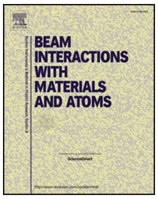
Nuclear Inst. and Methods in Physics Research B 415 (2018) 54–63

Contents lists available at ScienceDirect

Nuclear Inst. and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb



Radiation response of cubic mesoporous silicate and borosilicate thin films

Ayelén Manzini, Martín Alurralde, Vittorio Luca*

Comisión Nacional de Energía Atómica, Centro Atómico Constituyentes, Av. General, Paz 1499, 1650 San Martin, Provincia de Buenos Aires, Argentina

ARTICLE INFO

Keywords:
Mesoporous
Radiation
Borosilicate
Irradiation
Radiation damage
Thin films

ABSTRACT

The radiation response has been studied of cubic mesoporous silicate and borosilicate thin films having different boron contents prepared using the block copolymer template Brij 58 and the dip coating technique. The degree of pore ordering of the films was analysed using low-angle X-ray diffraction and film thickness measured by X-ray reflectivity. For films calcined at 350 °C, the incorporation of boron resulted in a reproducible oscillatory variation in the *d*-spacing and intensity of the primary reflection as a function of boron content. A clear peak was observed in the *d*-spacing at 5–10 mol% boron incorporation. For borosilicate films of a given composition an overall suppression of *d*-spacing was observed as a function of aging time relative to films that did not contain boron. This was ascribed to a slow condensation process. The films were irradiated in pile with neutrons and with iodine ions at energies of 180 keV and 70 MeV. Neutron irradiation of the silicate thin films for periods up to 30 days and aged for 400 days resulted in little reduction in either *d*-spacing or intensity of the primary low-angle X-ray reflection indicating that the films retained their mesopore ordering. In contrast borosilicate films for which the B (n, α) reaction was expected to result in enhanced displacement damage showed much larger variations in X-ray parameters. For these films short irradiation times resulted in a reduction of the *d*-spacing and intensity of the primary reflections considerably beyond that observed through aging. It is concluded that prolonged neutron irradiation and internal α irradiation have only a small, although measurable, impact on mesoporous borosilicate thin films increasing the degree of condensation and increasing unit cell contraction. When these borosilicate films were irradiated with iodine ions, more profound changes occurred. The pore ordering of the films was significantly degraded when low energy ions were used. In some cases the degree of damage was such that no low-angle reflection could be observed. This degradation of pore ordering was confirmed in scanning electron microscopy images of the irradiated films.

1. Introduction

Advanced nuclear energy systems, including new reactors and their corresponding fuel cycles (front- and back-end), will require novel materials that can tolerate extreme thermo-mechanical and chemical conditions as well as extremely high radiation fields without compromising significantly their chemical and physical properties over extended time frames [1,2]. In the context of reactor materials, ionizing radiation usually has highly undesirable consequences such as a reduction in strength, hardness, and fracture toughness as well as resulting in volume changes. It is not surprising therefore that since almost the beginning of the nuclear era researchers have devoted considerable effort to understanding the interaction of radiation with metals, ceramics, glasses and polymers. Yet many questions remain unanswered as to what really determines the radiation response of different materials and especially ceramics [3].

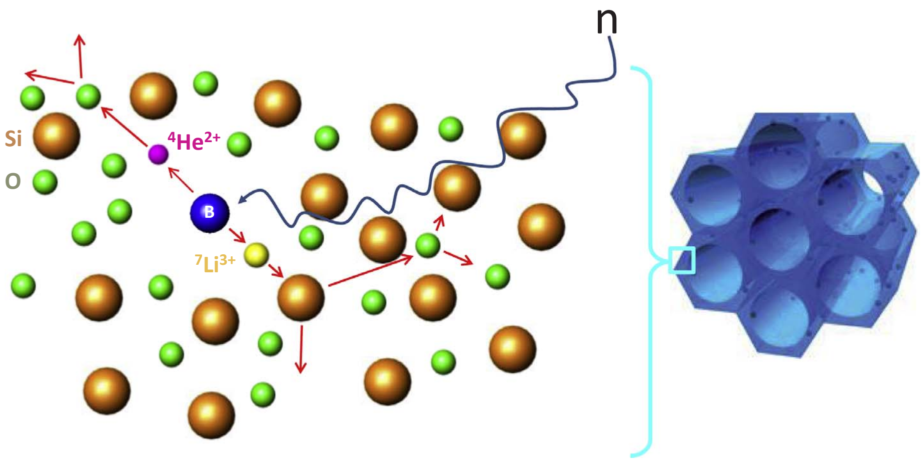
It is well appreciated that nanostructured materials with their high surface-to-volume ratios can have properties that can be quite different relative to their bulk highly crystalline counterparts. The literature is replete with descriptions of nanomaterials that show higher melting points, higher catalytic activity and so forth. It is not altogether surprising therefore that nanocrystalline materials might show different properties to their microcrystalline counterparts and therefore they have recently garnered great interest for potential applications in advanced nuclear energy system [4].

A poignant example of the potential that nanocrystalline ceramics may offer is provided by oxide dispersion strength (ODS) steels that contain oxide nanoparticles of around 5 nm [5,6]. ODS steels have attracted considerable interest in nuclear applications because of their improved resistance to radiation damage and high temperature creep. Although the exact reasons for enhanced stability of these materials is only beginning to be understood, it is apparent that the high concentrations of point defects associated with the nanoparticles and the nanoparticle-steel interface is important [7].

---

* Corresponding author.
E-mail address: vluca@cnea.gov.ar (V. Luca).

https://doi.org/10.1016/j.nimb.2017.10.026
Received 24 March 2017; Received in revised form 23 October 2017; Accepted 23 October 2017



Scheme 1. Depiction of the ^{10}B (n, α) reaction taking place within the pore walls of mesoporous borosilicate films.

Relative to bulk ceramics studies of the radiation response of nanocrystalline oxides is only in its infancy [8–14]. Therefore a comprehensive understanding of what governs radiation response in such systems does not yet exist although free surfaces are thought to play a significant role in annihilating defects.

Mesoporous metal oxides in bulk or thin film form have high surface areas and can have many potential applications including in the nuclear field [15]. For instance, potential applications could include as sorbents for the selective extraction and subsequent direct immobilization of radiotoxic isotopes [16], as coatings to mitigate the susceptibility of zircaloy to oxidation and the effects of iodine-induced stress corrosion cracking [17]. The present program of investigation is primarily directed toward the development of recyclable host matrices for isotope production and transmutations (see Fig. S1 of Supplementary material section) [18,19]. In these applications high surface areas are vital. However, the materials need to display unprecedented stability under irradiation preserving their physical and chemical stability over very long time frames. Mesoporous metal oxides and carbon-based materials prepared by supramolecular templating have ordered distributions of nanometer sized pores and began to be developed more than two decades ago. Although they have interesting properties and a myriad of potential applications [20], they have been little studied in the context of potential nuclear applications. It is necessary to distinguish supramolecularly templated mesoporous materials with periodic ordering from systems comprising a collection of randomly arranged nanoparticles containing intra-particle pores.

Periodically ordered mesoporous silicates are the most intensively studied of the mesoporous oxides but are known to have limited stability in water at ambient temperatures [21] and under hydrothermal conditions [22]. Mesoporous oxides of other metals on the other hand are far less susceptible to hydrothermal alteration. Highly porous and defective mesoporous metal oxides offer a unique opportunity to test the influence of length scale and porosity on radiation tolerance [14].

Ordered mesoporous silicate thin films and other compositions are easily prepared on silicon and other substrates through supramolecular self-assembly and sol-gel processing using surfactants as pore generators (porogens). Indeed the chemistry for the preparation of materials with a diverse range of structures is now very well established. The recently reported heavy ion irradiation (Xe, $E = 92$ MeV @ 10^{14} cm^{-2}) of hexagonal mesoporous silicate thin films has demonstrated the impact that subtle structural differences can have on modulating the tolerance of these materials to heavy ion bombardment [23]. More specifically it was observed that a 3D hexagonal (*P*6/*mmc*) SiO_2 film comprising spherical pores of about 2.5 nm in diameter was rendered completely amorphous while a 2D hexagonal (*P*6*m*) film comprising cylindrical pores having a diameter of 5.3 nm maintained order after comparable irradiations. No hypothesis for why the film with smaller pores was more easily damaged was ventured.

When considering the transmutation of a minor actinide or other element included within a porous host matrix, neutron bombardment provokes the transmutation of the incorporated element into more short-lived radionuclides giving rise to particle and/or photon emission. For instance ^{241}Am^{3+} ($T_{1/2} = 433$ y) forming part of a host structure may be transmuted into ^{242}Am^{3+} ($T_{1/2} = 16$ h) that decays to ^{242}Cm^{3+} ($T_{1/2} = 163$ d) and then to ^{238}Pu^{3+} ($T_{1/2} = 88$ y), or ^{129}I$^-$ ($T_{1/2} = 1.57 \times 10^7$ y) into ^{130}I$^-$ ($T_{1/2} = 12.36$ h) that decays to ^{130}Xe (stable). Typically a (n, α) reaction produces a primary knock-on atom (He) and a recoil nucleus giving rise to a series of collision cascades that cause local atomic displacements and structural damage. On the other hand, neutrons, and especially fast neutrons, can on their own possess sufficient energy to cause significant atomic displacements. In addition to the damage provoked within the host structure by the primary knock-on atoms and the recoil nuclei, the host structure needs to be able to accommodate the new species. This has recently been dubbed radioparagenesis and affects the long term performance of the waste form materials for radioactive waste immobilization [24–26].

Here we set out to assess and provide some insights into the influence of neutron and heavy ion irradiation on cubic mesoporous silicate and borosilicate thin films and to compare the damage in these materials to the previously studied hexagonal silicate phases [23].

Aside from irradiation of different cubic mesoporous silicates with swift heavy ions of similar energy to what was used in the aforementioned studies and also with lower energies for higher dpa, here we have examined the effect of high linear energy transfer (LET) alpha particles generated within the structure of B-substituted mesoporous silicates. Irradiation of the borosilicates with thermal neutrons generates low energy α particles due the ^{10}B (n, α) reaction as shown in Scheme 1.

This reaction generates α particles with energy of 1.47 MeV and ^{7}Li recoil atoms with energy of 0.84 MeV as well as prompt γ radiation (0.48 MeV). In comparison, the energy of the α particle emitted by the α decay of actinide elements is typically 4.5–5.8 MeV. The α particle that is generated has a considerably greater non-ionizing energy loss (NIEL) and therefore greater capacity to generate atomic displacements than the neutron itself. Such a strategy has been used previously in evaluating the influence of high LET radiation on solvent extraction systems [27] and more recently to study radiation damage in sodium borosilicate glasses [28].

One advantage of this methodology is that the distribution of α particles throughout the sample is uniform rather than being localized as might be the case using accelerator-derive heavy ion beams impinging on the surface of a film.

As an alternative it is also possible to simulate the release of fission fragments within an actinide host matrix using swift heavy ion