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Composition dependence of mechanical property changes in electron irradiated borosilicate glasses

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ABSTRACT

Mechanical properties evolution of three kinds of ternary Na_2O-B_2O_3-SiO_2 (labeled as NBS) glasses induced by 1.2 MeV electrons has been investigated by nano-indentation measurements. The glass samples were prepared with different values of the molar ratio $R = [Na_2O]/[B_2O_3]$ (0.4, 0.75 and 1.34), while the molar ratio $K = [SiO_2]/[B_2O_3]$ was kept constant as 4.04. The results indicated that both the mean hardness and the reduced Young modulus were decreased as a function of electron dose and the decrements are significantly related with the glass compositions. The toughness of all these three NBS glasses was slightly improved due to electron irradiation. The mechanical properties of glass samples with greater R value tend to be less affected under electron irradiation.

1. Introduction

Borosilicate glass constitutes a subject of widespread interest in several fields from articles of daily use to the precision optoelectronic field. In particular, it is found suitable for solidifying the radioactive high level nuclear waste (HLW) generated after the reprocessing of the spent nuclear fuel. As the first engineering barrier of the underground disposal repository, nuclear waste glass suffers irradiations and the principal sources of radiation in HLW are β-decay of the fission products and α-decay of the actinide elements, both of which may lead to physical and chemical changes in the glass waste form [1], among which β-decay is the mainly source of irradiation damage during the first 500 yr. of waste storage. Therefore, understanding the mechanical properties evolutions of borosilicate glasses under ionizing radiation is crucial for assessing its performance after long-term interactions with radiation environment [2–4].

When glasses are subjected to ionizing radiations, some of their mechanical properties can be changed as a function of glass compositions. Peuget et al. carried out a series of He ions external irradiation (mostly ionizing radiation) on the R7T7-type containment glass, micro-indentation results indicated that a slight decrease (approximately 3%) in the hardness when the flux was up to 1×10^{16} ions/cm^2 [3]. In addition, Yang et al. studied radiation damage of the borosilicate glass induced by He ions and electrons, the nano-indentation results showed that the mean hardness of He ions irradiated glasses was reduced about 14% while the hardness variation caused by electron was merely 4% when the electron dose accumulated to 1.0×10^9 Gy [5]. Gedeon et al. performed electron irradiation on the binary potassium-silicate glass (15 mol% K_2O + 85 mol% SiO_2) to study the reduced Young modulus and the hardness, experimental results indicated that the modulus variation was 17.82% below the initial value and the value of hardness was reduced by 8.06% after electron irradiation at 1.47×10^9 Gy [6]. Chen et al. reported decreases of hardness (about 6.6%) and reduced Young modulus (about 3.1%) in electron irradiated sodium aluminoborosilicate glass, which have been correlated with the formation of defects and the transformation of $[BO_4]$ group to $[BO_3]$ group [4]. Recently, Mir et al. reported the hardness variation in electron irradiated the three oxide sodium borosilicate (BS3) and the thirty oxide borosilicate glass (SON68) were 20% and 10% respectively, suggesting that the presence of transition metals and mixed alkali effect which tends to reduce the diffusion of light alkalis and irradiation damage [7].

Moreover, studies concerning the effect of the chemical complexity of borosilicate glass on its mechanical behavior after irradiation suggested that changes in the glass mechanical behavior after irradiation appear to be controlled by the behavior of the basic constituent, i.e. sodium borosilicate [3]. The structure of sodium borosilicate glass has been well described by Yun-Dell-Bray model [8–10], in which the molar ratios ($K = [SiO_2]/[B_2O_3]$, $R = [Na_2O]/[B_2O_3]$) are the most important composition-related structural

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parameters in this model. To reveal the particular relationship between these components and macro-properties, Kieu et al. described the fracture processes simulated by classical molecular dynamics in three ternary SiO_2-Na_2O-B_2O_3 glasses with different compositions [11]. These glasses were regarded as models of irradiated structures and analyzing their fracture behaviors provides valuable information for understanding the effect of composition on how the fracture toughness evolves under irradiation. However their K values increases as well as R values, the detailed mechanism between composition and mechanical properties is not currently clear.

In order to obtain a more systematic result, a series of electron irradiations were performed on three kinds of ternary Na_2O-B_2O_3-SiO_2 (labeled as NBS) glasses, of which the ratio $R = [Na_2O]/[B_2O_3]$ increased (0.4, 0.75 and 1.34), while the ratio $K = [SiO_2]/[B_2O_3]$ equaled to 4.04. This paper presents the results obtained by nano-indentation tests on the mechanical property evolutions of Na_2O-B_2O_3-SiO_2 glass system under electron irradiation.

2. Experimental

2.1. Chemical compositions and irradiation conditions

The NBS glass samples used in this study were prepared according to the following composition proportion (showed in Table 1). The errors in the compositions derived only from the raw materials' mass measurements. The accuracy of our analytical balance is 0.001 g. The selected glass samples were cut into squares of 10 mm size with the thickness of 1 mm. All the samples were fine polished and ultrasonic cleaned. Irradiation with 1.2 MeV electrons generated by D2.0 type high voltage transformer electron accelerator was conducted in the Institute of Modern Physics, Chinese Academy of Science. Different doses from 5.0×10^5 Gy to 1.0×10^9 Gy were used. For sake of reaching the low/high dose in reasonable time, the beam currents were selected about 1.0 mA and 10.0 mA respectively. The samples were cooled by water during the irradiation experiments. The penetration range of incident electron was calculated by ESTAR (Stopping-Power and Range Tables for Electrons) program [12], which is approximately 2.78 mm. In this way, the homogeneous irradiation of the glass sample was obtained in the present conditions of sample thickness and beam conditions.

2.2. Characterization methods

The mechanical properties of glasses were measured by the means of Nano-indentation testing which was performed using the Universal Nanomechanical Tester (UNAT, Advanced Surface Mechanics GmbH, now Zwick GmbH) equipped with a Berkovich indenter. To obtain indentation hardness as a function of contact depth, indentation loads in the range from 1 to 200 mN were applied. The maximum penetration depth of indenter is about 1.0 μm and the Nano-indentation followed a trapezoidal loading function with segment times 10 s, 5 s and 5 s for loading, dwelling and unloading, respectively. At least five indentations were carried out on each glass sample. The calibration of the indenter area function and the instrument stiffness was based on measurements on two reference materials (fused silica, sapphire) with known elastic modulus.

Table 1
Composition of sodium borosilicate glasses (mol%).

Sample	NBS1	NBS2	NBS3
SiO_2	63.38	69.64	74.31
B_2O_3	15.68	17.21	18.40
Na_2O	20.94	13.15	7.29
K	4.04	4.04	4.04
R	1.34	0.75	0.40

In order to contrast the change of indentation morphology, ultra high resolution field emission scanning electron microscope (SEM, HITACHI SU8020) was performed using secondary electrons. The experimental parameters used during imaging are shown in the corresponding pictures in Fig. 7. Due to the poor conductivity of NBS3 glass, a lower accelerating voltage was applied to obtain a more detailed picture.

3. Results

3.1. Hardness/Modulus of pristine samples

The hardness and reduced Young modulus curves of pristine NBS glasses are plotted versus the penetration depth in Fig. 1. The two groups of curves show the same tendency, i.e. the hardness/modulus of NBS2 is greater than the others and the NBS3 has the similar value with the NBS1. Due to the tip effect [4,5,13,14], the hardness and modulus curves in the region between 500 nm and 950 nm were selected to describe the corresponding values of these glasses. Table 2 presents the values of the average hardness and the average reduced modulus obtained from Fig. 1, the errors showed in this table are the statistical errors which are resulted from the multiple measurements on the same sample.

The hardness of NBS1 and NBS2 are in accordance with the previous study [15], in which Barlet et al. carried out a set of experiments to investigate the mechanical response of sodium borosilicate glasses as a function of their chemical composition, i.e. for a given K_{SBN} ($K = 2.50$) the hardness values decrease with increasing R_{SBN} ($0.69 \leq R \leq 1.85$).

3.2. Electron irradiation effects on the hardness/modulus

Fig. 2 presents the typical hardness curves of pristine and irradiated NBS glasses. As shown in Fig. 2, the hardness curves of irradiated glasses have the same tendency with the pristine ones, i.e. the hardness is almost constant beneath the surface influence zone area. However, the hardness values were obviously decreased in these three irradiated NBS glasses at the dose of 5×10^8 Gy, especially for NBS3 glass.

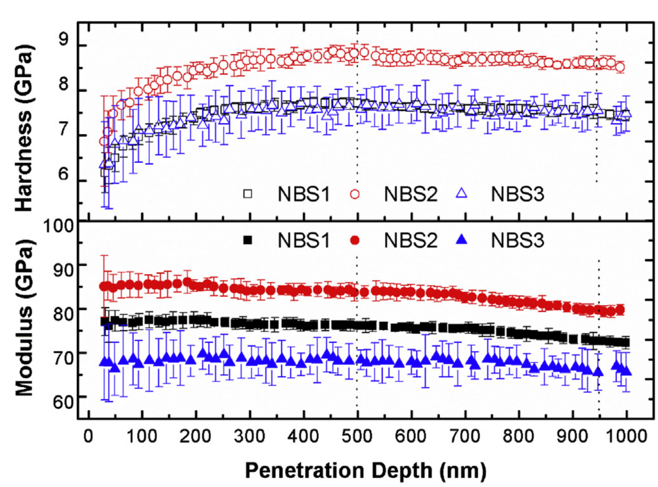

Fig. 1. Hardness (□, ○, Δ) and reduced Young modulus (■, ●, ▲) curves of pristine sodium borosilicate glasses.