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Growth of Beryllium Oxide Nano-structures during Thermal Treatment of Neutron Irradiated Beryllium

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Beryllium oxide nano-structures grown during high temperature oxidation of neutron irradiated beryllium have been investigated. Oxidation of non-irradiated and neutron irradiated (neutron fluence $(3-4) \times 10^{25}$ m^{-2}) beryllium was performed in a differential thermal analyzer in an atmosphere of air and its mixture with helium at temperatures up to 1050 °C. Structure of beryllium and its oxide was studied by the means of scanning electron microscopy (SEM). The growth of beryllium oxide nano-structures – "labyrinth type" layers and nano-rods on the inner surfaces of neutron irradiated beryllium was observed by means of SEM. The size of the rods was 10 nm – 100 nm in diameter and up to few micrometers in length. There were no or few BeO nano-rods found on the surfaces of non-irradiated pebbles after similar treatment. This indicates that neutron induced irradiation damages, such as dislocation loops, are responsible for the growth of BeO nano-structures.

Keywords: beryllium, beryllium oxide, neutron irradiation, thermal treatment, nano structure.

1. INTRODUCTION

Beryllium and its oxide are materials with a wide range of applications due to their unique properties. In particular, these materials are attractive for nuclear applications because of the excellent ability to moderate and multiply neutrons. Beryllium oxide possesses also an exceptional combination of optical, thermal, dielectric and mechanical properties that are very advantageous in electronic applications, as well as for development of gas sensors, lasers and even rocket engines [1].

At ambient temperature beryllium has a protective oxide layer of about 1 nm in thickness that prevents its further oxidation [2]. At low temperature oxide layer grows with its wurtzite type crystals epitaxy to the beryllium structure [3]. However, if the temperature increases, oxide crystals start to grow in a random orientation. The breakaway oxidation reaction occurs at ~750 °C and non-protective oxide layer starts to be formed [4]. 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 [5]. Beryllium oxidation below ~1000 °C is believed to follow parabolic rate law, whereas at the temperature beyond this – linear rate law [5]. In early studies of V. D. Scott on beryllium oxidation mechanism few beryllium oxide nano-rods grown around disorders of beryllium lattice were observed [6]. Author suggested that these disorders may take the form of screw dislocations parallel to the axis of the rod.

Neutron irradiation also causes disorders in the lattice of metals. High energy neutrons knock out the atoms in the lattice and generate defects such as vacancies and interstitials that further form dislocation loops. Such loops have been observed in neutron irradiated beryllium by several authors experimentally [7, 8]. Lattice damages raise surface energy and therefore can enhance its reactivity [9].

It can be expected that dislocation loops caused by neutron damage would aid growth of nano-sized beryllium oxide structures, however, other effects, e. g., influence of the gaseous species, helium and tritium, that are generated as a result of neutron induced transmutations also must be considered.

In this paper, the growth of beryllium oxide nano-structures during thermal treatment of neutron irradiated beryllium and changes of structure of irradiated beryllium have been studied.

2. EXPERIMENTAL

Beryllium pebbles of ~1 mm in diameter produced by Rotating Electrode Process REP (manufacturer NGK Insulators Ltd., Japan) were used. About 40 irradiated and 20 non-irradiated pebbles have been used in this study. Main impurities of the samples given by manufacturer are BeO with content of 2300 ppm (mass unit) and Mg – 300 ppm. Portion of the pebbles were irradiated at the High Flux reactor in Petten, the Netherlands. Irradiation conditions are given in the Table 1.

Table 1. Irradiation condition of beryllium pebbles [10]

Irradiation facility	High Flux Reactor
Irradiation time	294 full operation days
Neutron fluence ($E > 0.1$ MeV)	$(3-4) \times 10^{25}$ m^{-2}
Irradiation temperature	150 °C – 550 °C

Irradiated beryllium contains neutron induced transmutation products – helium and tritium (radioactive hydrogen isotope). Tritium content was measured by tritium monitor TEM 2100A with a proportional gas flow-through detector DDH 32. Tritium concentration is in range of 1 – 2 GBq·g^{-1} that corresponds to 8 – 16 appm (atomic unit). Both

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irradiated and non-irradiated pebbles have a large (up to 0.5 % of the total volume) void in the bulk of the pebble, which is formed during the cooling phase of the fabrication process. Few smaller voids with size up to 100 nm have also been observed in the bulk of the irradiated pebbles.

Samples were heated in the furnace of differential thermal analyzer TG/DTA (Seiko EXTAR 6300), which allows to follow oxidation process in a real time (Fig. 1).

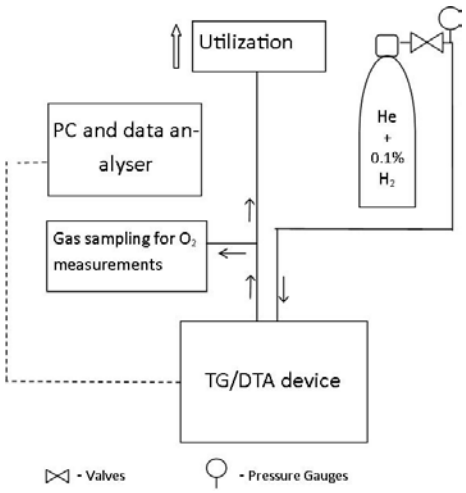


Fig. 1. Experimental setup based on TG/DTA device

Oxidation was studied by comparing the mass increase (TG signal) of the samples at similar conditions. Heating rate was 5 °C per minute. Oxidation was performed both in an atmospheric air and a diluted air by approximately 50 % with He and 0.1 % H_2 (system purged at a rate of 200 mL·min^{-1}). Dilution of air decreases the oxidation intensity therefore rate effect on the formed oxide structure can be studied. Hydrogen addition was necessary in order to perform simultaneous tritium release measurements. Composition of the diluted air gas samples from the system was measured by the means of mass spectrometry method and was as follows: He – (33 ±1) %, H_2 – (0.1 ±0,0) %, N_2 – (53 ±1)%, O_2 – (13 ±1) % and H_2O – (0.5 ±0.1) %) Several experiments were done in atmosphere of air diluted by argon and nitrogen to exclude effects of added gas.

Gradual heating of beryllium pebbles was performed up to 1050 °C. In order to observe structure evolution there were series of experiments where heating was stopped at lower temperatures.

Microstructure of the beryllium and its oxide was evaluated by means of Scanning Electron Microscopy (SEM) (Hitachi S-4800, 15 kV_{acc}, 15 µA). To study surfaces of inner pores and cracks samples were prepared either by polishing (first with SiC paper and then with diamond paste of 1 µm to 0.05 µm particle size) or alternatively – by mechanical fracture. Chemical composition of the samples was assessed by the means on Energy Dispersive X-ray (EDX) analysis (Quantax Esprit 1.9.) that are conjugated with the SEM.

3. RESULTS

Two stages of beryllium oxidation with different rates can be identified during thermal treatment of both neutron irradiated and non-irradiated beryllium under air atmosphere (Fig. 2.). The first stage involves slow oxidation that starts at ~650 °C. Oxidation rate significantly increases at ~950 °C that corresponds to the second stage of oxidation.

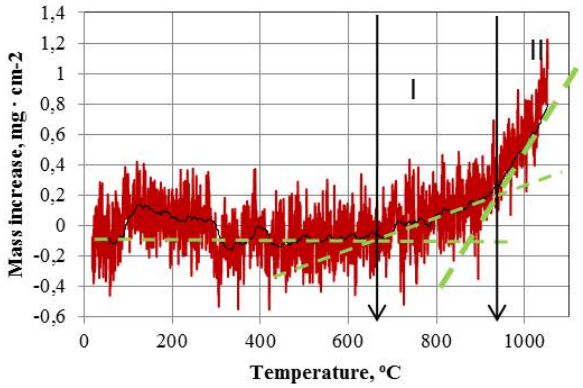


Fig. 2. Mass increase of non-irradiated beryllium pebble during thermal treatment up to 1050 °C in an air atmosphere. Oxidation stages are denoted as I and II (heating rate 5 °C·min^{-1})

The structure of oxide formed during these two stages was studied. SEM analyses of the samples were performed after gradual heating (5 °C·min^{-1}) up to 650, 750 and 850 °C to describe oxide structure formed during first stage and 950, 1050 °C – for the second stage.

It must be emphasized that macro structure of irradiated beryllium is less stable due to gaseous neutron transmutation products. During thermal treatment helium and tritium inclusions coalesces into bubbles and forms open porosity and cracks that increases the free surface of the pebble where oxidation can take place (Fig. 3).

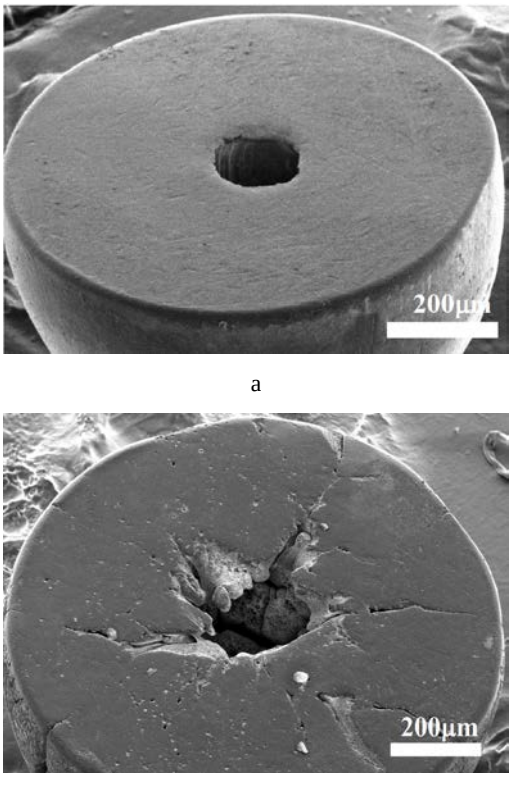
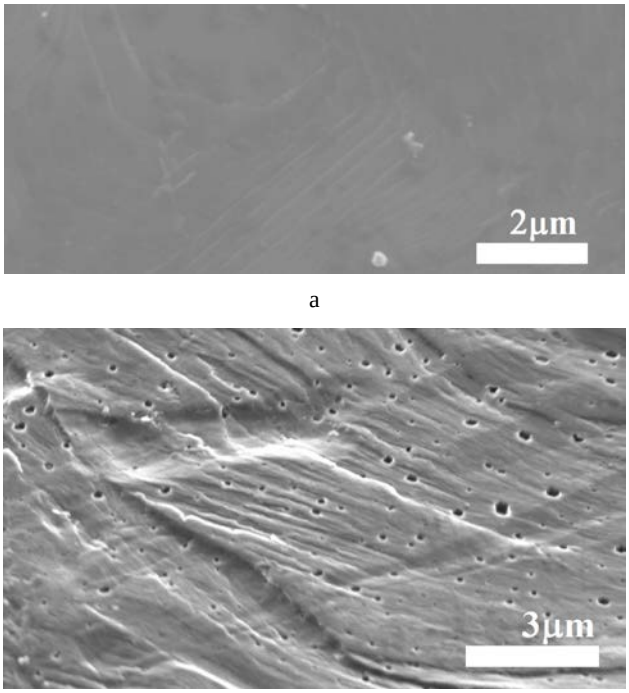


Fig. 3. SEM images of non-irradiated (a) and neutron irradiated (b) beryllium pebbles after thermal treatment at 1050 °C (heating rate 5 °C·min^{-1})

After thermal treatment at 650 °C and 750 °C in diluted air atmosphere oxide layer on the surface of irradiated beryllium do not differ from the non-irradiated beryllium treated in similar conditions. However, at 850 °C structure of neutron irradiated pebbles has changed dramatically – high porosity has appeared due to temperature driven coalescence and growth of helium gas bubbles (Fig. 4).



a

b

Fig. 4. SEM image showing the structure of non-irradiated (a) and neutron irradiated (b) beryllium after gradual thermal treatment up to 850 °C (heating rate 5 °C·min^{-1})

At 950 °C "labyrinth type" nano structures and start to appear on the inner surfaces of the pores and cracks of the irradiated beryllium pebbles (Fig. 5). The width of the "labyrinth branches" is approximately 100 nm.

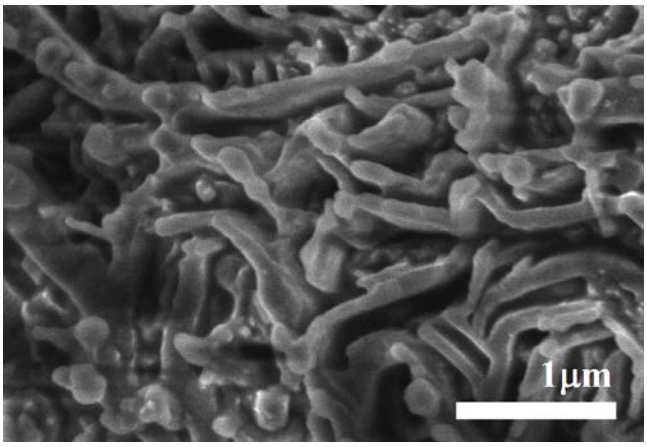
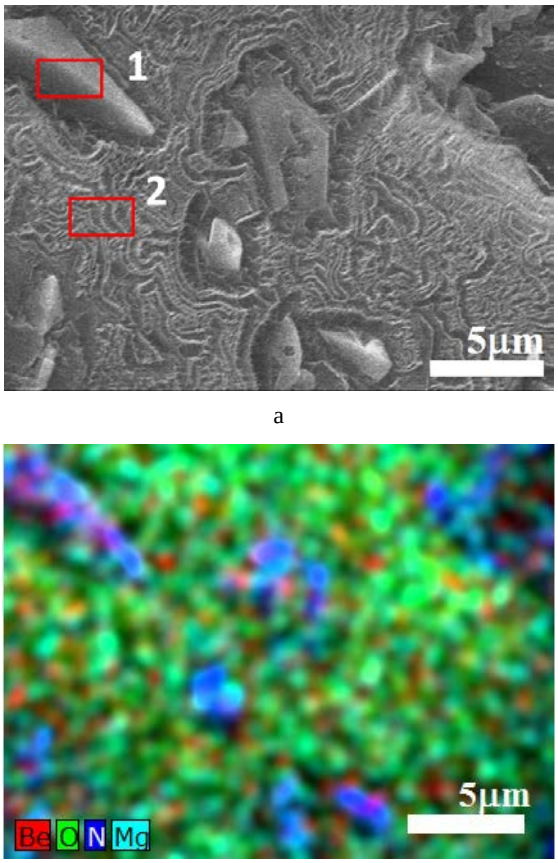


Fig. 5. SEM image of the "Labyrinth type" structure on the inner surface of neutron irradiated beryllium after gradual thermal treatment up to 950 °C (heating rate 5 °C·min^{-1})

EDX analysis revealed that these structures mainly consist of beryllium oxide (according to spectrum acquired from the area denoted as 2 in Fig. 6, a). Comparably large crystals (several micrometers in size) with high nitrogen content (up to 35 at% according to spectrum acquired from area denoted as 1 in Fig. 6, a) were found between these structures). It is known that in the hot air beryllium forms mixture of beryllium oxide and beryllium nitride therefore this nitrogen content corresponds to the Be_3N_2 formation [11].

No such "labyrinth type" nano structures were observed after thermal treatment in non- irradiated but otherwise identical pebbles.



a

b

Fig. 6. SEM image (a) and EDX mapping (Be, O, N, Mg) image (b) of the "Labyrinth type" structure and nitrogen containing crystals on the inner surface of neutron irradiated beryllium after gradual thermal treatment up to 950 °C (heating rate 5 °C·min^{-1})

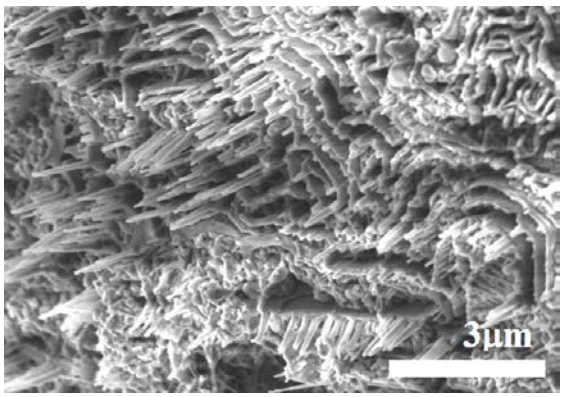


Fig. 7. SEM image showing start of beryllium oxide nano-rods growth from the labyrinth type structures at after gradual thermal treatment up to 1050 °C (heating rate 5 °C·min^{-1})

By further heating of neutron irradiated beryllium up to 1050 °C at a 5 °C·min^{-1} rate nano-sized beryllium oxide rods start to grow both from the "labyrinth type" structures and on surfaces without these structures. Length of the rods is up to 3 μm and diameter in range from 20 nm to 100 nm (Fig. 7).

After thermal treatment of neutron irradiated beryllium under normal air atmosphere no beryllium oxide nano-structures were observed.

4. DISCUSSION

The aim of this study was based on the assumption that neutron damage might facilitate the growth of beryllium oxide nano-structures during oxidation of irradiated beryllium. It was observed that during thermal treatment of neutron irradiated beryllium at high temperatures (above 950 °C) fraction of beryllium oxide forms in the shape of "labyrinth type" nano structures and rods with diameter in range from 10 nm to 100 nm and length up to several μm. It must be emphasized that no or few oxide nano rods were observed on the surface of non-irradiated beryllium after similar thermal treatment. The hypothesis was that these rods grow form dislocation loops formed in beryllium lattice during neutron irradiation. Several studies on the shape, size and density of the dislocation loops in the neutron irradiated beryllium have been performed by other authors. One of the studies revealed that loops of 20 nm – 40 nm in size with density of $1.2 \cdot 10^{14}$ loops per cm^{-3} are formed after irradiation with $2 \cdot 10^{20}$ n·cm^{-2} at 350 °C [12]. The size of these loops corresponds well to the rods observed in this study however the density of the rods is much higher. Nevertheless, it must be emphasized that pebbles used in this study have been irradiated at much higher doses (by approximately 4 orders: $(3-4) \times 10^{25}$ m^{-2}) therefore the density of the loops also might be higher. Moreover, in the studies of highly irradiated beryllium (neutron fluence 10^{25} n·m^{-2}) the density of dislocation loops is described as "very dense" [13]. Another issue is stability of these loops at high temperatures when oxidation resulting in growth of nano-rods occurs. Beryllium lattice itself is thermally stable if to compare with other light metals. Its phase transition and melting temperature is well above 1000 °C, as it is 1270 °C and 1285 °C, respectively. Therefore it can be expected that dislocation loops are still present at the annealing temperature above 1000 °C. Nevertheless, the role of gas inclusions as possible nucleation points also must be considered since a large amount of gaseous transmutation products are present. Small size gas inclusions are formed during irradiation. The size of these inclusions is in range up to 15 nm if the irradiation temperature is below 500 °C [14]. During thermal treatment these inclusions coalesce and form bubbles. At the temperature when the nano-rods start to form these bubbles has reached already several tens of micrometers, therefore it cannot be considered as a nucleation points for BeO nano-rod.

Another phenomenon observed is that nano-rods of BeO are mainly formed on the surfaces of cracks and pores connected to the outer surface. Exposure to atmosphere of these surfaces occurred only during cracking and formation of open porosity of the pebbles at the temperature where II stage of oxidation takes place. Therefore it can be assumed that beryllium oxide nano-rods forms only at high temperature on the clean surface of the beryllium metal.

The oxidation atmosphere also has an important role – nano-structures were formed only during treatment in diluted air when oxidation is less intense. Formation of beryllium oxide whiskers (similar structure as nano-rods) during thermal treatment under hydrogen atmosphere has been described in an early literature [15]. In this study addition of hydrogen to the purge gas has been also used, however, several experiments in different purge gas (argon) were done and formation of BeO nano rods remained.

The observed phenomenon of BeO "labyrinths" and nano-rod growth on the surfaces of neutron irradiated beryllium gives an important insight of metal behaviour under harsh environment such as neutron irradiation, oxygen containing atmosphere and high temperature. Moreover, these nano structures were formed mostly as a result of high temperature oxidation of pure beryllium surface where no initial oxide layer was present. It can indicate that mechanism of high temperature oxidation is more substrate structure sensitive – BeO formation is more favourable around dislocations than that for non-disordered lattice. Therefore, formation of BeO nano structures gives the opportunity to study different oxidation phenomena depending on underlying metal microstructure. However, more studies are needed to understand the mechanisms.

CONCLUSIONS

Formation of BeO nano-structures are facilitated by the structural changes induced by neutron irradiation of beryllium.

Crucial to this process are gaseous transmutation products that generate open porosity and cracks that increase the free surface.

Growth of beryllium nano-rods is mainly observed on the inner surfaces of the neutron irradiated beryllium.

Length of the nano-rods formed during isothermal treatment of beryllium at high temperature reaches several micrometers.

This is the first observation of BeO nano-rods growth during oxidation of neutron irradiated beryllium. However, more investigations are needed.

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