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Behaviour of neutron irradiated beryllium during temperature excursions up to and beyond its melting temperature

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ABSTRACT

Beryllium pebble behaviour has been studied regarding the accidental operation conditions of tritium breeding blanket of fusion reactors. Structure evolution, oxidation and thermal properties have been compared for nonirradiated and neutron irradiated beryllium pebbles during thermal treatment in a temperature range from ambient temperature to 1600 K. For neutron irradiated pebbles tritium release process was studied. Methods of temperature programmed tritium desorption (TPD) in combination with thermogravimetry (TG) and temperature differential analysis (TDA), scanning electron microscopy (SEM) in combination with Energy Dispersive X-ray analysis (EDX) have been used. It was found that there are strong relation between tritium desorption spectra and structural evolution of neutron irradiated beryllium. The oxidation rate is also accelerated by the structure damages caused by neutrons.

1. Introduction

Beryllium is a light metal with unique properties that make it attractive for the nuclear applications, including future fusion energy power plants.

Fusion power reactors will have to breed tritium to provide fuel for the fusion process. Due to its exceptional relevance, the question on the right tritium breeding concept has frequently been discussed. The European Union proposes two concepts of helium cooled tritium breeding blanket modules for testing in the International Thermonuclear Experimental Reactor ITER currently being under construction in France. In one of the concepts – "Helium Cooled Pebble Bed (HCPB) blanket", lithium ceramic pebbles are used as a tritium breeder and beryllium pebbles as a neutron multiplier [1]. Reference material is chosen to be 1 mm pebbles fabricated by NGK Inc. by Rotating Electrode Process [2].

Beryllium is one of the key components of tritium breeding process as it is a good neutron multiplier; therefore its performance under fusion reactor conditions is an important issue. Beryllium swelling, embrittlement and hardening as a result of the neutron irradiation are important issues regarding its mechanical performance, whereas tritium production and inventory is significant safety issue [3]. At the operational temperature of reactor a large fraction of tritium remains in the bulk of pebbles. In case of accidental temperature excursions this inventory of radioactive gas can be released in a short time and thus putting under the risk employees of the fusion reactor. In case of the accidental exposure to oxygen at high temperature beryllium oxide is formed. Beryllium oxide in the form of the dust can be considered as very toxic.

Beryllium pebble behaviour under accidental conditions, such as elevated temperature or/and air exposure, is of great importance since it provides information on the possible safety risks. Tritium release, microstructural changes, phase transitions and oxidation under accidental condition have been studied.

2. Literature review

2.1. Neutron induced effects in microstructure of beryllium

High energy neutrons knock out the atoms in the lattice and generate defects such as vacancies and interstitials [4]. There are several possible geometric configurations for clusters of vacancies and self-interstial atoms: planar dislocation loops (faulted or perfect) and three dimensional configurations as stacking fault tetrahedrons and cavities [5]. In beryllium irradiated at low temperatures (below 473 K) dislocation loops have been observed experimentally by several authors [6,7]. Moreover, the accumulation of the dislocations in different lattice planes depends on the type of the dislocation; vacancy loops are located on the basal planes, whereas interstitials on the prismatic ones [8]. Through the

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classical mechanism of vacancy accumulation – voids are formed. Accumulation of these voids on the grain boundaries leads to the embrittlement and swelling of a polycrystalline beryllium [7]. However, displacement damage is not significant factor for limiting beryllium pebble lifetime in fusion reactor since operation temperature will be comparably high. The main problem for beryllium performance under neutron irradiation is the gaseous products of neutron induced transmutations [9].

2.2. Gaseous products of neutron induced transmutations

As a result of neutron induced transmutations of beryllium helium and hydrogen isotope, tritium, are produced in considerable amounts. In the frame of the European Power Plant Conceptual Study, the peak integral gas production in beryllium, at the End-Of-Life of HCPB modules (40 000 h operation), has been assessed as 25 700 appm helium and 640 appm tritium, taking account in-pile tritium decay. The global tritium production in the whole of the blanket (390 tons of beryllium) is 23.8 kg [10].

It is assumed that initially helium and tritium form a dynamic solution throughout the entire lattice. Due to low solubility, helium tends to form gas clusters that performs as a nucleation site for further formation of bubbles [11]. In fact, grain boundaries are a strong sink for such defects, thus a large fraction of these clusters could be formed nearby them. Process of the bubble formation occurs via gas precipitation and a vacancy capture and this process is strongly temperature dependent [4]. After irradiation at temperatures below 200 °C no bubbles can be observed, whereas at the temperatures above this level – bubbles of few nanometres start to appear [6,12]. Interesting fact is that this tendency remains even at very long exposure time and large helium amount. In the low temperature (70 °C) irradiation experiment of beryllium that lasted for 15 years (helium content reached 2.2 at%), no bubbles were observed although significant swelling of the sample was obvious. Bubbles appeared only during post irradiation annealing of the sample [13]. Correlation between irradiation temperature and bubble size is also described in literature. Post irradiation examination of beryllium pebbles showed that bubble size in pebbles irradiated at ~700 °C are larger by a factor of 10 and more than those in pebbles irradiated at ~400 °C (diameter length range: 40–140 nm and 5–10 nm, respectively) [14]. Bubbles inside the grains were found to have a specific crystallographic form – a shape of hexagonal prisms. It is likely related to beryllium lattice parameters [11].

Swelling of beryllium due to helium accumulation also limits the lifetime of beryllium pebbles [4,15]. Mathematical approach of swelling models has been provided by several authors [4,16,17]. The parameters used in these calculations are neutron flux, initial porosity, amount of impurities, grain size [17]. It has been observed that swelling is less intense if the grain size of beryllium is smaller [12,15,18].

Tritium is assumed not to form its own gas inclusions since its overall concentration is very low if compared with helium. It is believed to accumulate as an interstitial atom or to be trapped by the structural or chemical traps. In contrast to helium tritium has a high chemical reactivity and it can form chemical bonds with impurities, mostly with beryllium oxide forming the hydroxide. It has been found that besides oxide layer on the surface BeO inclusions have a tendency to accumulate on the grain boundaries [6], therefore it can be expected that chemically bonded tritium can be found either on grain boundaries or in the surface layer. However, it is assumed that most of the tritium resides mostly in the helium gas inclusions [19,20]. This assumption is also in good agreement with experimental data on tritium chemical forms beryllium showing that in neutron irradiated tritium is accumulated mainly as a molecules [21]. To understand tritium behaviour in beryllium it is necessary to know such parameters as solubility, trapping energies and diffusivity. Some properties might be extrapolated from available data about protium or deuterium, however, isotopic effects must be taken into account [22]. In fact, it should be mentioned that in one of the first successful attempts to measure hydrogen solubility in beryllium tritium was used due to its simple detection based on its radioactivity [23]. Comprehensive overview of the experimentally obtained data on hydrogen solubility, diffusivity and permeation has been provided by R. A. Causey in 2002 [24]. Diffusion coefficient of neutron produced tritium in beryllium has been measured by several authors [25–27]. It is clear that overall tritium transport in neutron irradiated beryllium does not take place by a single mechanism of diffusion of tritium atoms dissolved in beryllium lattice. Trapping phenomena and influence of oxide layer have a crucial role. Theoretical model of tritium trapping on the imperfections of the lattice, such as vacancies, grain boundaries, etc. has been described [28]. Possible transport mechanisms of tritium in neutron irradiated beryllium has been studied by a number of authors, and a special computer codes or models have been developed [10,16,27,29–34].

2.3. Thermal desorption of tritium form neutron irradiated beryllium

Tritium and helium thermo-desorption spectra had been analysed widely in order to get comprehensive overview of the processes occurring during high temperature treatment of irradiated beryllium [4,10,26,32,35–40]. Earlier it was found that most of tritium releases together with helium, whereas helium can be released at temperatures close to the melting point of beryllium [41]. However, low temperature peaks of tritium release have been observed in a number of experiments. Some authors believe it is tritium located close to the surface and it is escaping through the micro cracks created by the irradiation or open porosity formed as a result of bubble coalescence along grain boundaries [37,42]. Other associates it with the diffusion of the tritium existing as an interstitial [10,35]. Tritium desorption process is affected by a number of factors, such as size and shape of the sample (diffusion length), structure (accumulation in the pores, grain boundaries, transportation along the cracks, etc), concentration of the helium gas inclusions and size of the gas bubbles (tritium accumulation together with helium), oxide content (tritium chemical bonding), etc. Therefore, desorption spectra might significantly differ. For instance, tritium desorption from pebbles of 0.1 mm mm in diameter, produced by Inert Gas Atomization method and irradiated with 2.70×10^{25} neutrons per m^{-2} starts at ~360 K, whereas from pebbles of 1 mm in diameter, produced by Rotating Electrode Process and irradiated with $(3–4) \times 10^{25}$ neutrons per m^{-2} – at 950 K [43]. Neutron induced damage and helium bubbles also leads to tritium retention in the pebbles [31,44]. Tritium desorption from pebbles in which tritium is loaded by thermo-sorption process occurs at much lower temperatures than neutron irradiated pebbles of the same production batch [45,46].

2.4. Beryllium oxidation

At ambient temperature beryllium has a protective oxide layer of about 1 nm in thickness that prevents its further oxidation [47]. However, if the temperature is raised above 1000 K a breakaway oxidation reaction occurs and non – protective oxide layer starts to be formed [48]. This dramatic increase of oxidation rate has been explained by the fracture of oxide layer due to differences of thermal expansions of metallic beryllium and its oxide [49]. Beryllium oxidation below ~1270 K is believed to follow parabolic rate law,