PhD Paul Pavel DINCĂ

DEUTERIUM RETENTION AND DESORPTION STUDY ON THIN FILMS RELEVANT FOR THERMONUCLEAR FUSION

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TABLE OF CONTENTS

INTRODUCTION

The sustainable development of civilization is strongly influenced by the available energetic sources. Due to the finite character of the current available energetic sources, the term of durable development implies the access to resources and their efficient exploitation to obtain a maximum energetic yield. This exploitation must be done as least as environmentally harmful possible by decreasing pollution through contaminants and radioactive materials and decreasing the CO_2 emissions respectively. For the last 60 years, the global energy production for high developed countries was mainly ensured by exploitation of energy sources based on fossil fuels like coal, oil and natural gas but less on nuclear (nuclear fission) and renewable energy sources (hydropower plants, windmill plants and solar plants) respectively. Despite of the massive investments during the last two decades in renewable energy sources, their input in the global energetic area remains modest due to the higher and higher energy requirements. Even though the nuclear energy obtained by nuclear fission is an attractive alternative for fossil fuels usage through reduction of the greenhouse effect, the problem of long-term storage for radioactive waste , with lifetimes of millions of years, still remains unsolved. Also, the risk for catastrophic accidents lead to reducing the input of this source within the nuclear energetic area for the last 20 years. Within this context, the nuclear fusion became an attractive source for energy production in the coming future. The immediate purpose of researchers within fusion community is to build a reactor able to generate on Earth, in a controllable mode, the same type of reactions that occur inside the stars. Thermonuclear fusion energy release is based on fusion of light nuclei. This phenomenon occurs when two or more nuclei have sufficient energy to overcome the Coulomb repulsive force, thus entering the action area of the nuclear attraction force. Hence one or more nuclei and subatomic particles are formed. The selected fuel constituents for producing fusion within thermonuclear reactors are deuterium and tritium. These two isotopes were proposed because of their effective high interaction cross-section.

The idea that the Sun is powered by fusion reactions that occur in its centre was first proposed by Hans Bethe in 1939, who later won a Nobel prize in 1967. This was first used in military purposes aiming to create weapons of mass destruction.

At the early 1950, the research within magnetic confined fusion for energetic domain has started simultaneously in three countries: US, Great Britain and USSR. The first conference in history on magnetically controlled fusion took place in 1958 and the interest in this field lead to an unprecedented international collaboration. In the next decades, many countries joined the EUROFUSION consortium, among them Romania. One of the most important outcomes of this collaboration was the *International*

Thermonuclear Experimental Reactor (ITER) construction, currently being finalised in the South of France, at Cadarache. It is intended to be the first experiment able to prove the economic sustainability translated through a positive energetic efficiency.

This PHD thesis aims to discuss a topic of interest for the optimum control of thermo-nuclear fusion reactors, namely nuclear fuel retention in fusion related materials: beryllium and tungsten. Currently, there are a series of experimental fusion reactors, and among them the most important are JET, ASDEX, TEXTOR. One of the most important research aims of these experimental reactors is the study of fusion plasma interaction with reactor's physical components under extreme conditions. A good understanding of this phenomena which can occur during plasma-wall interaction is crucial to select or develop certain materials able to withstand reactor conditions. An ideal material should have the following properties: low atomic mass, high thermal conductivity, high erosion resistance under plasma particles bombardment as well as neutron bombardment, high temperature resistance and low hydrogen isotopes retention. Currently, a single material cannot fulfil all of the above-mentioned criteria. The selected materials for ITER construction are beryllium and tungsten (W). In some cases, the interactions of particles with the exposed components can have minor consequences like elastic collisions with low energy loss, but for the most cases the consequences can be dangerous leading in time to physical sputtering, chemical erosion and material melting. These phenomena don't necessarily induce structural problems to the reactor (erosion of a 3 mm tungsten component occurs within 50 years of continuous running) but can lead to the contamination of the fusion plasma with wall and divertor materials determining a radiative cooling. Another unwanted aspect of material erosion is their redeposition on other surfaces within the reactor strongly influencing the predictions on nuclear fuel retention. This layers show physical and chemical properties different which are different in comparison to initial surfaces. Retention modelling in the redeposited layers becomes increasingly difficult to perform as more materials are involved. One of the main problems is represented by T retention . This radioactive isotope retained in large quantities in components may lead to an administrative closure of the thermonuclear fusion reactor for radiological safety reasons. Retention of tritium in the reaction chamber must be monitored and minimized both from an economic and security point of view. The post-mortem analysis of the components extracted from the experimental fusion reactors led to the identification of two main factors that lead to the accumulation of nuclear fuel in components: implantation of hydrogen isotopes and co-deposition. In this PhD thesis, both mechanisms responsible for nuclear fuel retention are studied, with particular emphasis on Be,W and mixed Be-W layers co-deposition with deuterium (D). Since the problem is mainly related to tritium one can question the use of D in experiments. The main reason are: D shows the same solubility properties in both Be and W, a higher abundance in comparison to T and doesn't need radiological safety

measures. For the realization of predictive deuterium retention models in the thin layers that can occur in fusion reactors, it is first necessary to obtain and study this layer in the laboratory frame.

Studies on deuterium retention in tungsten have been carried out in many research laboratories by the implantation of either thin layers or bulk material with deuterium ions. The most important conclusions of these studies are shown in the current PhD thesis. Also, a thorough and extensive investigation of the literature concerning deuterium retention studies performed on Be and Be-W layers is presented in the second chapter of this work.

The Elementary Processes in Plasma and Application research group (EPPA) from Low Temperature Plasma Laboratory within the National Institute for Lasers, Plasma and Radiation Physics (NILPRP) has a dedicated beryllium facility. This facility allows work with beryllium in vapour state and deposition of thin layers by various plasma assisted techniques.

One of the techniques employed to obtain layers needed for this study was thermionic vacuum arc (TVA). This physical vapor deposition method (PVD) was developed within Low Temperature Plasma Laboratory by Prof. Dr. Geavit Musa and subsequently was improved to obtain metallic coatings. One of the direct applications of this method in the nuclear fusion field was the development of beryllium coated marker and Inconel tiles which were installed on the first wall of the JET device in the preparation of the ITER like-wall project. TVA method shows many advantages as: excellent adhesion of the deposited films to the substrate; ion energy control; high purity films and high compactness degree. In addition, the deposition chamber allows the use of three independently controlled evaporation sources and thus, mixt films can be easily obtained. Another useful feature is represented by the in-situ monitoring of the evaporation rates which allowed simultaneous beryllium/ tungsten layers with well determined atomic concentrations.

The co-deposition of beryllium and tungsten with deuterium was realized using magnetron sputtering in DC and HiPIMS mode. This experimental configuration allowed the co-deposition of these materials together with nuclear fuel to simulate to some extent the material mixing in a fusion reactor..

The obtained thin films were characterised from structural, morphologic and compositional point of view using Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM). All of these techniques have been used to provide a complete picture of the influence of different plasma parameters on the deposited layers. These common investigation techniques are briefly described in the third chapter of the thesis. The focal part of this study was related to the analysis of deuterium retention mechanisms in samples through the analysis of the desorption behaviour with an experimental thermal

desorption spectroscopy system (TDS). Deuterium desorption spectra correlated with RBS results were also used to determine the deuterium inventory of samples, expressed throughout this study in atomic concentration.

The simulation of the phenomena occurring in the interaction of charged particles with the inner wall of the nuclear fusion reactor was accomplished by means of a special device capable of generating deuterium ions. This device was developed within the EPPA group to irradiate the pure and mixed beryllium and tungsten films obtained with TVA method. A constant deuterium flux is directed into the glass tube between two metal electrodes: a central one, made of W, and an outer one, made of stainless steel. In this geometry, a variable voltage is applied to the central W electrode while the outer steel electrode is connected to the ground. The ions leave the device through a sub millimetric hole located above the external electrode. The control of the ion energy is done by applying a negative potential on the sample. Deuterium plasma can be ignited in both direct current and pulsed mode. For the experiments, a pulse generator was used to control the frequency and duration of the pulse. In the first part of the results section the characterization of the deuterium plasma obtained with this device is presented. Optical emission spectroscopy measurements, spatial distribution of plasma potential and ionic composition are presented.

Another investigated problem concerned the deuterium retention in beryllium co-deposited layers at various deuterium flow values. The investigated layers had a thickness of 500 nm they were deposited on silicon substrates, respectively tungsten. Four co-depositions were performed at different deuterium flows: 2; 4; 10; 20 ml / min, in order to observe the influence of D flow on retention in co-deposited layers. The motivation for choosing beryllium co-depositions is based on multiple studies that have shown that nuclear fuel retention in this type of layers will account for the bulk of the ITER fuel inventory. Structural, morphological and compositional examinations of the samples were performed. Also investigations were carried out to assess the deuterium inventory in the samples.

A large study of deuterium retention in pure and mixed layers obtained from various combinations of beryllium and tungsten co-deposited by DC magnetron sputtering in a deuterium reactive atmosphere was performed for the first time. The aim was to investigate the influence of layer composition on deuterium retention. The samples were investigated from a structural, morphological and compositional point of view. The main mechanisms of deuterium retention were identified and the influence of the substrate on deuterium retention was analysed.

In addition to the D-T nuclear fuel, the mixed layers may also contain nitrogen (N), which will be injected near the diverter to mitigate thermal fluxes. Nitrogen present in Be-W type layers could affect the retention and desorption behaviour of hydrogen isotopes. In this PhD thesis there is a study of concerning the 2 μm thick beryllium

tungsten layers deposited on molybdenum, graphite and silicon substrates in a reactive atmosphere of argon-deuterium and argon-deuterium-nitrogen with the aid of two combined magnetron sputtering methods in HiPIMS mode and DC magnetron sputtering. The atomic ratio and layer thickness were controlled during the deposition process. We studied the structural changes induced by the presence of nitrogen in co-deposition as well as its influence on the retention mechanisms and the deuterium inventory in the samples.

All these studies mentioned above aim to improve the existing knowledge about the hydrogen isotope retention problem in ITER-like thermonuclear fusion reactors. In literature there is a limited number of studies on deuterium retention in mixed Be-W layers by implantation. Therefore, mixed layers of Be and W of varying concentration were prepared in the present thesis and were subsequently implanted with deuterium ions to investigate the retention behaviour. The main results are presented in Chapter VI. In spite of the fact that the retention of nuclear fuel in co-depositions of Be, W and Be-W will be the dominant component of implantation, there is a limited number of studies which deal with this aspect. For this reason, an extensive study on retention in these types of co-deposition was carried out following parameters such as deuterium flux, variation of Be and W concentration in co-deposition, layer morphology and structure and release behaviour of deuterium respectively.

Chapter I

The future of energy and nuclear fusion

1.1. The context of energy in the near future

The unique energy source that helped growing and development human civilization during the centuries until the XX th century was the one generated by the sun and changed into chemical energy by the plants through photosynthesis process. Wood burning has been the main drive for the development of human civilization helping to carry out a series of related activities besides domestic. James Watts' steam engine invention in 1764 helped to start the industrial revolution in the XIX th century. The steam engine was first used to pump water from galleries into coal mines, which subsequently led to larger drilling depths in the coal-rich deposits. In this way, in the first half of the XIX century, the coal mining production was significantly increased leading to the development of the industry (ferrous metallurgy, textile) as well as sea freight and inland (locomotives and steam vessels). Thus, the use of coal as a raw material in energy production has led to increased comfort and mobility of human civilization. Since the second half of nineteenth century, the discovery and exploitation of petroleum deposits has revolutionized public and domestic lighting. At the same time, it has gradually replaced the coal usage in transportation area. The products obtained by oil refining, gasoline and diesel together with the development of internal combustion engines (Otto, Diesel) have contributed decisively to the development of road and maritime transport, and are also used for boosting heavy machinery (in construction and mining). They have also led to air transportation development through the use of kerosene which is mostly used nowadays to supply the airplanes powered by reaction engines. The energy deposit represented by internal energy of natural gases is mainly used in home heating as well as in electricity production. Although, in the transportation sector, coal has been replaced by petroleum products, it gains an overwhelming importance in the energetic field for being used from the XX century in electric power generation within coal-based power plants.

The fossil fuel has led to an unprecedented development of human civilization regarding life expectancy, comfort improvement as well as world interconnection. All these highlight an increased dependency on this type of natural resources. Fossil fuels are considered non-renewable resources due to the conditions and time (millions of years) required for the regeneration of the deposits. It is estimated that during civilization evolution, from the primitive age to the present day, the energy consumption level has increased several million times. It continues to grow worldwide very fast. For example, in the past 100 years, the coal consumption needed in industry and energetic field increased approximatively 40 times, at the same time the predictions for the half XXI century based on a constant population growth, on an access to energy for the people in underdeveloped countries, it is estimated an increase of energetic consumption twice bigger comparing to the beginning of the century. Some of the energetic potential of hydrocarbons used in energy industry is lost due to low conversion yield. Thus, about 66% of energy amount is

lost on the energetic chain from producer to consumer. These losses are caused by the conversion from caloric energy to electric energy and due to the low efficiency of domestic and industrial consumers. Under the circumstances, where global oil and natural gas resources will be exhausted in the next decade, another problem is represented by oil and natural gas centralized exploitation especially from politically unstable countries towards decentralized consumption that can lead to worldwide economic instability with the diminishing of resources. For example, over 50% of the EU`s total energy consumption is provided by non-EU countries. Another issue related to the hydrocarbons exploitation as raw source for energy production is carbon dioxide release in the atmosphere (CO_2) by burning them. CO_2 emissions lead to the greenhouse effect contributing to Earth's surface global temperature increase. Since the beginning of the industrial revolution, the amount of CO_2 released in the atmosphere has led to a global heating of 0.6^oC. Based on the current energy policy and on the grounds of energy accelerated consumption, it is estimated that until the first half of XXII century, the temperature is expected to rise between 1 to 5^oC and it could have global dramatic consequences. In this way, the progress and development in the near future as well as environment will be endangered if the current energetic strategies are not changed. In order to reduce the CO_2 emissions and allow their attachment to ocean and Earth's surface during more generations, it is necessary to reduce the consumption with at least 2/3 from the current consumption of oil, gas and coal. This strategy is not feasible in the closer future without a fast development and mass production of new renewable energy sources. At the same time, intensive work is done for making conventional energy source more efficient that will lead to lower consumption of conventional raw materials. Despite the adverse effects directly resulting from fossil fuel burning (climate change, environment pollution and increased mortality rates due to air pollution in major cities), the need for warmth, comfort and electricity, essential to civilization will counterbalance all these negative aspects. At the same time, the reduced cost of fossil fuels and their derivatives help them have exclusivity on energetic market and inhibit the development of new alternative energy sources and technologies [1]. Parallel to energy sources based on fossil fuel, two other sources with high significance in global energy production appeared. One of them uses water potential energy. Thus, hydroelectric power plants convert the energy of large volumes of water drops into electricity. The first hydroelectric power plant in the world was built in Lancey, France in 1869 and generated a nominal power of 5 kW. The high energy demand after the Second World War combined with technological development allowed the transportation of the electric energy over large distances and led to a massive increase in electric energy production by this means. Currently, the hydroelectric power plants produce about 18% of the global requirements compared with 65% produced by fossils fuels. This source exploitation degree, varies according to the available hydrographic basin. Thus, only 10% of the hydrographical potential economically advantageous is in operation now. Although there are multiple benefits (river flow is regulated by removing the flooding risk, the accumulated water can be used for agriculture and fresh water supply), there are also disadvantages such as stopping river transport, wide land area flooding and negative effects on fauna by stopping certain fish migration. Despite low maintenance and production costs (the cost per kW is 5 times lower comparing to coal power plants) the needed investments to open

a hydroelectric power plant with high economic return are massive and the initial investment is covered over a few decades. These costs can currently be supported only by highly industrialized countries. Another problem is unequal distribution of hydrographic potential on the planet.

Among all sources that majorly contributed in electric energy production, the nuclear energy is the youngest energetic branch. It got a considerable development starting with mid XX century and until the beginning XXI century. This type of energy is obtained by controlled fission of radioactive elements using uranium, thorium and plutonium as nuclear fuel. The most important and used material is uranium. Exotherm reactions obtained from kilogram of uranium gives the same caloric power equivalent to 2000 tons of anthracite (superior coal). Presently, the nuclear energy contribution in the world energy total is 18%, and is decreasing since the beginning of the XXI century. The nuclear power plants are able to provide electric energy 1/3 cheaper than the one produced by thermoelectric power plants. The high construction costs and important investments in radio-protection measurements mean that most of the nuclear power plants are constructed in highly industrialized areas. The side effects on environment as well as low production costs make from this source of energy a viable alternative to fossil fuels. Despite this, the accidents at Chernobyl and Fukushima have contributed to diminish the public confidence in nuclear energy. For the last years, another factor that has led to a decline in the contribution of nuclear energy in global production was the decrease in fossil fuels prices. Another concern is the fear of nuclear weapons due to the plutonium production in nuclear reactors. Also, at the current consumption, the known uranium stocks will be exhausted in the next 50-70 years. A solution to this problem is thorium cycle much cleaner compared to uranium, solution that can also reduce nuclear weapons proliferation problem. The fourth generation of nuclear reactors that will use thorium as primary fuel are now only on research stage. This reactor generation that uses thorium cycle has the potential to solve uranium mineral resources problem, thorium being at least 3 times more abundant than uranium. The present thorium deposit could sustain human energetic consumption for several thousand years.

An emergent field of global energy is renewable energy sources. Interest for this type of energy has increased once with oil price increase in 1970s. The largest energetic share of these sources is being mainly exploited for geothermal energy, wind energy and solar energy.

The geothermal energy is harnessed using geothermal power plants. They use the caloric energy emanated from Earth's crust at great depths. This clean energy has started to be exploited since 1904 in Italy. Among the power generation component, this type of power plant can supply heat to cities and communities around them. Geothermal energy’s disadvantage is that economically can be exploited only in areas with high volcano activity (high geothermal gradient). For example, over 60% from the geothermal energetic potential of the planet is in Pacific Fire Circle area. The share of geothermal energy in world energetic production is currently 0.3%, with highly increased values in countries such Island.

The solar energy uses solar energetic potential to produce electricity. This conversion is possible due to photoelectric effect. This inexhaustible energy source shows

the advantage of being available on a global level. The most advantaged areas are low-cloud ones situated at low latitudes. Thus, energy potential distribution shows a maximum in the tropical, subtropical and dessert areas and a minimum at the poles. This type of energy has advantages in energy supply of small communities, but they are not effective for use in industry and for domestic consumption in large cities because of the large area that must be covered with solar panels. Although it is presented as a clean energy source, the space needed to install photovoltaic panels is huge, affecting the ecosystem. Also, without a consistent contribution to industry and due to the rare elements required to build them, the manufacturing cost is mostly covered by the energetic field powered by fossil fuels. Another disadvantage is the time of the year when this energy source is available. Thus, due to issues related to the storage of electricity, its supply is mostly diurnal.

Wind energy exploits the energetic potential provided by wind. Due to the wind power plants, airflows can be utilized at a speed of more than 5m/s. It shows a series of advantages: unpolluting characteristic reduced noise level and doesn't require cooling. Compared to solar energy, wind energetic power plants are limited to high latitudes areas, sea areas and permanent winds areas. Among disadvantages, should be mentioned the intermittent functioning conditioned by the air currents velocity, the low efficiency compared to thermoelectric power plants, the high initial cost leads to log retrieve time of the initial investment and 30% more expensive electric energy comparing to that obtained from fossil fuels. Despite these disadvantages, this type of energy is in full development due to large-scale projects initiated by high industrialized countries. Currently, the wind energy production contributes with 0.3% to world total.

Besides the three main renewable energy sources (geothermal, wind and solar) in the sea areas it is trying to exploit the energy generated by the ocean. The huge energetic potential of the flux and the reflux is currently caught by mareometric power plants. Landscaping an area where these power plants can be established requires major investments. From economic point of view, they can be built in natural bays with narrow access points to obtain the highest efficiency. Also, the capture of energy generated by sea currents and waves represents a highly energetic source for the future. The major problem in developing and valuing this energy is mainly represented by its transport from source to consumer.

The renewable energy sources currently represent less than 1% of the energetic total globally preponderantly produced in developed countries. Avery small percentage compared to 65% obtained from fossil fuels combustion. These continue to gain popularity despite conventional sources due to ecological point of view. An example in this way is Germany, whose energetic development strategy says that starting with 2050, over 80% from the entire energy amount needed is to be provided by renewable energy sources. Although ambitious, this project is considered by many people to be unrealistic in terms of current technical difficulties. Currently, due to high extraction and manufacturing energetic costs for rare materials and elements needed to make components for exploitations of these sources significantly contributes to global heating (most of the components are manufactured in China and India whose industry is mainly powered by coal-based power plants). Another major problem is also the difficulty of storing electricity. Thus, the discontinuous energy production character

makes them unusable in industrial environment. In order to ensure a sustainable development of human civilization it is mandatory to ensure both domestic and industrial demand using complementary energy sources. At the same time, to reduce the greenhouse effect and pollution caused by the energetic sector, for the next decades the CO_2 emission must be drastically reduced.

A promising source able to provide energy both for domestic and industrial use without greenhouse effect or radioactive residues with long times of life is nuclear fusion.

1.2 Nuclear fusion

Nuclear fusion is the most promising option to generate high amount of energy in the near future to supply both the industrial and the domestic energy demand. In order to understand the difficulties that fusion researchers and engineers are facing to develop the technology needed to build a thermonuclear power plant, it must be mentioned that this process feeds the Sun and the rest of the stars in the Universe. Inside the stars the necessary conditions for achieving fusion are in their centre. Thus, due to gravitational force, the central temperature inside a star makes possible that the atomic nuclei to collide and fuse them to release energy in form of neutrons.

To obtain fusion on Earth a gas mixture of hydrogen isotopes (deuterium and tritium) is heated to a temperature of about 100 million degrees Celsius. In order to achieve the fusion conditions, the magnetic confinement of hot gas is used in a controlled environment using powerful magnets. In this way the plasma charged particles are prevented from reaching the chamber confinement walls. The most promising device to attain the mentioned conditions is “tokamak”. This concept comes from Russia representing a magnetic ring chamber.

Looking ahead, from the point of view of fossil fuel resources decrease and global heating, thermonuclear fusion has many advantages that makes it a very attractive energy source. In the future, the nuclear fusion power plants will have zero CO_2 emissions, giving an answer to global heating problem due to greenhouse effect emissions. The only secondary product of fusion reaction is the release of small amounts of chemically inert helium (which does not contribute to air quality degradation). Another aspect worth mentioning is nuclear fuel abundance. Deuterium can be extracted from water and tritium can be obtained from lithium (high abundance in Earth`s crust), these resources being virtually inexhaustible (millions of years). Also, the energetic efficiency obtained per kilogram is clearly superior compared to fossil fuel. A kilogram of nuclear fuel is equivalent to 10 million kilograms of coal.

Compared to nuclear fission power plants, both radioactive products and safety concerns are solved. Thus, in the thermonuclear reactors the only radioactive products will be inner chamber walls, but the generated radioactive isotopes lifetime is smaller than 100 years. Also, there is no risk of nuclear accidents with severe environment and human consequences (Chernobyl and Fukushima) due to small nuclear fuel amount present each moment (equivalent to a stamp weight). Previously, the main economically benefits of fusion power have been mentioned.

Nuclear fusion is defined as the physical process where two light nuclei are combined to form a heavy nucleus. The process is exotherm in nature, being released

a large amount of energy. The nucleus resulted from the fusion of the two light nuclei must have a bonding energy per nucleon higher than it because the number of nucleons is bigger and each nucleon feels the attraction force generated by the others. This process is energetically friendly only for the elements with atomic mass (A) below iron (Fe), because this element has the biggest bonding energy per nucleon. Anyhow, there is a mass difference between reactants and reaction products. This so-called "mass defect "represents the energy released in the fusion reaction according to the Einstein equation of equivalence between mass and energy $E=\Delta mc^2$ [2]. The energy production in the centre of the Sun is based on hydrogen atoms fusion reaction. Despite the high natural abundance and low repulsion electromagnetic forces between two nuclei, this reaction is not practical for energy production on Earth due to small interaction section. Another feasible and energy-efficient alternative to hydrogen is its isotope use, mainly deuterium and tritium. Deuterium natural abundance in ocean represents 1 atom at 6500 hydrogen atoms. A major advantage of deuterium compared to hydrogen is the effective section significantly higher for fusion related nuclear interactions. At the same time, the biggest effective interaction section is shown by D and T. Based on this consideration, it is anticipated that in the first phase thermonuclear reactors will be operated using D-T reaction [2].

$$ {}_{1}^{2}D + {}_{1}^{3}T \rightarrow {}_{2}^{4}He(14.05MeV) + {}_{0}^{1}n(3.54MeV) \tag{1.1} $$

From equation 1 results the He fusion products with kinetic energy of 3.54 MeV and a neutron with 14.05 MeV energy. We also need to point that the relation 1.1 does not represent the final objective of fusion research, this showing multiple disadvantages and make it less ideal to long term exploitation. For example, tritium as hydrogen radioactive isotope is present in nature in neglectable quantities being produced in higher layers of the atmosphere due to the interaction with cosmic rays. This production mechanism for tritium is presented in 1.2:

$$ {}_{7}^{14}N + {}_{0}^{1}n \rightarrow {}_{6}^{12}C + {}_{1}^{3}T \tag{1.2} $$

The amount of gas required to initiate the fusion reaction in thermonuclear reactors will be provided by tritium obtained in fission reactors using heavy water as a moderator. Excepting this initial supplement, during the entire operating process of a thermonuclear reactor, tritium must be continuously generated from lithium (Li) according to 1.3:

$$ {}_{3}^{7}Li + {}_{0}^{1}n \rightarrow {}_{2}^{4}He + {}_{1}^{3}T + {}_{0}^{1}n \tag{1.3} $$

One disadvantage of D-T fusion reaction is represented by the deterioration and activation of the materials used inside the tokamak. Thus, the energetic neutrons produced in the reaction lead to limiting the lifetime of the thermonuclear reactor. Subsequently the main purpose of the entire research work in fusion field is to make DD reaction feasible in order to obtain electricity directly from fusion products. At this point, DD reaction is not feasible due to low effective cross-section that require high operating temperatures, the relative power density being also low [3].

From building a thermonuclear fusion reactor point of view, there are two major constraints regarding its design. The first one is heating nuclear fuel until reaches the necessary condition for DT ignition and the second one is about the confinement of previously heated particles [2]. To overcome the electromagnetic repulsion force between the D and T positively charged nuclei, plasma is heated to a temperature of $1.5x10^8$ K corresponding to a average ion energy of 8 keV. A direct consequence of these intense temperatures is that nuclear fuel particles must be confined to prevent their interaction with reactor inner walls. Thus, the most efficient magnetic set-up for future fusion commercial reactors will be tokamak. Tokamak design includes a torus vacuum chamber that uses toroidal and poloidal magnetic field for plasma confinement. In this configuration, plasma will be resistively heated by electric currents that flow through it (Ohmic heating), with additional heating with neutral particles injection and radio-frequency (RF) induction [4]. From scientific point of view, tokamak was proved as feasible for nuclear fusion since 1950, plus obtaining energy for the first time through controlled fusion in Joint European Torus (JET) entrusted this design. Currently, no tokamak reactor has proved its feasibility from an energy point of view. Essentially, all tokamak reactors consume more energy than they release. Thus, the brake-even limit where Q=1 (the input power equals with the released power) was not yet reached in any tokamak reactor. The most successful experimental tokamaks so far were JET and Fusion Test Reactor (TFTR). The main interest and research direction of the fusion research community is ITER (International Thermonuclear Experimental Reactor).

Among the main technical ambitious objectives of ITER include: an extended combustion time, between 300 and 500s in inductive operating mode at Q>10, proving operating capacity in continuous regime using non-inductive heating Q>5 respectively. ITER was designed for a production capacity of 500MW using the DT reaction, its final purpose being reaching and improving plasma fusion ignition and maintenance as well as proving the economic feasibility of this type of energy.

Chapter II

Nuclear fuel retention in plasma facing materials

2.1 Plasma facing materials

Despite efforts to improve fusion plasma confinement in order not to interact with the first wall of the reactor, the results will never be perfect. Thus, PFC-exposed Plasma Facing Components are subjected to intense heat and particle flux. This aspect makes the development of PFCs one of the key issues of fusion science and technology [5,6,7]. All components must withstand long-lasting operations without significant dust production and without retaining a large amount of nuclear fuel. A complete description of all plasma-wall interaction processes requires, in addition to theoretical predictions, experimental observations and computational simulations. Plasma-wall interaction processes are extensively studied in experimental fusion reactors, JET, TEXTOR, ASDEX, as well as in linear plasma accelerators PISCES and Magnum-PSI. Understanding the phenomena that occurs during plasma-wall interaction provides the information needed to develop new materials or select from existing ones. Compatibility between fusion plasma and surrounding materials is one of the main issues in the development of a fusion reactor. The ideal characteristics of the materials exposed to plasma are as follows:

- **High thermal conductivity**: capacity to transport high energy fluxes from plasma to cooling system
- **Low erosion to plasma particle bombardment:** low erosion leads to component life improvement as well as a plasma reduced contamination.
- **High temperature resistance:** Plasma facing components must show good mechanic characteristics at high temperatures to prevent their damage.
- **Neutron bombardment resistance:** Neutron bombardment leads to material straining and embrittlement as well as their activation.
- **Low tritium retention:** Tritium retention in plasma facing components can limit reactor's life.
- **Low atomic mass.**

There is currently no material that meets all of the above conditions. In ITER, the divertor will be exposed to thermal fluxes with maximum values between 10-20 MW / m^2 and constant particle fluxes of 1024 DT / m^2s. In other areas of the reactor, such as the first wall, the conditions are not as extreme will allow flexibility of choosing more types of materials. A compromise will be the use of two materials in the current ITER design [8,9,10]. The wall of the first wall of the reactor (700 m^2) will be covered with beryllium tiles, while tungsten tiles (155 m^2) will be used to construct the divertor. The distribution of materials in the fusion reactor is shown in Figure 2. The diverter castellation illustrated in Figure 2.1 b will be replaced several times throughout the operation of ITER due to activation.

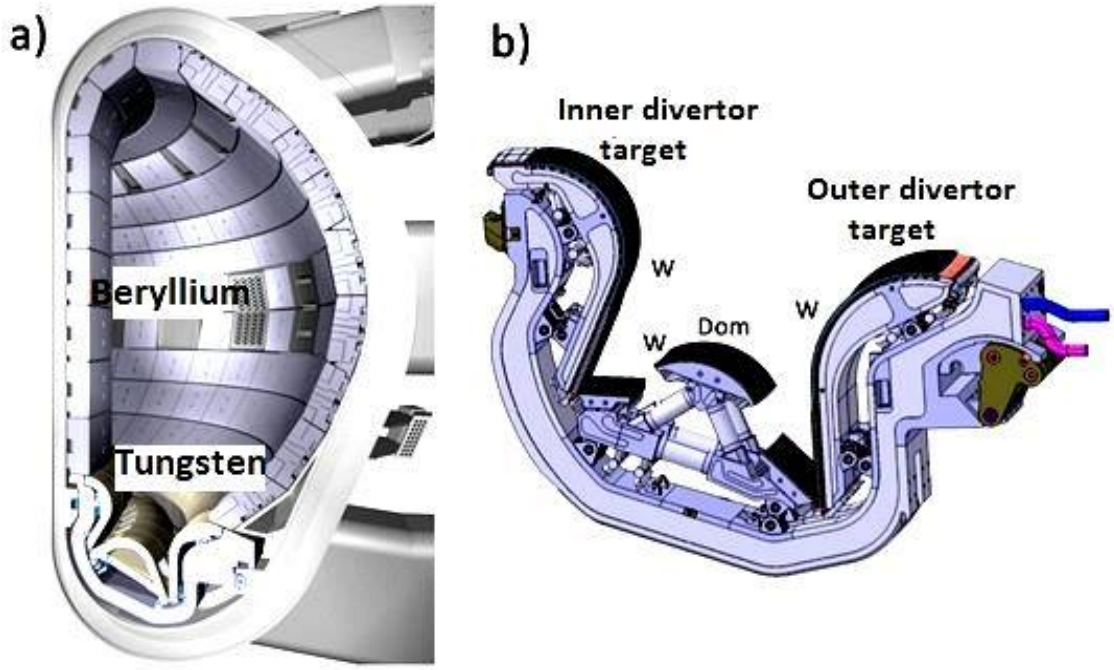

Fig. 2.1 *a) ITER chamber section b) Divertor section assembly*

Beryllium can withstand thermal loads of 1MW / m^2 obtained under normal operating conditions [11]. Beryllium tiles can be used up to thermal loads of 7.5 MW / m^2 that can be reached at the start of the fusion reaction [12]. Due to the low atomic number, beryllium provides low plasma contamination, as well as low nuclear fuel retention compared to carbon. The low melting point does not present beryllium as a useful material in the divertor area where the dissipated power can reach 10 MW / m^2 and may exceed 20 MW / m^2 during edge localised modes. An additional advantage of beryllium is the ability to retain oxygen from plasma through the formation of stable oxides (BeO). Tungsten has the highest melting point of all elements and has a high erosion threshold, making it ideal for divertor components. Unfortunately, tungsten loses its ductility to temperature changes, also forms H and He bubbles on the surface due to neutron bombardment from plasma [13].

When charged or neutral particle fluxes come into contact with plasma facing materials, a variety of processes occur at their surface. Part of the incident particles interact elastically with the atoms of the material being reflected back into the plasma with a minor energy loss. In the vast majority of cases, interaction processes are much more complex with adverse implications on materials such as physical sputtering, chemical erosion, melting, and embrittlement [14,15,16]. A schematic presentation of the processes involved is presented in Figure 2.2.

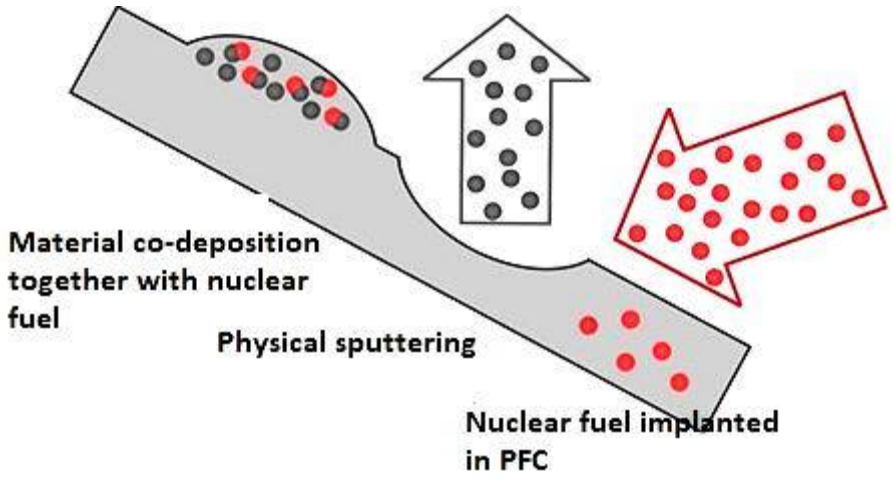

Fig. 2.2 *Schematic representation of the main processes occurring at the interaction of fusion plasma with PFC's*

Loss of material due to physical and chemical erosion results both in the reduction of material lifetime and in plasma contamination. The erosion of PFC includes a large number of processes, of which the most important are the following:

● **Physical sputtering**. This mechanism involves the sputtering of atoms from the surface of the material as a result of the energy transfer between the incident particles and the atoms on the surface. The sputtering process occurs for any type of material and its efficiency (the number of particles ejected per projectile) depends on the energy and incidence angle of the projectile, on the masses of the ion and the target atom and the surface bonding energy [17,18]. A good approximation for sputtering is given by the binary collision model where the masses of target and projectile atoms play a dominant role.

● **Chemical erosion**. Chemical erosion is the reaction that produces volatile compounds in the target. Compared to sputtering, chemical erosion is a process that is strongly dependent on the nature of the material and the surface temperature. For example, the carbon currently used in most fusion reactors is most vulnerable to chemical erosion. When hydrogen isotopes bombard the carbon wall, a series of hydrocarbons are formed which are thermally released into the plasma. A similar process is also observed under the action of oxygen bombardment leading to the formation of CO and CO_2 compounds. Also, tungsten can be chemically eroded at high temperatures in the presence of oxygen impurities, leading to the formation of volatile oxides WO and WO_3 [19,20].

● **Material melting.** Under the influence of intense heat fluxes, the surface temperature may exceed the melting point of the material. The material melted in this way can be expulsed into the plasma as small droplets or can recrystallize, producing a surface with new physical properties.

The eroded particles entering the plasma are later re-deposited on the walls of the reactor or are pumped out by the vacuum system. Re-deposits can occur on surfaces near the original erosion areas, but in most cases the eroded particles are transported along

magnetic field lines over long distances. Re-deposited layers also can be eroded again. The erosion or net deposition for a given surface on the divertor is defined as the balance between the incident material flow and the flow of eroded material. Such areas of net erosion can be observed in the divertor area and in the plasma limiter area, whereas net deposition can be observed in areas receiving a low flux of plasma particles, the voids between the castellations or the vacuum pump ducts [21]. Redeposition changes the chemical and physical composition of the newly formed surfaces. Nuclear fuel and plasma impurities are co-deposited together with eroded species to form mixed materials as well as chemical compounds [22]. The influence of co-deposited layers becomes more important as more materials are used in the manufacture of PFC's. Materials used in ITER may lead to the formation of mixed alloys with poorly defined properties [23].

Fuel retention in the reactor chamber is defined as the amount of hydrogen isotopes retained PFC' s. This aspect becomes extremely sensitive when tritium is considered as nuclear fuel [24,25].

Retention of tritium in the reaction chamber must be monitored and minimized from both economic and security point of view. Only a small portion of 1-2% of the injected tritium will contribute to fusion reactions while the remaining 98-99% will be recycled by the plant. ITER has a maximum administrative limit of 700 grams of tritium due to safety reasons [26]. Estimates of tritium retention in ITER, extrapolated from the data obtained for JET and TFTR [27,28] indicate that this limit is reached after 20-50 pulses for a reactor chamber composed of components made entirely of carbon. The predictions for a metal enclosure (made up of Be-W) indicate that several hundreds 400 second pulses (ratio D / T = 1 and Q = 10) are required to reach 700 g of tritium. Under normal vacuum conditions, residual gases in the chamber are absorbed by the walls. These volatile species are can be thermally removed from the walls. Also, regardless of surface temperature, there will always be a quasi-balance between absorbed and desorbed particles. In the case of thermonuclear reactors, where plasma-wall interaction or material migration play a decisive role, fuel retention during a single discharge can be estimated from the global balance of particles [29]. These estimates cannot be used for predictions on long-term retention where plasma disturbances and wall- conditioning play an important role. Thus, post-mortem analysis of reactor components, especially net deposition areas, contributes decisively to studies on long-term retention.

From the post-mortem analysis of the components of some experimental fusion reactors such as JET and ASDEX, two main factors have been identified that lead to the accumulation of nuclear fuel in the reactor:

- Co-depositions. The physical and chemical erosion of the PFC constituent materials leads to redepositiont on the walls of the reactor, resulting in the formation of non-homogeneous layers with high nuclear fuel content. Co-deposition is thus recognized as the main mechanism for the retention of nuclear fuel.
- Implantation, followed by diffusion and trapping. Energetic particles can be implanted into solid materials and after a series of elastic collisions they can remain in the material [30]. For the typical hydrogen isotopes energies (0.1-1Kev), the depth of implantation in beryllium is between 3 and 30 nm. This depth is even smaller if we take

into account large Z elements such tungsten [31]. Diffusion of ions at greater depths in the material depends on its nature and properties [32].

The problem of nuclear fuel inventory mainly concerns tritium, but due to precautions and high prices, the experimental study of the problem is limited to working with a common isotope of hydrogen, namely deuterium.

2.2. Deuterium retention in tungsten

The first fusion experiments initiated in the USSR using a tokamak device used stainless steel as a plasma facing material. In parallel, the properties of high atomic mass refractory metals, such as tungsten and molybdenum were investigated in order to replace stainless steel [33]. All this time, there was concern that the sputtering of tungsten by bombardment with energetical particles will contaminate the plasma, which will lead to a radiative cooling. Initially, due to these concerns, the use of tungsten was limited to low-flux areas, and the research was mainly focused on the study and implementation of low atomic number elements such as beryllium and carbon. Over the past 20 years, good understanding of plasma-wall interaction and low energy used (below 100eV), where physical spraying of tungsten is nearly 0, has expanded its use in the divertor area [34]. Studies have shown that tungsten plates for the diverter area can survive at thermal loads of 16 MJ / m^2 for 2000 cycles [35]. The erosion time of a 3 mm thick tungsten tile will be 170 years under the relevant ITER conditions. This resilience under extreme operating conditions makes this material an important candidate for the construction of future fusion commercial reactors, where component life will play an important role in the success of this technology.

Tungsten is a refractory metal with some exceptional properties. One of these properties is the extremely high melting point (3683K the largest of the metals and the second after the carbon) and one of the highest densities (19,254 g / cm3). The most commonly used form of tungsten is polycrystalline form. In this form, its properties greatly depend on the method used for processing as well as the treatment applied after processing such as recrystallization or quenching. Another advantage is the excellent properties at high temperatures, including the lowest vapor pressure and the highest breaking strength of all metals. Also, under high temperature conditions, tungsten has excellent hardness, flexibility and resistance to deformation. At low temperatures, tungsten is very brittle, especially if thermal treatments have been applied before and very rigid with Young modulus ~ 410kPa . Tungsten also has some interesting chemical properties for fusion. At room temperature it is resistant to the action of oxygen, water, acids and alkaline solutions. Reacts with the carbon at very high temperatures of 2000 K to form tungsten carbide, which means it can be used together with carbon in the thermonuclear reactors because these temperatures are hard to attain in a controlled fusion regime.

While the mechanical and chemical properties of tungsten are well known by the scientific community, the properties of diffusion of hydrogen isotopes, as well as their interaction with the material, are not well documented.

The technique used predominantly in literature to study the interaction of hydrogen isotopes with tungsten is ion implantation. The popularity of this technique in the

scientific community comes from the excellent control of important parameters such as ion fluency and energy. Relative to the large ions fluences encountered in the divertor area ~ 10^{29} DT / m^2 it can be concluded that implantation is an inadequate process for simulating those conditions due to the small ion fluences obtained in the different experimental configurations [36]. Furthermore, these plasma conditions may vary depending on the type and size of the fusion reactor. Thus, most studies using tungsten ion implantation are not focused on simulating the conditions of the divertor exposed to fusion plasma, but rather focus on understanding the mechanisms of nuclear fuel retention. The ultimate goal of these experiments is to understand the physics behind these processes and to extrapolate useful results for fusion reactors.

Studies conducted at different fluences of deuterium ions at room temperature (300 K) on 25 μm samples of polycrystalline tungsten indicated that total deuterium retention tended to the saturation point (6 x 10^{20} D / m^2) at higher fluence 10^{23} D + /m^2. This behaviour was observed in the literature by varying the energy of the incident ions between 300 eV / D - 1 keV / D being independent of the thickness of the samples used [37]. Instead, the samples implanted at 500 K indicated that the fluence of ions retained in the material is proportional to the square root of the incident fluence. Also, deuterium retention in tungsten did not reach the saturation point up to the incidence fluence of 3x10^{24} D /m2. This saturation point is reached due to the diffusivity limit of deuterium in tungsten.

While the literature results are similar for several commercially available and irradiated samples at room temperature, it can be concluded that the high deuterium retention in tungsten at high temperatures is mainly affected by the deuterium ion diffusion in the material, which its turn is affected by the distribution of impurities and the structure of the material.

In addition to determining the dependence of deuterium retention on the incident ion fluence, a series of experiments aimed at studying the influence of ion energy, flux and implantation temperatures on deuterium retention in W. In one of the papers published on this topic [38], various ion beam energies (below the threshold of 960 eV, where defects creation occurs) were used in studies to assess the ion fluency dependance. For room temperature irradiation, the ion beam energy was varied from 100 eV to 500 eV only to led to a negligible increase in deuterium retention. Instead, the same increase in energy mentioned above led to a three-fold increase in retention values for samples irradiated at 500 K. From the results of the author, apparently ion energy becomes a major factor at high temperatures despite the fact that this energy is below the threshold of creating defects in the material. This interesting phenomenon can be generated by the contribution of two important factors; better diffusion of energy ions at 500 K, possibly coupled with the distribution of impurities C and O in the material. The second factor can be explained by a more efficient energy transfer between D and C through elastic collisions. Thus, C and O impurities may be responsible for the defects created in the material, which leads to the conclusion that increased retention is due in large part to defects created by impurities. At lower energies (100-200 eV) a linear decrease in retention in W with a temperature increase from 300 to 500 K was observed. An

interesting result is that deuterium retention at higher temperatures was not observed in the irradiation experiments at temperatures higher than 700 K.

The most widely used method in the literature for investigating deuterium retention is thermal desorption spectroscopy. The depth profile of samples obtained by nuclear reaction analysis can be a powerful complementary tool for measurements obtained by thermal desorption spectroscopy. Thus, the depth profile can provide information on the diffusion of deuterium ions into the material, which helps elucidate the mechanisms governing the deuterium retention in tungsten. In literature, the depth at which specimens irradiated at energies between 0.2-1.5 keV show deuterium retention, can be divided into three areas [39]:

- Surface retention between 200 and 500 nm
- Retention next to the surface 0.5-3μm
- Bulk retention >3 μm

In [40] tungsten polycrystalline specimens, irradiated at room temperature with an incident beam energy of 200 eV / D, exhibit a surface retention between 1-5 at% and 0.1% in the immediate vicinity of the surface. For ion fluence greater than 10^{24} D / m^2, a decrease in deuterium retention of about 3 times was observed in the immediate vicinity of the surface. The observed bulk retention shows a linear dependence on the fluence of the incident ions up to a saturation value of 6 x 10^{-3} at% for a fluence greater than 10^{24} D / m^2.

Surface deuterium retention for tungsten samples of 25 μm was measured in [41]. The depth profile obtained for samples irradiated at room temperature (500eV ion energy and 10^{24} D / m^2 ion fluence) indicated that deuterium retention had a peak at 80 nm with a concentration of 3%. It was also observed that deuterium was retained in the material and at a depth of more than 500 nm to bulk. For the same parameters at 500 K, a uniform distribution of deuterium throughout the sample (from one surface to the other) was observed with a concentration of approximately 0.1%. This uniform concentration suggests that all traps in the material are occupied by deuterium diffusion. However, this phenomenon does not occur at fluences lower than 10^{24} D / m^2 and 500K sample temperature, suggesting that bulk material only saturates at high fluences.

The most important aspect of the deuterium inventory is related to the effects of surface modification on tungsten retention mechanisms. A series of recent studies have shown that deuterium irradiation of tungsten has the effect of creating "blisters" that have the effect of modifying the retention properties [42,43,44]. They indicated that the surfaces of tungsten samples exposed to large fluences of low-energy deuterium ions (below 960 eV) lead to the formation of blisters [45]. Moreover, it appears that they have highlighted a correlation between deuterium retention and blister formation at different irradiation temperatures. Thus, the exposure to the deuterium ion bombardment on a range of energies, fluence and temperatures led to the author's statement of the following conclusions:

- At energies of 1kev/D+ at room temperature blister formation was observed for fluences of 10^{23} D/m^2, where blister size increases with ion beam energy.
- Blisters occur at low energies 100 eV/D and fluences of 10^{25} D/m^2, where blisters size increases with ion beam energy increase.

● At temperatures over 873 K blisters do not form.

In the paper [45] a systematic study was conducted to investigate the influence of ion-induced defects on deuterium retention. For experiments with ion energy (500eV / D +) an increase in D retention for tungsten samples previously exposed to high ion fluences compared to those exposed at low fluences was observed. Additionally, blisters have been observed on the surface of the material as a result of exposure to large ion fluences. However, there seems to be an exception to the rule for pre-irradiated samples at 10^{25} D / m^2 and $3x10^{25}$ D / m^2 respectively. The problem of blistering is important because it can affect the nuclear fuel inventory and may lead to the exfoliation of tungsten PFC's, the main negative effect being plasma contamination.

2.3 Deuterium retention in beryllium

Beryllium is a low-density metal that was first used in nuclear applications, fission reactors, and nuclear weapons because of its neutron reflector property. In recent years, the applications of this "miracle" metal have diversified, being used today in the automotive, aerospace, defense, medicine and electronics industry. Due to its unique properties and its fusion plasma compatibility (low beryllium concentrations in plasma do not lead to strong radiative cooling) was considered and used in the past to protect internal components in experimental fusion reactors such as JET and UNITOR. Currently, as a fusion application, beryllium was used to build the JET first wall. In the future, it will be used to make the PFC's for the ITER experimental reactor.

The proposal of beryllium on the list of materials of interest in the field of fusion has generated the need to carry out studies of the solubility of nuclear fuel in this material. In the study [46], which includes a synthesis of hydrogen isotope retention experiments in beryllium, it is concluded that: under relevant ITER conditions, the nuclear fuel concentration is saturated in beryllium in the immediate vicinity of the surface. Ion bombardment in this area will cause damage to the material, resulting in a greater number of ions returning in the plasma. At the same time, the amount of hydrogen isotope retained in the immediate vicinity of the surface depends mainly on the temperature of the material and less on the energy of the implanted ions. Thus, it was observed that the deuterium retention at high temperatures of the implanted specimen is lower than that obtained at low temperatures. Also, deuterium retention was lower for irradiated specimens having a porous structure than dense specimens. Another important conclusion of this study is that retention in comparison with tungsten does not depend on the fluency of the incident ions. The study of irradiated metallic beryllium and oxide samples showed that the implanted hydrogen species are in both molecular and atomic form. Molecular species form bubbles in the cavities, their size being dependent on the irradiated layer production method. Instead, the atomic hydrogen species are either attached to impurities (BeOD or CO and CO2) or are caught in the crystalline defects of the structure. Material desorption of atomic species occurs at temperatures above 600 K.

In the same study [46], in addition to data from beryllium irradiation experiments, the author made a synthesis of experimental data obtained by co-depositing beryllium with nuclear fuel and other plasma impurities. The main results of these investigations indicate that deuterium retention in co-deposited beryllium layers depends on the