Understanding the evolution of mechanical properties under irradiation in nuclear glasses via experiments

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Abstract: More than 80% of France's electricity needs are met via nuclear power plants. Due to France's nuclear power program it maintains a high level of energy independence and one of the lowest costs of electricity in the world. Furthermore, with today's worry about global warming, it also lays claim to an extremely low level of CO_2 emissions per capita. However a big disadvantage to nuclear energy is the long term storage of the nuclear waste. The high-level wastes are stored in a complex borosilicate glass matrix to protect the environment from radioactivity for hundreds to thousands of years. But glass is a brittle material which the life time can be limited by micro cracks generated during the fabrication. This glass must also resist to leaching by groundwater. It's why it is important to understand the mechanisms of crack propagation in a corrosive environment. The aim of this study is the comprehension of how the toughness is affected by the structural changes on simplified borosilicate glasses under irradiation and variation of the chemical composition of the glasses.

Simplified borosilicate glasses are irradiated to simulate alpha and beta decays using He^{2+} ions and electrons. The subcritical stress corrosion fracture properties of glasses are studied using DCDC samples which permit fracture growth in this regime. The experimental measurements of the crack propagation velocities as a function of the applied stress intensity factor is presented as a $v=f(K_I)$ curves. To understand how structural modifications are linked to failure mechanisms RAMAN, NMR and EPR spectra are investigated.

Keywords: Fracture, stress corrosion, irradiation

1. Introduction

Originally spent fuel was supposed to remain in spent fuel pools for 10-15 years. However many countries have left the fuel in for more than 20 years, and there is no end in sight. Spent fuel contains Uranium (~95%), Plutonium (~1%), Minor Actinides (~0.1%; Neptunium, Americium, and Curium), and Fission Products (~4%), and it poses a significant security risk as seen during Fukushima. France has chosen to close the fuel cycle by reprocessing spent fuel. Uranium (~95%), Plutonium (~1%) are reprocessed into MOX fuel, and the minor actinides and fission products are imbedded into nuclear glass packages (NGP, a complex Borosilicate Glass matrix frequently called R7T7 in France). These systems are subject to self-irradiation stresses which arise due to α disintegrations and β/γ decay processes of minor actinides (^{237}Np, ^{241}Am, and ^{244}Cm to name a few) and fission products in NGP. Piecewise studies concerning the structural modifications and how they affect the material properties have been conducted; however the origin and the extent to which these modifications affect the glass are not fully understood [1, 3, 5, 8, 9, 13, 16, 18, 19].

Numerous studies carried out investigate the impact of alpha and beta irradiation at macroscopic and microscopic scales[6, 15, 17, 18]. Variations in mechanical properties include: (1) up to 30% decrease of the hardness depending on irradiation doses and (2) about 60% increase in the toughness before stabilization.

Some authors concluded these evolutions are due to variations of the glassy molecular structure.

Over the past century multiple methods have been discovered and implemented and moreover today are widely used to study structural variations. Two techniques which will be implemented herein are Electron Paramagnetic Resonance (EPR) which is a very sensitive tool for the analysis of paramagnetic defects in glasses and Raman spectra usually employed in the examination of vibrational, rotational and other low frequency modes in complex sodium borosilicate glasses. From these spectra, scientists are able to extract information on the electronic defects, and some structural characteristics about local entities, local angles, local coordinations [7][5]…. Moreover after heavy ions irradiation scientists have evidenced[9][8][14, 17]: (1) decreasing of Si-O-Si angle; (2) depolimerization of the borate network; (3) change in sodium's role (network compensator/modificator)…. These structural evolutions are proposed to explain the modifications of the macroscopic properties. These recent conclusions contradict some older experiments that suggest these variations are due to electronic process[1].

To better understand the source of the changes in the macroscopic properties, and in particular the hardness of nuclear glasses, simplified borosilicate glasses are subject to a controlled external irradiation. Herein we will report results on samples which undergo electron irradiation. Hardness results are acquired via Vickers indentation tests. An investigation is also underway concerning how the fracture behavior at macroscopic scale and the structure modification at microscopic scale are linked.

2. Experimental methodology

2.1) Glass samples:

Nuclear glass packages are complex systems which contain more than 30 different oxides and undergo self-irradiation. In order to understand the role of each oxide the composition has to be simplified. A reasonable simplification of the NGP is sodium borosilicate glasses (SiO_2-B_2O_3-Na_2O), or SBN glasses, as these are the three main components of the NGP system. Herein we will concentrate on three compositions: SBN14, SBN35 and SBN55 (see table 1) which are defined by R_{OG} ($[Na_2O]/[B_2O_3]$) and K_{OG} ($[SiO_2]/[B_2O_3]$). It should be noted that due to the crucibles used in the glass fusion processes, a minimal amount of iron was found in all samples. Secondly as crucibles are recycled SBN35 and SBN55 also have a minimal amount of zirconium. The amount of iron and zirconium has been quantified and it is less that .1% molar mass.

To simulate electronic damage due to self-irradiations, the glasses are externally irradiated via electrons. Electron irradiations were conducted at LSI Sirius. Sirius is a 2.5 MeV Van de Graaff accelerator. At 2.5MeV electrons can penetrate the full our sample thickness (0.8mm thick). Thus our samples are considered homogeneous irradiation. An integrated dose of 0.5, 1, 1.5 or 2 GGy irradiation dose was reached on each sample with a 12 µA beam. During irradiation the sample temperature was maintained at less than 40°C.

OG name	SiO_2	Na_2O	B_2O_3	R_{OG}	K_{OG}
SBN14	67.73	14.23	18.04	0.79	3.76
SBN 55	55.3	29.99	14.71	2.04	3.76
SBN 35	43.95	35.42	20.63	1.72	2.12

Table 1: Composition of glasses (% of molecular oxides)

2.2) Marco-hardness tests:

Microscopic indentation tests were conducted using an Anton Paar MHT-10 Microhardness Tester. These tests were performed on glass specimens irradiated with electrons, and the load mass varied from 10g to 100g. The duration of each load was 15 seconds. The hardness values are determined as follows:

$$H_v = \frac{2*F*\sin(\frac{\theta}{2})}{d^2} \qquad (1)$$

where F is the applied force in Newtons, θ corresponds to the angle of the indenter (136° herein), and d is the averaged diagonal length of the residual print in mm (figure1). Hardness values presented herein are the average of 10 tests with a load of 50g.

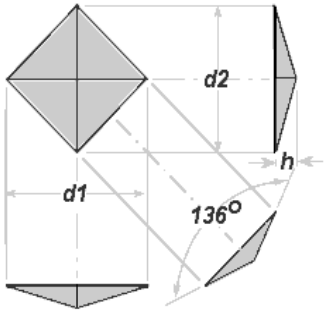

Figure 1 : Sketch of the Vickers diamond pyramid indenter

2.3) Structural measurements

Structural quantifications have been conducted via two techniques herein: RAMAN and EPR measurements. These measurements provide us with some insight on local variations and defects creation.

RAMAN measurements:

Raman spectroscopy measures the vibration modes of a system; moreover, it depends on Raman (inelastic) scattering of visible light. The incident photon interacts with the electron cloud; the return to a lower level emits a photon shift if the final state is different from the initial state. The frequency shift is called the Stokes shift. To improve the weak Raman intensity why several techniques are invoked (filters, high power...). Herein a Jobin Yvon HR 800 spectrometer was used to acquire RAMAN spectra. The wavelength of the laser on the instrument was 532 nm. Also the laser power was maintained at a low level to avoid heating of the sample.

EPR measurement:

Electron Paramagnetic Resonance (EPR) techniques permit a detailed identification of paramagnetic defects on the atomic scale in solids. Within the literature, there are several common defects which EPR spectroscopy can detect: oxygen hole center, E' centers, hole centers associated with boron atoms, hole centers near alkaline ions, etc**[4, 12]**Hence, the aim of this work is to inspect the paramagnetic defects as a function of the irradiation dose, and secondly how the paramagnetic defects vary as a function of the chemical composition in SBN samples. Electron Paramagnetic Resonance (EPR) spectra were obtained to

evaluate the paramagnetic defects due to electron irradiation. EPR spectra are obtained using an X band (v~10GHz) ESP300 Bruker spectrometer. Multiple spectra were run at different powers (1µW, 1mW and 10mW) to enhance or subdue defects.

2.4) Stress corrosion cracking

In moist environments, subcritical crack propagation, or stress-corrosion fracture, is feasible, i.e. $K << K_c$, due to the stress enhanced corrosive action of water molecules on the stretched molecules within the PZ[10]. The stress-corrosion cracking regime is of primary importance in the storage of nuclear waste since it can modify the storage quality over the long term. In this regime, the crack velocity can be very small, down to a few picometers per second. The global form of the curve $v(K,T,H)$ in OG (where K, T, and H refer to stress intensity factor, temperature and humidity, respectively) has partially rationalized over these last 4 decades[20][11] for a recent review]. It was shown to exhibits three regions:

- Region I where the crack velocity is set by the rate of the stress enhanced chemical reaction between water molecules and stretched chemical bonds in the OGs.
- Regime II where the crack velocity is limited by the transport of water molecules to the crack tip.
- Regime III where the velocity raises sharply with K.

The experimental set up which will be employed herein has been tested frequently over the past 10 year within the Complex systems and Fracture Group. These experiments are performed on DCDC (Double Cleavage Drilled Compression) specimens. Samples will be placed between the jaws of a compressive Deben machine (Figure 2). The force will then be gradually increased up to the initiation of two cracks that propagate symmetrically on both sides of the hole. During the propagation of cracks, a CDC camera will be used to gather information on the velocity of the crack front. Thus with this information we can plot the velocity versus the stress intensity factor (K_I).

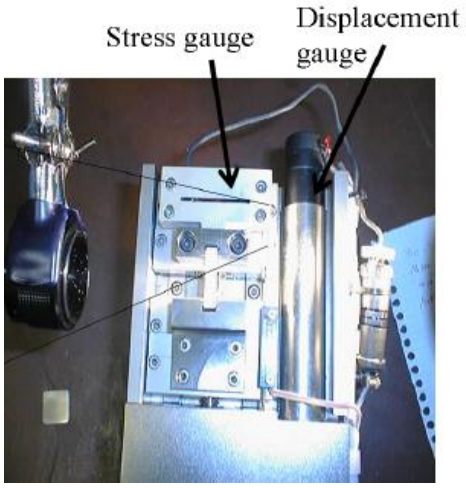

Figure 2 : Experimental setup used to fracture glass sample at low velocity in stress corrosion.

3. Experimental results

In SBN samples presented herein electrons should uniformly irradiate the system; hence leaving homogenous samples to be examined. This is contrary to light and heavy ion irradiation (not presented herein) which only penetrate the samples by a few μm. SBN55 and SBN35 irradiated from until 0 to 2GGy were found to have little to no variation on the hardness. On the contrary the SBN14 composition presents another behavior: the hardness decreases by about 20 % at 1 GGy (figure 3).

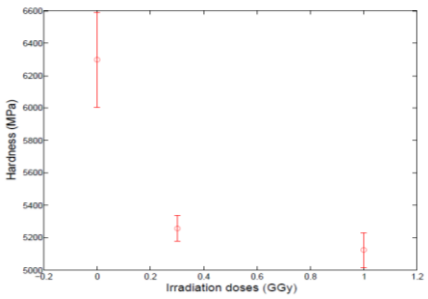

Figure 3 : Hardness variation (MPa) versus electronic irradiations doses for SBN 14 glass

In order to quantify and qualify some of the smallest variations, i.e. variations in the paramagnetic defects of the glasses, we will study the EPR spectra. In all cases non-irradiated glasses revealed defects due to contamination during elaboration (Zr^{3+} and Fe^{3+})[2]. SBN14 irradiated glasses (figure 4a)) did expose E' centers, Oxygen hole centers, hole centers near alkaline ions [4]…. A dependence on the irradiation dose is revealed. Moreover we find an evolution in paramagnetic defects versus the chemical composition (figure 4a et 4b) right).

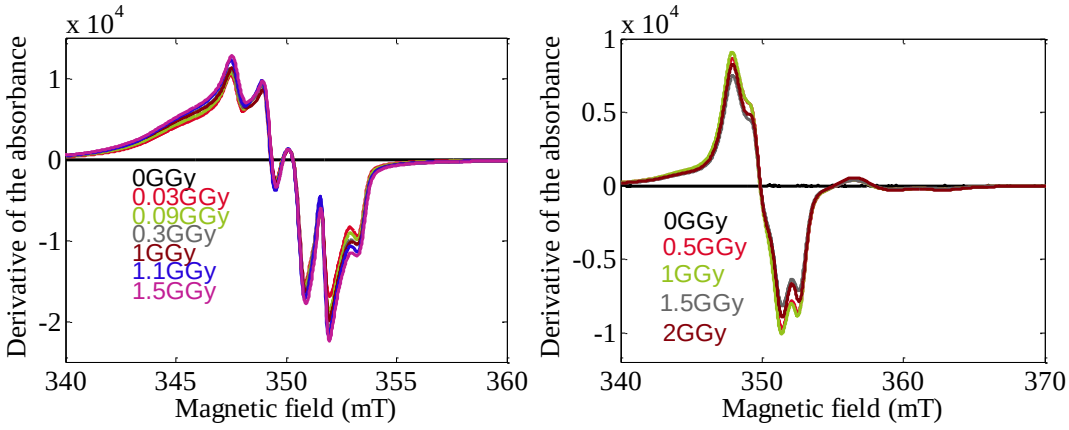

Figure 4 : EPR spectra for a) SBN 14 and b) SBN 35 at 1μW.

Figure 6 depicts the RAMAN spectra for SBN35 at irradiation doses 0, 0.5, 1, 1.5 and 2GGy,. Herein minute dependencies are found on the dose for SBN35 samples.

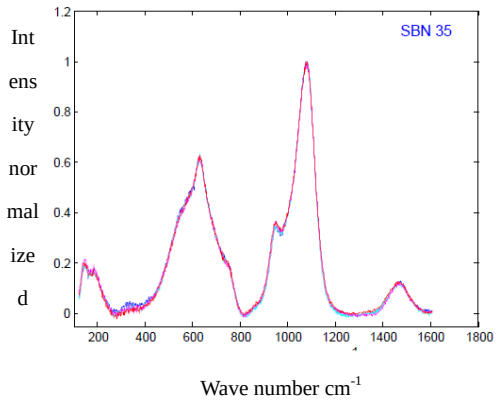

Figure 5 : RAMAN spectra for SBN 35 at different doses: 0, 0.5, 1.5 and 2GGy

4. Discussion and conclusion

Electronic damages induced in glass vary with composition. No influence until 2 GGy have been observed for two borosilicate glasses SBN35 and SBN55. The SBN 14 presents a marked behavior.

The variations affect the macroscopic scale with a decrease of the hardness value and an increase of the toughness which can be explained by the variation at microscopic scale. To understand the relation between electronic damages and glass compositions other studied are needed. Finally let us add that stress corrosion fracture studies are still underway and will be presented at the conference.

5. Acknowledgements

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