Comenius University in Bratislava

Faculty of Mathematics, Physics and Informatics

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Dissertation Thesis Overview

A computational study of interactions in Be-W-D system relevant to fusion reactors

to obtain the academic Philosophiae doctor degree

in the study program:

4.1.11 Chemical Physics

Place and date:

Bratislava, 2015

This thesis was performed at the Department of Nuclear Physics and Biophysics, of the Faculty of Mathematics, Physics and Informatics at Comenius University in Bratislava (FMFI UK) within a full-time PhD study program.

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The defense of PhD thesis will take place on ..... at ..... h at the council for defense of PhD thesis of the doctoral study of the study program **4.1.11 Chemická fyzika** approved by the head of the council **prof. RNDr. Ján Urban, DrSc.** at **Faculty of Mathematics, Physics and Informatics, Comenius University in Bratislava, Mlynska dolina F1, 842 48 Bratislava, room ...**

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Introduction

The main goal of the international project *ITER*[1] is to develop and build a demonstration fusion energy power plant which will be fuelled by the fusion reaction between the hydrogen isotopes, deuterium and tritium. This fusion occurs in a hot plasma with temperature of 150 million K confined by a strong magnetic field within a reactor based on the *tokamak* concept, a toroidal shaped device. Products of this reaction are helium nuclei and neutrons. The energy of helium shall maintain the plasma temperature; the neutron escaping from the plasma due to its neutral electric charge, caught by tokamak's inner walls, called also a *blanket*, and subsequently slowed down. Its kinetic energy transforms to heat which dissipates through cooling towers or, if in commercial use, will produce steam and subsequently electricity. Such a plant has a few advantages: an ecological fuel, more secure usage. It is energetically superior to other ways of producing electricity. Unfortunately, inner walls are never fully protected from the plasma. The flow of plasma particles, neutrons, and heat through the magnetic field caused by a turbulence of the edge plasma will damage the blanket. Special, detachable *first walls* are planned for the protection of the blanket that must face the incoming particles and heat, and thus, to minimize unwanted damage. Beside that, excess of helium and other hot waste will be dislocated from walls to a *divertor* at the bottom part of tokamak.

The research on beryllium and tungsten materials belongs to important area of fusion reactor physics, especially as the project *ITER*[1] is concerned. Those materials, together with carbon, are referred to as *plasma-facing components* (PFCs) and are planned to be used for the blanket and the divertor in vacuum vessel of the tokamak device. Primarily, they will serve as a protection against the plasma. Mutual interactions between plasma particles and PFCs, designated as *plasma-wall* interactions (PWIs), will be the source and cause of various surface processes in the walls. Nevertheless, not only plasma particles, but also impurities added to control the plasma will play their roles in these complex systems. Thus, knowledge of the characteristics of these processes will help to reach an optimal design for the ITER fusion reactor in terms of longer life, easier maintenance, and better quality of fusion reaction. Currently, beryllium is planned to be used for the first walls, tungsten and carbon for the divertor.

Beryllium and tungsten were chosen because of their physical and chemical properties to effectively face these interactions. Only a few materials can stand temperatures up to 3000 K. Tungsten is one of them. Beryllium has also a relatively high melting point (1560 K). Both represent an excellent choice for ITER and will be tested during the demonstration phase. Experiments with these materials run in already existing tokamaks: JET (Culham, UK), TEXTOR (Julich, GE), and Tora Supra (Cadarache, FR), each with different setting of design. Unfortunately, controlled experiments with Be and W within tokamaks are very hard to perform. On the other hand, linear devices like PISCES-B are used for more controlled experiments.

Under the circumstances that beryllium and tungsten parts have to withstand during the runtime, like heat loads or high particle fluxes, diverse processes and interactions take place that result in erosion of these materials. Initial starters are the impinging particles from plasma and the accumulated waste in the divertor. Then, processes on different time (ps to s) and length (Å to μm) scales occur. This ranges from *sputtering* and erosion of material, implementation and retention, to forming of new alloys with different properties that are often not desired and to dust formation. Life time of PFCs, dust production from eroded PFCs and tritium inventory in vacuum vessel are the most problematic issues of ITER design. Furthermore, too fixed, expensive, and regulated experiments caused by beryllium toxicity are amongst the disadvantages of experimental research that result in increasing use of computational material science and theoretical approaches to simulate and model these processes in order to explain physics behind them. However, also continued improvement and development of the theory to justify the results is needed.

On the other side, molecular data are of great importance as well. To model more complex processes by fluid or plasma codes, input data in the form of structures, dissociation energies, or electron-impact ionization cross sections of small molecules or clusters of atoms relevant to these processes is needed. At this point, very few experiments were done, i.e. spectroscopy, to obtain such data for beryllium, tungsten, or Be-W clusters, as well as beryllium hydrides, and deuterides. The need for such data is a repeatedly issued on IAEA and EFDA meetings.

1 Objectives

The modelling of beryllium-tungsten mixed materials is a central topic of this dissertation thesis which is relevant to fusion reactor physics in a sense that these materials are planned to use as the wall materials. In consequence, Be-W mixed alloys will be present in the divertor part of the reactor and the properties of such surfaces should be studied to find out if the change of material characteristics will influence the stability of the inner walls or quality of plasma reaction. On the other hand, the controlled experiments and most of the atomic or molecular data about Be-W mixed alloys are unavailable or not easily obtained. Therefore, theoretical methods are often used to fill those gaps in knowledge, though sometimes it means only the first guess in a long way of the particular research. This thesis presents the possibilities of theoretical approaches in providing the data for Be-W mixed materials and in explaining the nature of processes recorded in experiments on these materials. For this purpose, we chose our first goal as follows:

a) To model D irradiation of Be-W mixed materials using Molecular Dynamics. This approach suits best the nature of the processes we were interested in, i.e. sputtering of Be and BeD molecules from the surface, implantation of D in such surface and its influence of sputtering yields. Particularly, Be_2W and $Be_{12}W$ surfaces were chosen for low energy (10 - 30 eV) D ion bombardments at 300 K.

Another point of view on Be-W materials can be provided by analysing Be-W clusters with quantum-chemical methods. Therefore, the second aim of this thesis is:

b) To find out the characteristics of Be_2W-$Be_{12}W$ clusters, i.e. how these Be-W clusters evolved and changed as the number of beryllium atoms was increasing or if there is some specific size of cluster where metallic behaviour becomes visible or its properties become similar to those of the bulk Be-W mixed materials. The Density Functional Theory method was used for time-efficient optimization of clusters. Various molecular properties were calculated in order to describe these clusters.

The following goals are closely related with previous parts and illustrate how useful the theoretical methods for estimating properties of small molecules that cannot be

obtained experimentally are:

c) Calculation of total electron-impact ionization cross sections for Be_2W-$Be_{12}W$ and for small beryllium hydrides based on the Binary-encounter-Bethe method. These data were specially requested to improve various codes for modelling plasma-surface interactions.

d) Analysis of the dissociation of BeD_{1-3} molecules to help understand the sputtering results from MD simulations and experimental data and explain the differences between them. Again, *ab initio* methods, MP2 and DFT, were used because no experimental data exist about BeD_{1-3} molecules.

2 Methodology - Computational tools

DL_POLY 3.09[2] was used for all MD simulations. This program which is written in Fortran language, can be freely modified. It uses the link-cell algorithm and is well parallelized for large systems. The ABOP potential was used for our Be-W mixed surfaces which has been already used for similar modelling of Be, W and Be-W mixed materials. TURBOMOLE package v6.5[3] was used for local minima searching via simulated annealing in BO MD, and also for geometry optimizations and vibrational analysis at the DFT level of theory. For CCSD(T) calculations, as well as for input parameters for electron-impact cross sections, the Gaussian 09 program[4] was used. Furthermore, a code was written for cross sections calculations and fitting based on modified J. Burkard's Fortran subroutines[5]. The scripts for analysing data and other purposes were written mostly in Perl, AWK, and bash programming languages.

MD simulations were carried out on LEO2 and LEO3 supercomputers at Innsbruck University which could be used for our goals within the collaboration with prof. M. Probst. Some *ab initio* calculations were done there as well. For all other more time-consuming computations we used the computer cluster at the Department of Nuclear Physics and Biophysics.

2.1 Our contributions

We have written the following modifications and scripts for running and analysing MD simulations. Additionally, corresponding manuals and/or user guides were written:

- Modification of *DL_POLY* 3.09 - added ZBL repulsive potential and the electronic stopping in FORTRAN
- Set of bash and Perl scripts for easily running long-lasting bombardment MD simulations in *DL_POLY* 3.09 on supercomputers LEO2 and LEO3, including scripts for detecting sputtering events and basic statistics.
- The description of implementation of the ABOP potential and all other modifications in *DL_POLY* 3.09 program [6].
- The usage manual for bombardment simulations scripts and their modification for other systems and supercomputers[7].
- Unified set of scripts for automatic analysis of bombardment simulations, their statistics, trajectories, visualisation. Almost all of them written in Perl, the rest are bash and AWK scripts.
- Unified set of scripts for MD optimization using SA algorithm in TURBOMOLE as well as scripts for automatic geometry optimization and extracting the data from output files.

3 Applications and Results

This section deals with the application of the discussed methods to achieve the objectives of this thesis, the characterization of Be-W mixed materials under D bombardment. It also deals with properties of small Be-W clusters as well as dissociation and total electron-impact ionization cross sections of small beryllium hydrides, as such data are important to explain the behaviour of these mixed materials during fusion reactor operation. The following results represent the main achievements accomplished during our research. The publications in the appendix C, to which we contributed, may be also perceived as an additional information and an example of a bigger picture of collaboration in fusion plasma research.

3.1 MD modelling of irradiation of Be-W mixed materials

As mentioned above, Be-W mixed materials will be present in ITER fusion reactor. Therefore the properties of possible Be-W mixed materials facing the ion fluxes, especially D irradiation, are in demand. This section summarizes the effects of D irradiation of Be_2W and $Be_{12}W$ samples. A systematic study was performed in which the samples underwent 1000 cumulative and non-cumulative D bombardments with low impact energies in the range 10-30 eV at 300 K. The Be_2W sample was terminated by mixed Be-W layer, $Be_{12}W$ was amorphous.

MD simulations with the ABOP potentials for Be-W[8] and Be-Be II (Be-H II)[9] was used to carry out these simulations. MD modelling can offer insight into some of the processes taking place during the D irradiation, such as sputtering or D implantation. However, because of the short time-scale in MD, the essential processes for alloying or structure formation like diffusion could not be described. On the other side, still a handful of detailed structural properties or implantation profiles could be extracted.

The MD modelling of Be-W mixed materials, particularly Be_2W and $Be_{12}W$ surfaces, showed the important effects of surface deuteration in amorphous $Be_{12}W$. According to the bombardment simulations it affected the be sputtering yields as well as D re-erosion and D reflection rates. However, this effect was almost negligible in Be_2W surface, which had a very structured, crystalline form, its structure remaining unchanged over time during the simulations. The significant changes of surfaces were dependent on energy, too. The breaking point was 15 eV impact energy for Be_2W and 20-25 eV for $Be_{12}W$. Almost 50-60 % of all incident D ions were implanted only in top 5 Å at lower impact energies, after the breaking point it decreased quickly to $\sim$ 10-20 %. The other characteristics changed as well: D depth profiles showed an emerging of second peak approximately 10 Å under the top layer in $Be_{12}W$ or shifting of the peak deeper in Be_2W, also an evident decline of D reflection yield in $Be_{12}W$ for lower energies. The sputtering yields in non-cumulative bombardments in $Be_{12}W$ for higher energies were different from those at lower energies. Furthermore, the BeD:Be ratio peaks were at 15 eV in Be_2W and at 20-25 eV in $Be_{12}W$. A close relation between deuteration of surface and impact energy was suggested to explain the preferred way of sputtering.

No visible structure changes were observed after 1000 impact. However, the conclusion can be made that 1000 impact and corresponding fluencies were too small to estimate the whole effect of surface bombardment in these cases. Also temperature and angular dependencies were not modelled here due to the computational costs of the simulations and therefore macroscopic parameters obtained were limited. Subsequent MD modelling will concentrate on these issues because such dependencies are very useful for the other codes like ERO that model erosion of PFCs.

3.2 Dissociation of small beryllium deuterides molecules

The following section deals with results of other MD modelling of D irradiation of Be surfaces performed by finish group led by K. Nordlund. The details of these simulations are described in the paper I in Appendix C to which we contributed with dissociation calculations. The dissociation energies and thermodynamics of small beryllium deuterides were calculated because the experimental data from JET experiments with beryllium[10] were not consistent with the MD results. Particularly, the released BeD molecules outnumbered the remaining Be-containing molecules (BeD_2 and higher) at low temperatures (<500K) in experiments as well as in MD modelling, however, it was different at higher temperature (600-1000K). BeD_2 and BeD_3 eroded more frequently than BeD molecules in MD simulations. Contrary to that, no other molecules beside BeD were observed in experiments. Therefore the dissociation and stability of these molecules were checked by quantum-chemical methods because of the lack of experimental thermodynamical data for beryllium deuterides, BeD_{1-3}.

We determined the bond length for Be-H(D) to be 1.338 Å which is in excellent agreement with the experiment. The changes of enthalpies of formation for BeD and BeD_2 molecules from both used method were in agreement with experimental and calculated data, though still the chemical accuracy is not satisfied since experimental enthalpy of formation for Be is not very accurate. The studied dissociation channels of small beryllium deuterides were calculated as well. It was shown that if the results from MD modelling of D irradiation of Be surfaces are corrected on the basis of this analysis, the BeD:Be ratio of sputtered species is in agreement with JET experiments with beryllium. That is, BeD_3 if formed at all, easily dissociates into BeD + D_2

and BeD_2+D, and BeD_2 into Be+D_2. The same conclusions were reached using pure calculated values as well as if experimental values for atoms and D_2 molecule were used, though the Gibbs free energies obtained by the former method resulted in a more rapid decrease in dependence on temperature, especially if the reactions contain D_2 molecule.

3.3 DFT calculations of Be-W clusters

The properties of Be-W mixed clusters could be of great help in analysing the possible scenarios of erosion and damage of materials in ITER tokamak, where Be-W mixed materials will be probably formed, even when no experimental data about them are currently known. Eroded molecules from such surfaces could do another damage or aggregate into dust particles. The results are the first systematic study about Be-W mixed clusters using quantum-chemical methods. In order to find out the basic characteristics of BeW to 12W clusters, out of which the further details about behaviour of these clusters, particularly the way metallic properties emerge, can be extracted, the optimization of these clusters is necessary. The simulated annealing within *ab initio* MD was used to obtained the most of possible configurations.

Overall, there are a few common sign for all so far described properties, concerning geometries as well as energy characteristics of clusters. First of all, a visible change of clusters in behaviour occurs clusters larger than Be_7W. The average Be-Be bond length increases up to 3.2 Å for Be_7W, then drops by 0.2 Å, but the bond length kept increasing. it was also visible if only the first neighbours were considered. The W-Be bond length was constant around 2.2 Å. For larger clusters it began to increase. This was evident in MD/ABOP structures as well as in geometries optimized at the DFT level of theory. Similar tendencies were served for binding and stabilization energies that showed the least values for Be_7W cluster. One of possible reasons for this could be the change of the preferred position of W atom, from the centre of small clusters to the edges of larger clusters. Another reason may be that from Be_7W on, a metallic nature of clusters is already present.

3.4 Total electron-impact ionization cross sections for small clusters

Electron-impact ionization cross sections represent another kind of data that are valuable for research on Be-W mixed materials within fusion physics as well as in other industries. Such data for Be, W, or W-Be clusters are not easily measurable. However, there are some theoretical methods as BED (BEB) or DM for calculating these properties. This part of the thesis presents the results of computing EICS for small beryllium deuterides and Be_{1-12} clusters using BEB method. The publication II in Appendix C compares the use of BEB and DM methods for small beryllium clusters as well as with experimental data for single Be atom.

3.4.1 Total electron-impact ionization cross sections for small beryllium hydrides

The resulting BEB cross sections had peaks 2.6, 3.1, 3.0, 5.5 and 5.7 $\times 10^{-16}\, cm^2$ at 43, 48, 56, 51 and 58 eV for Be, BeH, BeH_2, Be_2H_2 and Be_2H_4, respectively. On the other hand, DM methods yielded 3.96, 4.0, 4.8, 8.6 a 9.4 $\times 10^{-16}\, cm^2$ at 31, 44, 50, 46 a 56 eV in the same order as for BEB. The difference between both methods is about $\sim$ 25 - 40 % with DM values higher than BEB. The same differences were for single orbitals as well. Nevertheless, such a disagreement is typical when cross sections calculation are concerned.

3.4.2 Total electron-impact ionization cross sections for Be-W clusters

The peaks are for all clusters very similar, at $\sim$ 40-48 eV, the values can be divided into three groups:

1. BeW-Be_6W - $\sim$ 13-20 $\times 10^{-16}\, cm^2$ at 42-48 eV
2. Be_7W - $\sim$ 25 $\times 10^{-16}\, cm^2$ at 43 eV
3. Be_8W-Be_{12}W - $\sim$ 30-40 $\times 10^{-16}\, cm^2$ at 41-44 eV

Again, there is a visible gap between small clusters and larger clusters. Moreover, Be_7W was singled out of both groups. There were only small differences whether pure

HF orbitals energies or IPs from CCSD(T) calculations were used for the lowest binding energy.

4 Conclusions

The interactions between deuterium, beryllium and tungsten have been studied by atomistic modelling with analytical potential energy functions as well as with quantum-chemical methods. The former approach has served to describe fusion relevant plasma-surface processes, the latter to find out the basic properties of small Be-W clusters and beryllium deuterides.

Regarding the plasma-surface interactions, the results from Molecular Dynamics modelling of low energy D irradiation of Be-W mixed materials are presented. In particular, Be sputtering yields from Be_2W and $Be_{12}W$ surfaces are quantitatively very similar to those from pure Be surface as well as if a release of beryllium deuderides is concerned. The swift chemical sputtering plays its role in low energy Be sputtering. No W atoms were sputtered. The effect of surface deuteration in $Be_{12}W$ was observed affecting the sputtering yields dependence on energy. Also different ways of implantation of D atoms were noticed in both surfaces. In order to accomplish these simulations the simulation protocol and many different scripts for analysis were developed.

Quantum-chemicals methods were applied to compute thermodynamical properties of neutral BeD_{1-3} molecules for which no suitable experimental data exist. The calculated dissociation energies for various possible dissociation channels explained the difference between experimental and simulated ratios of single Be to BeD molecules at temperatures > 500 K. In this regard, we found out that larger beryllium deuterides, BeD_2 and BeD_3, dissociated easily into BeD and Be, which are the most preferred products at high temperature. After correction based on this analysis according our analysis of energetic data, they agree with experimental measurements, though obviously also experiments aimed on detecting BeD_2 molecules should be performed in future.

In addition, quantum-chemical methods were used to find and optimize local minima of Be-W clusters, BeW-$Be_{12}W$. The set of properties were extracted to describe these clusters behaviour in dependence of size. The visible different character of small clusters, up to Be_7W, and the remaining ones is noticed in structure properties as well as in energy. However, if some characteristics may point out the metallic behaviour of larger clusters, the sample was not big enough to determine it more precisely.

The calculation of electron-impact ionization cross sections represents another use of theoretical methods. These cross sections were computed for small beryllium hydrides as well as Be-W clusters and have been already partly included in cross section databases.

To sum up, the atomistic simulations and quantum-chemical calculations were used to obtain the characteristics of Be-W mixed materials as well as Be-W small clusters. In the view of recent development of fusion plasma codes as well as their use for further understanding the processes occurring during experiments, the need of data to compare more complicated models with experiments is question of great importance. However, plasma-facing materials like tungsten or beryllium are not easily experimentally manageable in order to get sought-after properties at the environmental conditions where they are most desirable. Thus, concerning these materials, theoretical approaches can provide the information to support experimental research and development of various codes. Particularly, the sputtering yields and surface properties dependencies on surface temperature can be obtained from the atomistic simulations. The molecular properties of species present in fusion reactors and the interaction of plasma impurity seedings with the PFCs are examples, for which there are currently no available empirical data, but which can be calculated using quantum-chemical methods.

5 List of Contributions

The following works to which we contributed and are discussed in my thesis are listed here:

I. Atomistic simulations of the effect of reactor-relevant parameters on be sputtering, Journal of Nuclear Materials
E. Safi, C. Björkas, A. Lasa, K. Nordlund, I. Sukuba, M. Probst
Journal of Nuclear materials, http://dx.doi.org/10.1016/j.jnucmat.2014.10.050.

II. Electron impact ionization cross sections of beryllium and beryllium hydrides
Thana Maihom, Ivan Sukuba, Ratko Janev, Kurt Becker, Tilmann Märk, Alexander Kaiser, Jumras Limtrakul, Jan Urban, Pavel Mach, Michael Probst
The European Physical Journal D, 67:2(2013)

Other publications:

- Teoretické štúdium klastrov berýlia a vodíka: Be_nH_1
  I. Sukuba
  Študentská vedecká konferencia FMFI UK, Bratislava 2011 : Zborník príspevkov. - Bratislava : Fakulta matematiky, fyziky a informatiky UK, 2011. - S. 147-153. - ISBN 978-80-89186-87-7

- Disociácia molekúl BeD_{1-3}
  Ivan Sukuba
  Študentská vedecká konferencia FMFI UK, Bratislava 2014 : Zborník príspevkov. - Bratislava : Fakulta matematiky, fyziky a informatiky UK, 2014. - S. 108-112. - ISBN 978-80-8147-023-3

Other contributions:

- MD modelling of D irradiation of Be-W mixed materials
  Joint Working Session of WPJET1/WPJET2/WPMST1/WPPFC on integrated plasma-wall modelling, Tervaniemi, Finland

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