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# Extreme ion irradiation of oxide nanoceramics: Influence of the irradiation spectrum

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ABSTRACT

Oxide nanoceramics combine the enhanced radiation tolerance of nanocrystalline materials with the chemical inertness of oxides, and are promising materials for highly corrosive and intense radiation environments. In this work, nanocrystalline $Al_2O_3$ thin films are irradiated at 600 °C with either 12 MeV $Au^{5+}$+18 MeV $W^{8+}$ or 4 MeV $Ni^{2+}$ ions. The radiation damage exposure exceeds 450 displacements per atom. A comprehensive analysis of the irradiated samples is accomplished by X-Ray Diffractometry (XRD), Transmission Electron Microscopy (TEM) and Scanning-TEM (STEM). Results are compared in an effort to establish correlations between the irradiation spectrum and the response of this class of materials to radiation environments. The results show that grain growth is the main microstructural change induced by ion irradiation in the material, regardless of the ion utilized in this work. The phase evolution may be depth-dependent, and depends strongly on the ion utilized and on the irradiation spectrum. 12 MeV $Au^{5+}$+18 MeV $W^{8+}$ irradiations favor the formation of γ-$Al_2O_3$ and α-$Al_2O_3$, while 4 MeV $Ni^{2+}$ irradiations yield mainly δ-$Al_2O_3$, accompanied by small α-$Al_2O_3$ centers. Molecular dynamics simulations of displacement cascades are used to support discussions on the mass effect brought about by the different ions.



## 1. Introduction

The lack of suitable materials for extremely hostile conditions stands as one of the most challenging issues for the development of advanced nuclear systems, including both fission and fusion reactors [1,2]. Most difficulties arise from the high temperatures, the highly corrosive reactor coolants, and the radiation damage caused by intense neutron radiation fields. Accordingly, current research efforts in the field are focused on the quest for new classes of materials with improved radiation tolerance, such as bulk metallic glasses [3], complex oxide compounds [4], MAX phase ceramics [5], and many others. In particular, there is a strong interest for nanocrystalline materials, for which the very high density of interfaces is expected to promote radiation tolerance [6–8]. Among nanomaterials, oxide nanoceramics have attracted much attention, and are currently considered as candidate materials for a variety of applications in advanced nuclear systems, ranging from fuels [4,9] to high-level radioactive waste forms [10], or corrosion-resistant coatings [11,12].

The response of oxide nanoceramics to radiation fields is commonly studied using ions. There is a strong drive in the scientific community to simulate neutron-induced damage using ion irradiation as a predictive tool, basically because ion irradiation offers advantages in terms of flexibility, time and cost. On the other hand, it is common acceptance that the outcomes of ion and neutron irradiations may not always be considered equivalent to all extent and purposes. In particular, irradiation experiments are strongly influenced by the irradiation spectra (given by the ion mass and energy). Additional variations of the outcomes are

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determined by a tradeoff between temperature, dose and dose rate [13,14]. Thus, special care is required when designing ion irradiations to simulate neutron-induced damage. This is particularly true in the case of ceramic insulators, which are extremely sensitive to ionizing radiation. Ion irradiation experiments done in the nuclear (i.e. displacive) or combined energy loss regimes should be favored over irradiations done in the electronic (i.e. ionizing) energy loss regime –at least if the goal is to simulate neutron-induced damage in oxide nanoceramics.

The structural response of nanocrystalline oxides to ion irradiation in the nuclear or combined energy loss regimes is most often characterized by an increase of the average grain size. The increase follows a sub-linear dependence on the damage exposure. This observation has been reported, for example, for yttria-stabilized zirconia (YSZ), zirconia and ceria [9,15–18]. For these oxides, grain growth is observed even at temperatures as low as 160 K. Incidentally, grain growth has also been found in nanocrystalline metals irradiated at room temperature [19].

One of the mechanisms underlying the grain growth in nanocrystalline oxides has been unraveled recently by molecular dynamics simulations of ion-irradiated ceria [17,18]. These simulations suggest that the grain growth observed experimentally is first driven by the rapid interaction of radiation-induced disorder with grain boundaries, followed by conventional curvature- or grain-rotation-driven mechanisms. It has also been found that the extent of grain growth is dependent on the combined effect of the electronic and the nuclear energy loss components of the irradiation spectrum, which may be competing, additive or even synergistic [16,17]. In the specific case of ceria and zirconia, the effect is additive [17].

In this work, the structural features of $Al_2O_3$ nanoceramic thin films are evaluated in detail as radiation damage exposure approaches the extreme. Since no neutron irradiation studies are reported for nanocrystalline $Al_2O_3$, previous ion and neutron irradiations of sapphire are taken as a reference for designing the ion irradiations in this work.

Neutron irradiation at high temperature is known to produce a series of undesired effects in alumina, the most important being gross fracturing (related to impurity content and temperature) and void swelling [20]. The latter is a direct consequence of the development of a dense array of dislocation loops, accompanied by the precipitation of vacancies to form voids [21–26]. In the case of sapphire, irradiation growth (i.e. anisotropic swelling) is observed along the c-axis of the polymorph's structure. The anisotropic expansion of randomly oriented grains induces grain separation [20]. Surprisingly, the structural rearrangement leads to an increase of fracture toughness [25], which has been attributed to the concomitant interaction of cracks with compressive strain fields around the dislocation loop arrays, and to crack blunting through crack-void interactions. An increase of compressive strength along the c-axis is also observed [24], and can be explained by an inhibition of the propagation of r-plane twins. On the other hand, the stress state induced by irradiation growth is relaxed through and micro-cracking [25,26], which limits the usefulness of polycrystalline alumina in advanced nuclear systems. An interesting solution to these issues is reducing the amount of impurities in the material and, especially, reducing grain size [20]. These findings provide an encouraging basis for the development of oxide nanoceramic components for advanced nuclear systems.

Extensive work has shown that the microstructural features induced by neutron irradiation of single-crystal or polycrystalline sapphire can be reproduced with ions [27–32] –specifically, voids and dislocation loops [31,32], as well as grain boundary cracking [33]. Importantly, it is found that the irradiation spectrum has a prominent effect on the microstructural evolution of sapphire [27]. This effect can be easily visualized in terms of three important variables, namely the type of ion, the energy of the ion and its electronic-to-nuclear stopping power ratio (ENSP). In general, heavy ions release a larger amount of damage energy per unit length as compared to light ions of the same energy. Both the penetration depth in the material and the ENSP ratio are lower for the former. In addition, for a given ion, higher energies imply higher ENSP ratios. Importantly, a highly ionizing component in the irradiation spectrum (i.e. a high ENSP ratio, for instance above 100) suppresses dislocation loop formation and enhances loop growth [27]. Thus, in order to emulate the effect of neutron irradiation (which creates a high density of small dislocation loops [25]) a low ENSP ratio is recommended, as also mentioned earlier in this section. In particular, the anticipated ENSP ratio for alumina in advanced nuclear systems is around 4 (which includes the contributions of both primary knock-on atoms and $\gamma$ rays) [27]. Lastly, a low absolute electronic energy loss component (ideally below $9.5 \pm 1.5$ keV/nm) is desirable to avoid complete amorphization [34], nanoscale hillock-like defects or swift ion track amorphization [35,36]. These phenomena are not observed in alumina irradiated with neutrons at reactor relevant temperatures, and often take place in the electronic energy loss regime. It should be noticed, however, that amorphization is also possible upon ion irradiation in the nuclear energy loss regime. Amorphization may take place above a critical ion threshold fluence [37–39], provided that the irradiation temperature were low enough (i.e. room temperature in Refs. [37,38], and below in Ref. [39]). However, this is strongly determined by a tradeoff between dose, dose rate and irradiation temperature, as stated above. For instance, plasma-sprayed alumina is not amorphized by neutron irradiation at 4 K by a fast neutron fluence of $1.8\times10^{22}$ n.m$^{-2}$ [40]. In addition, low-temperature amorphization is not relevant for reactor applications, where temperatures typically exceed 300 °C.

In our previous investigation [41], we have shown that ion irradiation of nanocrystalline $Al_2O_3$ in the combined energy loss regime induces grain growth. From the mechanical point of view, the grain growth observed causes an increase of stiffness, together with an increase of hardness that is well fitted by the Hall-Petch relationship. The mechanical analyses in Ref. [41] are accompanied by preliminary phase characterizations by XRD. The latter reveal that the initially XRD-amorphous material fully crystallizes into $\gamma$-$Al_2O_3$ first, and then evolves into a mixture of $\gamma$-$Al_2O_3$ and $\alpha$-$Al_2O_3$, as grain size increases sub-linearly with damage exposure. Notably, ion-irradiation of nanocrystalline $Al_2O_3$ in the combined energy loss regime may also induce grain shrinking, provided that the irradiation is done at low temperature [42]. Concerning the initial stage of irradiation effects (i.e. crystallization of the amorphous phase), it is worth mentioning that ion beam induced crystallization is commonly observed in amorphous alumina films. The crystallization may be homogeneous and epitaxial if the films are free-standing [43] or epitaxial when the layers are in contact with sapphire substrates [37,39,44,45]. Notably, the crystallization may be achieved in the nuclear [37,44,45], in the combined [39] and in the electronic [43] energy loss regimes, both at relatively high [39,44,45] and low [37,43] temperatures. This behavior may be explained by considering that amorphous alumina is a highly metastable form of the material. Small injections of energy may be sufficient to overcome the energy barrier associated with the formation of more stable polymorphs [43].

Here, nanocrystalline $Al_2O_3$ thin films are irradiated at 600 °C either with 12 MeV $Au^{5+}$+18 MeV $W^{8+}$ or with 4 MeV $Ni^{2+}$ ions. The main goal of the work is to achieve a detailed comparison of the outcomes of two different types of irradiation from a structural point of view, extending the preliminary analyses done in our previous work [41], in an effort to establish correlations between