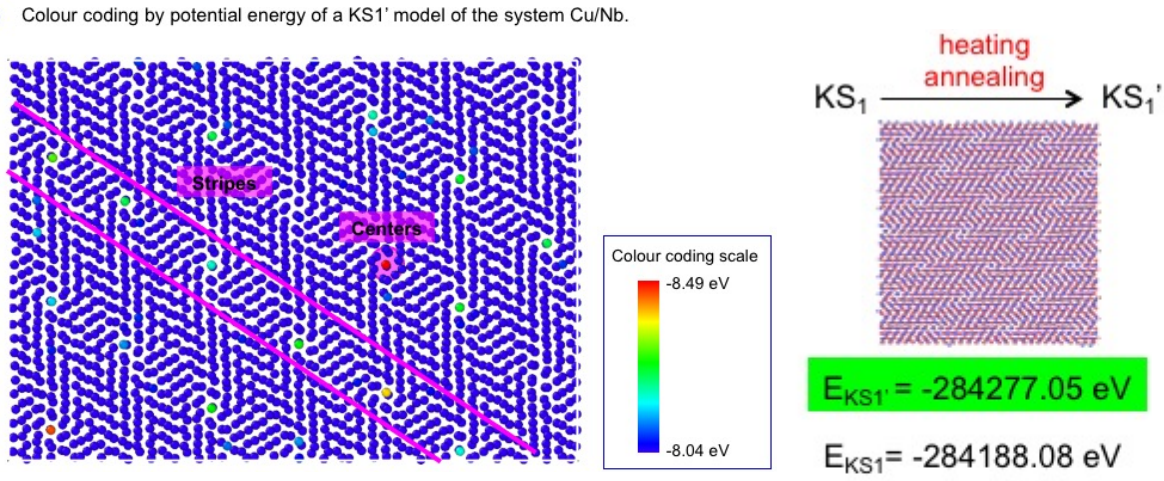


On the other hand, the Nishiyama-Wassermann (NW) orientation aligns the close-packed ⟨110⟩ rows of the fcc overlayer (or equivalently, the ⟨1120⟩ rows of the hcp overlayer) to the ⟨100⟩ rows of the bcc substrate [18].

In this work, we have decided to explore the most probable (minimum energy) degeneration of the interface structure based KS1, in order to find the best guess of a relaxed interface and test its ability to trap He atoms. To achieve such a conformational space exploration we have run canonical Molecular Dynamics trajectories at high temperatures (from 700K up to full melting), and used an empirical embedded-atom method (EAM) potential developed by Demkowicz and Hoagland and validated in previous works [19]. Our process started from the KS1 structure and then underwent through long processes of energy dissipation by means of Langevin dissipative dynamics, ending with an energy minimization stage.

Noteworthy, all the temperature trajectories lead after minimization and dissipation to the same stable derivation of the KS1 structure, that we have denominated KS1'. This new CuNb interface structure (see Figure 3) shows a clear ordered structure with low energy undercoordinated centers aligned in stripes. Strikingly the global energy of the structure is accounted as -284277,05 eV, while the relaxed KS1 structure predicted in [8] accounts for a slightly higher energy -284188,08 eV.

Figure 3. Visualization of the KS1' interface configuration looking normal to the interface plane. Interface at left is coloured according to the atomic potential energy scale shown. The structure is organized as a degeneration of KS1', underlining the preservation of patches of undercoordination aligned in stripes. Strikingly the global energy of K1' is lower than previously reported KS1 structure [8] (right).



Confirmed mechanism of He trapping ability by CuNb interfaces

Once we have explored the most suitable prediction of interfacial structure for a CuNb model bi-layer, we will try to demonstrate its ability in adsorbing He atoms in time. To that end, Helium atoms were introduced in the Cu/Nb KS1' multilayer composite following a step-by-step procedure which reproduces a torrent of helium atoms. The main goal of this procedure was to minimize the helium bubble and aggregation formation in the bulk and, as consequence, to maximize the diffusion of He atoms from the bulk to the interface speeding up the time sampling of an hypothetical situation of He flux and saturation at the interface.

Saturation by means of He insertion was modelled in steps, running continuous molecular dynamics trajectories at fixed temperature (500K) after inserting He atoms in the bulk central region. Each 2.5ns of trajectory production phase defines a step in which a random insertion of a fixed number of helium atoms is carried out. Note that the insertion mechanism is designed far enough from the interface in order to do not influence the natural interfacial trapping of He. Moreover, at each random He distribution generated for insertion, a removal of previous bulk He atoms resulting from old steps but not migrated to the interface is imposed, in order to avoid the formation and coalescence of big helium bubbles in the bulk, that could make difficult the 'He aging process at the interface'.

After 50ns of simulation of helium saturation aging process, a detailed analysis provided us useful information concerning saturation phenomena of the interface as well as the behaviour of helium

atoms in a Cu/Nb compound when a high number of helium atoms is present in the system. The overall behaviour of the Cu/Nb interface is depicted in figure 4.

Figure 4. Views of the relaxed Cu-Nb KS1' interface looking normal to the interface plane are showed. Dashed lines and circles are used to highlight the position of the stripes and the patches of undercoordination presents in the KS1' structure. Helium atoms (green) accommodated at the Cu/Nb interface (red and blue respectively) in the endpoint of the most representative steps of a MD simulation: a) step 1 (2,5 ns), b) step 5 (12,5 ns), c) step 10 (25 ns). d) A collection of spheres centered in the characteristic patches of undercoordination of relaxed KS1' interface were constructed. The percentage of these spheres that contain helium atoms was computed and averaged at each step for all the MD trajectories. The corresponding curve was smoothed.

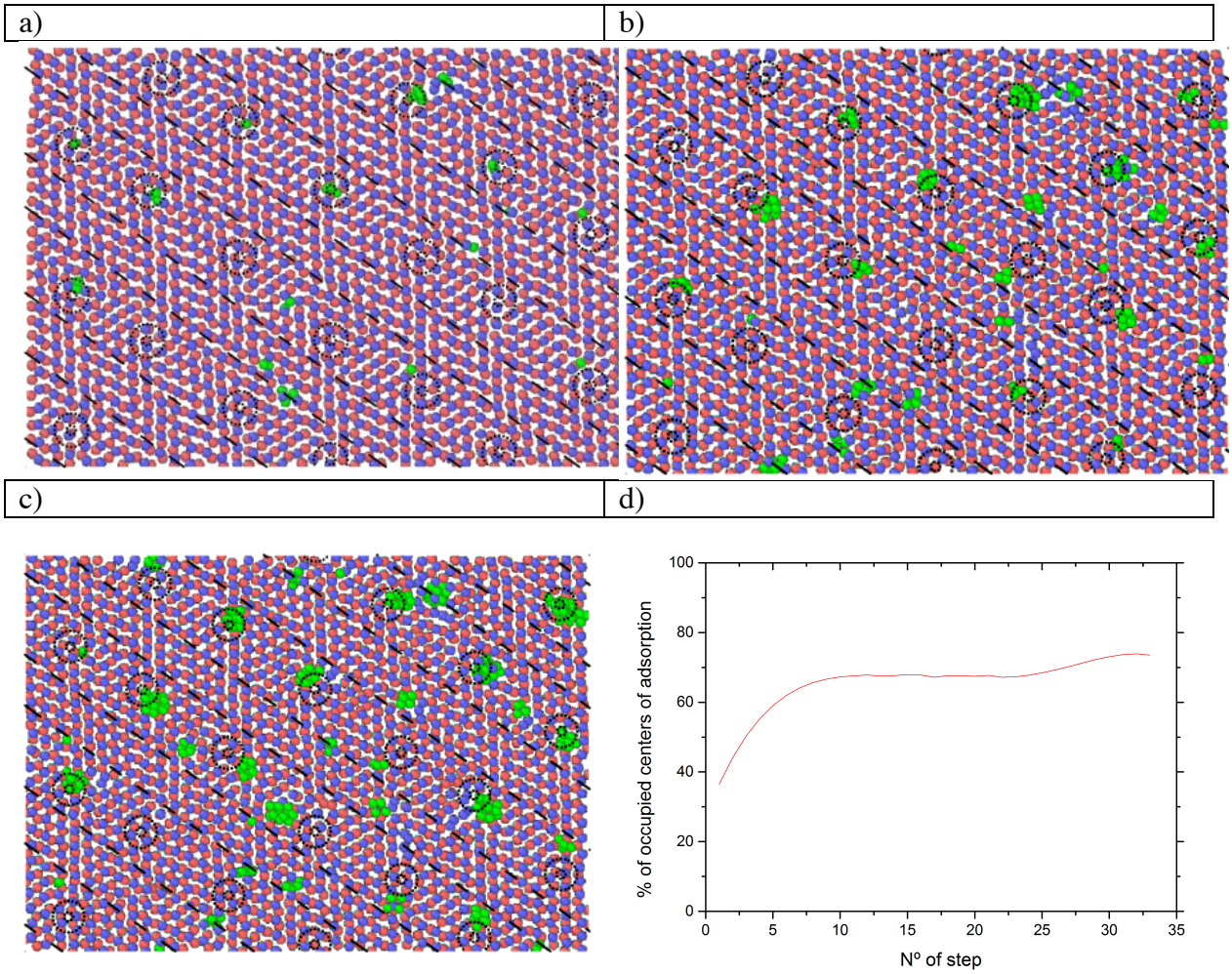


Figure 4 shows views of the relaxed KS1' interface configuration looking normal to the interface plane at the endpoint of steps 1 (2,5ns), 5 (12,5 ns), 10 (25 ns) of a MD full trajectory. Visual inspection reveals that at step 1 (see figure 4(a)), He atoms diffusing from the niobium bulk are trapped at the KS1' interface structure. They are preferentially located near of the patches of undercoordination presents in the KS1' interface model. Moreover, location along the stripes that connect the different patches by diagonal is preferred than other locations at unspecific positions. From step 1 to 5 (see figure 4(a) and 4(b)), the number of the occupied patches of undercoordination

(from now called *'centers of adsorption'*) increases as well as the population of helium atoms in the mentioned centers. From step 5 to step 10 (see figure 4(b) and 4(c)), both the number and the population of the occupied centers of adsorption increases until that, at step 10, the major part of the centers are already engaged. Incoming helium populates the stripes or the already occupied centers of adsorption. Movements from stripes to specific centers are also detected.

These results suggest the existence of two stages for the helium accommodation in the Cu/Nb interface model. At the first stage, the helium atoms start occupying the centers at the interface until the major part of the adsorption centers are already occupied. In this stage, the population at each center increases by the formation of helium platelets. In the second stage, the number of occupied centers remains essentially constant but the helium population at each center increases by the helium bubbling formation. Furthermore, the transition from one stage to another seems to be related with the number of occupied centers.

As a result of the whole modelled process, a saturation mechanism in preferential sites have been identified as also clearly reflects Figure 4 d). Virtual spheres of 3 and 6 A of diameter were defined around each adsorbing center and the number of helium atoms inside them accounted. The built in graph, Figure 4 d), depicts the averaged He saturation evolution of the adsorption centers for the different MD trajectories sampled. The ability of the CuNb interface to trap and harbor helium atoms is not only confirmed, but also defined to be strongly dependent on the surface density of adsorption centers.

The reported adsorption mechanism certainly leads to a saturation process of helium bubble formation at particular locations in the interface, thus suggesting a possible design strategy in NMMCs to maximize helium arresting. On the other hand, it must be also noted that a selective spatial adsorption may influence and strain the network of misfit dislocations resulting both on different mechanical properties and limiting the radiation resistance properties of the interface [15,17,19].

Computational methods

Molecular Dynamics trajectories and computational experiments where generated using LAMMPS code [20]. Data were visualized using OVITO [21]. The Cu-Nb multilayer material was modelled by two crystalline blocks: the copper layer is modelled by 21 {111} fcc planes with 27048 atoms in total and the niobium layer is modelled by 26 {110} bcc planes with 25350 atoms in total. These layers were brought into contact from above and below, forming two interfaces with a Kurdjumov-Sachs (KS) orientation relationship. The simulation cell was periodic in all directions so that there were two equivalents KS1 interfaces.

KS1' structure exploration was accomplished by several cycles of heating using both isobaric-isothermal ensemble (NPT) and heating in the canonical ensemble (NVT), followed by relaxation and annealing using Langevin dissipative molecular dynamics [22]. Relaxed dimensions of the simulation cell after thermalization were 101.84x 71.58 x 104.52 Å.

The Cu–Nb interactions were modelled via the empirical embedded-atom method (EAM) potential of Demkowicz and Hoagland [19]. The Cu–He and Nb–He interactions are modelled by the empirical pair potentials of Kashinath and Demkowicz [23].

Conclusion and future perspectives

Our work brings on the desk important conclusions and raises the need of further studies in order to understand the suitability of NMMCs, and particularly Cu-Nb, as a nuclear material of possible application in next generation of emerging nuclear systems.

The structural details at the interface of NMMCs are still a subject of strong debate in the community, and since the spatial arrangement and order of atoms at the interface is what defines their properties, further insights on the design of interfaces with controlled misfit dislocation patterns by tailoring interface crystallography and composition is needed. Such a knowledge would allow the design and prediction of composite materials with exceptional properties, such as radiation resistance, extreme thermo-mechanical stability, or high strength and ductility. Our work not only confirms previous studies about the interface structure of Cu-Nb [8], but also reports a new possible structure for such an interface of the KS1 type.

On the other hand, Cu-Nb model interfaces have been reported to exhibit an effective radiation damage recombination mechanism [8,19], as well as serving as good mechanisms to arrest and adsorb helium atoms [7], being both properties promising for a nuclear material. One of the aims of this study was to probe the effectiveness and mechanisms underlying the interaction of helium atoms with a CuNb interface.

Our results not only confirm the ability of Cu-Nb interfaces to attract and trap helium atoms, but also contribute to a deeper understanding of the mechanisms of Cu-Nb adsorption. A clear preference for helium adsorption at undercoordination sites of lower energy has been reported, what brings two important conclusions: (1) there should be a limit in the adsorption of helium imposed by the spatial distribution of '*adsorption centers'* generated at the interface. These centers constitute a well localized *mosaic* saturated in helium, and create further points of helium bubble nucleation. (2) Such an effect can be used as a design factor and strategy for looking into more effective helium trapping interfaces.

However, a possible drawback has been also identified thanks to our results, suggesting the need of further investigations. Since the helium is massively adsorbed in the sites close to the location of the misfit dislocation intersections, known to be the responsible of the defect recombination mechanisms and the superb mechanical properties of NMMCs, a clear local structural distortion is expected, resulting in a possible detriment on the exhibited self-healing properties of this kind of materials, and possibly imposing a limit, not yet clear, in their use as a nuclear material.

Acknowledgements

The authors gratefully acknowledge support from European Union, Project FP7-RADINTERFACES, GA 263273

References

[1] I.I Chernov, A.N Kalashnikov, B.A Kalin, S.Yu Binyukova, Gas bubbles evolution peculiarities in ferritic–martensitic and austenitic steels and alloys under helium-ion irradiation, Journal of Nuclear Materials, Volume 323, Issues 2–3, 1 December 2003, Pages 341-345

[2] R.K. Klueh, R.E. Stoller, D.S. Gelles, R.L. Klueh, K. Ehrlich, F. Abe, Fusion Reactor Materials Part AFerritic/martensitic steels: promises and problems, Journal of Nuclear Materials, Volume 191, 1992, Pages 116-124

[3]Basic Research Needs for Advanced Nuclear Energy Systems (Washington, D.C.: Office of Basic Energy Science Workshop, U.S. Department of Energy, July 31 to August 3, 2006),www.sc.doe.gov/bes/reports/list.html.

[4] Proceedings of Plasma–Surface Interactions in Controlled Fusion Devices 15, J. Nucl. Mater. 313–316 (2003) 92, 97.

[5] Laser Fusion Materials, Special issue on Materials Devel- opment for Inertial Fusion Energy, J. Nucl. Mater. 347 (2005) 289.

[6] D.L. Smith, S. Majumdar, M. Billone, R. Mattas, Performance limits for fusion first-wall structural materials, Journal of Nuclear Materials, Volumes 283–287, Part 1, December 2000, Pages 716-720.

[7] Zhang, X., et al., Nanostructured Cu/Nb multilayers subjected to helium ion irradiation, Nuclear Instruments and Methods in Physics Research B 261 (2007) 1129-1132.

[8] Demkowicz, M.J., R.G. Hoagland, and J.P. Hirth, Interface structure and radiation damage resistance in Cu-Nb multilayer nanocomposites, Physical Review Letters 100 (2008).

[9] Hattar, K., et al., Arrest of He bubble growth in Cu-Nb multilayer nanocomposites, Scripta Materialia 58 (2008) 541-544.

[10] D. J. Bacon, A. F. Calder, and F. Gao, "Defect production due to displacement cascades in metals as revealed by computer simulation," J. Nucl. Mater., vol. 251, no. 97, pp. 1–12, 1997.

[11] J. Fikar and R. Schäublin, "Molecular dynamics simulation of radiation damage in bcc tungsten," J. Nucl. Mater., vol. 386–388, pp. 97–101, 2009.

[12] J. Fikar and R. Schaeublin, "Molecular dynamics simulation of radiation damage in bcc tungsten," Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms, vol. 255, no. 1, pp. 27–31, Feb. 2007.

[13] A. M Ito, Y. Yoshimoto, S. Saito, A. Takayama1 and H. Nakamura. Molecular dynamics simulation of a helium bubble bursting on tungsten surfaces. Physica Scripta, Volume 2014, Number T159. 2014

[14] Demkowicz, M.J. and R.G. Hoagland, Structure of Kurdjumov-Sachs interfaces in simulations of a copper-niobium bilayer, Journal of Nuclear Materials 372 (2008) 45-52.

[15] M. J. Demkowicz, J. Wang, and R. G. Hoagland, in Dislocations in Solids, edited by J. P. Hirth (Elsevier, Amsterdam, 2008), p. 141.

[16] X.-Y. Liu, R. G. Hoagland, J. Wang, T. C. Germann, and A. Misra, Acta Mater. 58, 4549 (2010)

[17] A. Misra, M. J. Demkowicz, X. Zhang, and R. G. Hoagland, "The Radiation Damage Tolerance of Ultra-High Strength Nanolayered Composites" JOM The Journal of The Minerals, Metals & Materials Society (TMS) no. September, pp. 3–6, 2007.

[18] A. J. Vattré, N. Abdolrahim, K. Kolluri, M. J. Demkowicz.Computational design of patterned interfaces using reduced order models Scientific Reports 4, Article number: 6231 (2014)

[19] M.J. Demkowicz, R.G. Hoagland, Simulations of collision cascades in Cu–Nb layered composites using an eam interatomic potential. Int. J. Appl. Mech. 1 (2009).

[20] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics

J. Comput. Phys. 117 (1995) 1.

[21] *A. Stukowski*. *Visualization and analysis of atomistic simulation data with OVITO - the Open Visualization Tool Modelling Simul. Mater. Sci. Eng. 18 (2010), 015012*

[22]C. Pastorino, T. Kreer, M. Müller, and K. Binder. Comparison of dissipative particle dynamics and Langevin thermostats for out-of-equilibrium simulations of polymeric systems. Phys. Rev. E 76, 026706 – Published 24 August 2007

[23] A. Kashinath, M.J. Demkowicz, A predictive interatomic potential for He in Cu and Nb. Modell. Simul. Mater. Sci. Eng. 19 (2011) 035007.