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Specific outcomes of the research on the radiation stability of the French nuclear glass towards alpha decay accumulation

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ABSTRACT

This paper presents an overview of the main results of the French research on the long-term behavior of SON68 nuclear glass towards alpha decay accumulation. The effect of the radiation damage induced by alpha decay and also helium build-up were investigated by examining glass specimens, doped with a short-lived actinide ^{244}Cm, irradiated by light and heavy ions. Additionally, atomistic simulations by molecular dynamics have provided further information on the atomic-scale effects of the macroscopic phenomena observed.

These studies have shown that some macroscopic properties vary with the accumulation of alpha decay, but then stabilize after integrated doses of the order of 4×10^{18} α g^{-1}. For example, the glass density diminishes by about 0.6%, its Young's modulus by about 15%, and its hardness by about 30%, while its fracture toughness increases by around 50%. The SEM and TEM characterization showed that the glass is still homogeneous. No phase separation, crystallization or bubbles formation was noticed up to an alpha decay dose corresponding to several thousand years of disposal of nuclear glass canister. Moreover the initial alteration rate of the glass is not significantly affected by the glass damage induced by alpha decays or heavy ions irradiations.

The comparison of the macroscopic evolutions of the Cm doped glass with those obtained for glasses irradiated with light or heavy ions (from either experimental and molecular dynamic studies) suggests that the macroscopic evolutions are induced by the nuclear interactions induced by the recoil nuclei of alpha decay.

The analysis of the behavior of the glass structure subjected to ballistic effects with various spectroscopic studies, together with the results of atomistic modeling by molecular dynamics, have identified some slight changes in the local order around some cations. Moreover a modification of the medium-range order has also been demonstrated through changes in the bond angles between network formers and broadening of the ring size distributions, indicating increasing disorder of the glass structure. This structural evolution induced by alpha decays would be driven by the reconstruction of the glass disorganized by displacement cascades of the recoil nuclei, freezing a glass structure with a higher fictive temperature. This "ballistic disordering (BD) fast quenching" event induces a new glassy state characterized by a higher enthalpy state. Accumulation of α decays induce similar phenomena of "BD-fast quenching", increasing the fraction of the sample volume characterized by a "high enthalpy state". At dose around 4×10^{18} α g^{-1} the entire sample volume has been affected by "BD-fast quenching" events at least once, which explain the stabilization of the evolutions of glass structure and properties.

Helium behavior was also studied by measuring the helium solubility constants and diffusion coefficients. Helium atoms are incorporated into the glass free volume with a solubility constant that varies less than 10% around a value of about 10^{11} at cm^{-3} Pa^{-1} and a density of solubility sites accessible for helium around 2×10^{21} sites cm^{-3} which is larger than helium production in a glass package. Helium diffusion experiments performed on infused and Cm doped SON68 glasses indicate that helium migration is controlled by a classical thermally activated diffusion process, whose activation energy (e.g. 0.6 ± 0.03 eV) is not affected by an alpha decay dose of around 10^{19} α g^{-1}.

Helium implantation studies suggest that helium trapping could exist in nanometer size bubbles. SEM and TEM analysis performed on a Cm doped glass damaged by an alpha decay dose of around 10^{19} α g^{-1},

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showed a homogeneous glass without crystallization, phase separation or bubbles with a spatial resolution limit of 10 nm. Bubbles of significant size seem very unlikely to form at room temperatures. But, the ability to form helium bubbles of nanometer size, at temperature below the glass vitreous transition temperature cannot be excluded. However, all these studies agree on one point, the absence of macroscopic consequence on the glass integrity of accumulation of high helium concentration in the glass.

1. Introduction

In France the ultimate waste (fission products, FP, and minor actinides, MA) arising from reprocessing spent fuel from PWR reactors is immobilized by vitrification in a borosilicate glass matrix known as R7T7, after the names of the two vitrification units in the AREVA plant at La Hague [1]. Vitrification of the solutions containing fission products and minor actinides is the reference process for durable confinement of the radioactive elements arising from reprocessing of spent PWR fuel [1]. The process was developed in France in the 1970s and 1980s, and led to the formulation of a sodium aluminum borosilicate glass matrix containing more than thirty oxides.

The presence of radioactive elements implies different irradiation sources: α decay of the minor actinides (mainly Np, Am, and Cm), β decay of fission products (FP), and γ transitions accompanying β and α disintegrations. An order of magnitude less significant are (α, n) reactions, spontaneous or induced fission reactions, and (n, α) reactions, the most common of which is the ^{10}B (n, α) ^{7}Li reaction.

To guarantee the long-term behavior of containment glasses in a nuclear waste repository, studies have been conducted since 1970 in Europe, in the USA and in Japan, on the effects of irradiation in nuclear glasses. The most recent comprehensive review was carried out by Weber et al. [2]. This review shows that the main source of change in glass properties is associated with alpha disintegrations of the minor actinides. Certain macroscopic properties in all the glasses are sensitive to the accumulation of alpha decay, also known as alpha self-irradiation. This is the case for the mechanical properties, internal energy, and density, with variations depending on the chemical composition of the glass. The impact of alpha self-irradiation on the glass microstructure and its chemical reactivity with water was poorly documented, sometimes with contradictory results. Cognitive gaps were also highlighted, most importantly with regard to the origin of the observed changes in these properties.

Since the mid-1990s a CEA research program has sought to clarify the evolution of the properties of French R7T7 glass under alpha self-irradiation and to understand the underlying causes. The effects of this type of irradiation must be accurately assessed and the robustness of the results must be demonstrated in order to guarantee the long-term behavior of the glass. This paper presents the current state of knowledge of R7T7 glass behavior when subjected to alpha self-irradiation, i.e. radiation damage and helium build up.

After an overview of the research methodology and the materials concerned, the effects of radiation damage induced by alpha decays on the macroscopic properties and structure of the glass are described and discussed. The sum of this information allows us to propose a phenomenological explanation for the origin of the observed changes based on a mechanism of thermal quenching of the ballistic disorder created by the displacement cascade associated with the recoil nucleus of an alpha decay. Moreover the helium behavior in glassy matrix was also investigated by studying its solubility and diffusion properties.

2. Alpha decay radiation damage

2.1. Methodology and materials

The objective is to determine whether or not the glass properties will be modified by the accumulation of alpha decay after geological disposal. It is therefore indispensable to accelerate the time scale to simulate the potential consequences over very long periods — typically ten to several hundred thousand years. A multifaceted approach was adopted for this purpose, consisting mainly of specific laboratory-scale experiments simulating the aging of containment glasses, and atomistic simulations designed to understand the observed phenomena at atomic scale. Coupling these approaches makes it possible not only to assess the impact of self-irradiation of the glass on its macroscopic behavior and thus evaluate the long-term persistence of its radionuclide containment properties, but also to understand the atomic origin of the phenomena involved, which is indispensable for the development of long-term behavior models.

2.1.1. Actinide-doped glasses

Short-lived actinides are incorporated in the glass to quickly accumulate the highest possible alpha decay doses. This methodology is the most representative because the entire glass volume is irradiated in the same way as in a nuclear glass, involving all the components of alpha disintegration: recoil nuclei and alpha particles. Conversely, the use of radioactive samples limits the possible characterization techniques to those available in this environment. In addition, the faster integration of decay doses in these materials than in a repository environment raises issues relative to the effect of the dose rate, which must be evaluated. This is done by fabricating glass samples with different dopant concentrations to study not only the effects of accumulated decay doses but also the effects of dose accumulation rates.

Between 2001 and 2004, four batches of SON68 glass (R7T7-type glass in which fission products are simulated by nonradioactive elements) doped to 0.04, 0.4, 1.2 and 3.25 wt% $^{244}CmO_2$ were fabricated in the Atalante high-level waste laboratory (DHA) [3]. They will be called *X*CmSON68 in the paper where *X* is the weight percent of $^{244}CmO_2$ in the glass. Their macroscopic properties (density, modulus of elasticity, hardness, fracture toughness, initial alteration rate), and their microstructure and structure were examined periodically over time. Their chemical compositions are indicated in Table 1, and the elaboration process are described in detail in Refs. [3–5]. Their periodical characterizations up to 2012 allowed to investigate the effects of alpha decay doses corresponding to around 100,000 years of disposal of nuclear glasses.

2.1.2. External irradiation

The second area of study uses nonradioactive (“inactive”) surrogate glass compositions in which irradiation stresses are simulated by external irradiation with ions. The objective is to investigate the macroscopic and microscopic changes induced in the material. This approach also allows experimental characterization of the glass by spectroscopic techniques (Raman, NMR, XANES) to assess the behavior of the atomic structure of the glass under irradiation. In addition, different types of irradiation can simulate the different