Effects of Electron Beam Irradiation on Impact Value of Borosilicate Glass

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The effects of homogeneous irradiation of electron-beam (EB) with low voltage on the Charpy impact value (a_{uc}) of borosilicate glass were studied. When it performed in short bursts to maintain a low temperature, EB irradiation at a dosage from 0.04 to 0.22 MGy increased the a_{uc} value and enhanced its reproducibly. Based on the electron spin resonance (ESR) spectra, EB-irradiation formed apparent dangling bonds constructed with sodium atoms with high density of outer-shell electrons and terminated oxygen atoms of silica network in the borosilicate glass. When the intermolecular repulsive force generated the partial relaxation against residual and deformed strain, as well as expansion in front of crack tips near the sodium atoms, the initial a_{uc} enhancement of the borosilicate glass by the irradiation can be explained. Furthermore, the strong resistance to radiation damage of borosilicate glass was qualitatively confirmed. Although the large start point of irradiation dose to decrease the a_s value was 0.08 MGy for silica glass, it was 0.22 MGy for borosilicate glass. Consequently, the boron addition enhanced the resistivity to irradiation damage. [doi:10.2320/matertrans.MAW200914]

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1. Introduction

Borosilicate glass can be used as thin glass of large-area liquid-crystal displays of televisions,¹⁾ as well as an electronic insulator. However, the low fracture toughness of the glass has been a serious problem, when it is used to manufacture broad thin glassy sheets.²⁾ Thus, strengthening transparent thin sheet glass is an important technique in manufacturing large-area liquid-crystal displays.¹⁾

The brittle fracture, which is the result of nucleation and propagation of cracks,³⁻⁵⁾ is observed in steels, which is constructed with bcc iron and carbide, by deformation of both low temperature and high strain rate. Since it is very difficult to eliminate the crack origins, strengthening is often inhibited by crack propagation.^{6,7)} General strengthening has been performed by fiber reinforcement⁶⁾ and transformation-induced toughness.⁷⁾ Furthermore, it is useful to add residual compressive strain on the surface of the glass by physical and chemical reinforcement processes.⁸⁾ However, process conditions related to pressure, composition, temperature, time and dependent on the materials, must be selected in a complex manner.

On the other hand, the shot-peening is one useful tool to randomize the metallic glasses.⁹⁾ It enhances the saturated magnetization,¹⁰⁾ and also softens the glass, homogeneously.¹¹⁾ However, it is difficult for shot-peening to randomize the ceramics without fracture.

To randomize the glassy network structure without fracture, irradiation by an electron beam (EB-irradiation), which has limited small mass, has been used as the ball of shot-peening.^{12,13)} Homogeneous EB-irradiation with low-voltage generates dangling bonds^{12,13)} and then eliminates the crack, resulting in strengthening.^{12,13)} In addition, our research unit recently starts to report that the high stress resistance to crack origin nucleation as well as to crack propagation dominates the high fracture resistance of borosilicate glass.¹⁴⁾ However, the influence of EB-irradiation on the Charpy impact value (a_{uc}), one of indicator of practical

fracture resistance, has not been reported for borosilicate glass. The a_{uc} value of a material is an important property in terms of practical applications. As a basic research, effects of EB-irradiation on a_{uc} value of silica glass, which is not so easy to form thin sheet because of high glass transition temperature (T_g) at 1333 K, have been reported.¹⁵⁾ The EB-irradiation enhances the a_{uc} value.¹⁵⁾ Since the EB-irradiation generates the stress relaxation and compressive stress at dangling bonds in silica network structure, the a_{uc} enhancement of silica glass by EB-irradiation can be explained.¹⁵⁾

On the other hand, effects of additional elements on a_{uc} values of silicate glasses (crown, soda and alkali free glasses) have been studied.^{16,17)} The dissolution driven by the added alkali elements in the one of silicate glass (Crown glass (71 mass% SiO₂, 11 mass% Na₂O, 7 mass% CaO, 5 mass% K₂O, 4 mass% ZnO, 2 mass% BaO)) easily occurs.¹⁶⁾

Although the alkali metals desolve in liquid-crystal, the other silicate glass (soda glass (64.4 mass% SiO₂, 8.07 mass% B₂O₃, 7.00 mass% K₂O, 6.48 mass% Na₂O, 4.68 mass% ZnO, 4.18 mass% Al₂O₃, 4.08 mass% TiO₂, 0.14 mass% Fe₂O₃, 0.58 mass% Sb₂O₃)) is often applied to popular liquid-crystal displays with low price, is easily to form the thin sheet because of low T_g value at 830 K. The EB-irradiation with small dose (0.043 MGy) tremendously enhances the a_{uc} value of soda glass.¹⁷⁾ When the EB-irradiation cuts the ionic bonding between terminated alkali ions and its chained oxygen atom of silica network structure, the repulsive force probably occurs between the alkali atoms with high density of outer-shell electrons and terminated oxygen atom. Since the intermolecular repulsive force generates the relaxation with compressive stress in front of silica network structure near sites of alkali metals (Na and K) with chemical weak bonding energies to oxygen of Na-O (252 kJmol⁻¹)¹⁸⁾ and K-O (167 kJmol⁻¹),¹⁸⁾ the enhancement of a_{uc} value can be explained.¹⁷⁾

However, the alkali dissolution is a serious problem for wide liquid-crystal TV display with long life. To prevent dissolution, elements of Al and Ca add instead of alkali metals, since the chemical bonding energies of Al-O

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(507 kJmol⁻¹) and Ca-O (397 kJmol⁻¹)¹⁸⁾ are larger than those of Na-O (252 kJmol⁻¹) and K-O (167 kJmol⁻¹).¹⁸⁾ Thus, the thin sheet of alkali free glass (60.0 mass% SiO₂, 17.0 mass% Al₂O₃, 8.0 mass% B₂O₃, 8.0 mass% Sr₂O₃, 4.0 mass% CaO, 3.0 mass% MgO) is often utilized for an expensive liquid-crystal TV display with long life. Furthermore, the EB-irradiation with small dose (0.043 MGy) enhances the a_{uc} value of alkali free glass.¹⁹⁾ However, the maximum a_{uc} value improved by EB-irradiation is not high enough to utilize for super-wide thin glass for its display.

In order to improve the maximum a_{uc} value by EB-irradiation, a borosilicate glass (80.6 mass% SiO₂, 11.9 mass% B₂O₃, 4.4 mass% NaO and 3.1 mass% Al₂O₃) is expected, because the bonding energy of boron-oxygen (805 kJmol⁻¹)¹⁸⁾ is larger than that of silicon-oxygen (794 kJmol⁻¹).¹⁸⁾

On the other hand, since the small bonding energy of sodium-oxygen is 252 kJmol⁻¹,¹⁸⁾ the Na addition in the borosilicate glass decreases the T_g value of 833 K and then induces the good productivity. Furthermore, since EB irradiation with small dose easily cuts the ionic bonding between terminated sodium ions and its chained oxygen in silica network structure, the repulsive force probably occurs between the sodium atoms and terminated oxygen atom of silica network. When the intermolecular repulsive force generates the stress relaxation with compressive stress in silica network structure, it is possible that EB irradiation with small dose may easily enhance the a_{uc} value of borosilicate glass. Namely, both strengthening by boron addition and shortening the start dose of EB-irradiation to strengthening by sodium addition can be expected for borosilicate glass.

To confirm that, it is possible to strengthen transparent thin glassy sheets for a super-wide liquid-crystal display, the possible beneficial effects of EB irradiation on the a_{uc} value of borosilicate glass have been investigated.

2. Experimental Procedure

2.1 Sample preparation and impact test

The atomic fraction of positive ions of borosilicate glass samples (Kobayashi Tokushu Glass, Co., Ltd., Japan) was 8.85 at% for B, 81.83 at% for Si, 4.74 at% for Al and 4.58 at% for Na. The sizes of samples measured was 20 × 10 × 1.0 mm. To evaluate the impact-fracture toughness, the Charpy impact values of the glass samples with and without EB irradiation were measured by using a standard impact-fracture-energy measurement system (JIS K 7077-1991). The Charpy impact value is expressed by the following equation:^{15-17,19)}

$$E = WR[(\cos \beta - \cos \alpha) - (\cos \alpha' - \cos \alpha)(\alpha + \beta)/(\alpha - \alpha')] \quad (1)$$

where, E , W , R , β , α and α' are, respectively, the impact fracture energy (kJ), the hammer weight (N), the length (m) of hammer weight point from the rolling center, the start angle before impact, the maximum angle after impact, and the maximum angle of the blank test. The Charpy impact value (kJm⁻²) is given by the following equation:

$$a_{uc} = E/(b \times t) \quad (2)$$

Here, E , b (= 10 mm), and t (= 1.00 ± 0.005 mm) are the impact fracture energy (J), sample width (mm), and span distance (sample thickness, mm). The distance between the supporting points was 11.45 mm.

2.2 Electron-beam irradiation

The borosilicate glass sheets were homogeneously irradiated by using an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co., Ltd., Tokyo).^{15,17,19)} The specimen was homogeneously irradiated with an electron beam through a titanium window attached to a 240-mm-diameter vacuum chamber. A tungsten filament in a vacuum was used to generate the electron beam with an electrical potential of 170 kV and an irradiating current of 2.0 mA. To prevent their oxidation, the samples were kept in a nitrogen atmosphere of 0.1 MPa with a residual concentration of oxygen of less than 400 ppm. The flow rate of the nitrogen gas was 1.5 Ls⁻¹.

The sample, was positioned in an aluminum plate holder (0.15 m × 0.15 m), and transported on a conveyor at a speed of 9.56 m/min. Because the minimum dose of EB irradiation was 43.2 kJg⁻¹ (1.13×10^{13} em⁻² = 43.2 kGy), each burst of irradiation was performed for a short time (0.23 s) at 0.043 MGy to avoid excessive heating of the sample. As a result, the temperature of the sample surface remained below 323 K just after irradiation. Both surfaces of the samples were repeatedly irradiated to increase the total irradiation dose. The interval between the end of one period of irradiation and the start of the next was 30 s. The dosage was proportional to the yield determined from the irradiation current, conveyor speed, and number of irradiations. The yield was calibrated using dose-meters with radio chromic nylon film (FWT-60-00: Far West Technology Inc., Goleta, CA, USA).

The electron number density (em⁻²) was expressed by the following equation in metals.²⁰⁾

$$Ng = DE/Cg \quad (3)$$

Here, Ng (em⁻²) is the irradiation dose, DE (Svs⁻¹) is the dose equivalent, and Cg is the dose equivalent per transferred coefficient of particle flux $\{0.1649 \times 10^{-13} [(Svs^{-1})/(e(m^2s)^{-1})]\}$.²⁰⁾

2.3 Evaluation of dangling bonds

To obtain more precise information on atomic-scale structural changes in the glass, the density of the dangling bonds was measured by means of an ESR spectrometer (JES-FA2000, Nippon Denshi Ltd., Tokyo).^{15,17,19)} The microwave frequency range used in the ESR analysis was the X-band at 9.45 ± 0.05 GHz with a field modulation of 100 kHz. The microwave power was 1 mW. The magnetic field was varied from 318.7 to 328.7 mT. The spin density was calculated by using the Mn²⁺ standard sample. Only ESR spectra are given, not spin densities. Based on the standard calibration material [4-hydroxy-2,2,6,6-tetra-methylpiperidine-1-oxyl (TEMPO, 089-04191, Wako Pure Chemical Industries Ltd., Tokyo)] and Mn²⁺ in the MnO, the density of dangling bonds is estimated by double integration of the intensity of the ESR signal.¹⁵⁾

Fig. 1 Relationships between Charpy impact value and fracture probability at each EB irradiation dose.

3. Results

3.1 Impact value of borosilicate glass before and after EB-irradiation

Evaluating the probability of fracture (P_f) is a convenient method of quantitative analyzing experiment values relating to fracture. P_f is expressed by the following equation, which is a generalized form of the median rank method:²¹⁾

$$P_f = (I - 0.3)/(N_s + 0.4) \quad (4)$$

where n and I are the total number of samples ($n = 33$) and the order of fracture of each sample, respectively. Here, the order of fracture is the aligned number of fractured samples from low to high impact value. When the I values are 1, 12, and 33, the P_f values are 0.020, 0.350, and 0.979, respectively.

Figure 1 plots the relationships between the P_f values and the experimental Charpy impact values (a_{uc}) of borosilicate glass irradiated at each dosage. The a_{uc} values at all P_f values for borosilicate glass irradiated at 0.043–0.22 MGy exceed the corresponding values before irradiation.

Figure 2 presents the experimental impact values (a_{uc}) of the borosilicate glass for various electron-beam (EB) irradiation dosages at each P_f value. EB irradiation from 0.04 to 0.22 MGy probably enhances the a_{uc} value of borosilicate glass from 0.02 to 0.98 of P_f value. The a_{uc} value at a P_f of 0.020 of borosilicate glass irradiated at a dosage of 0.13 MGy is about 1.37 times greater than that before irradiation. Additional EB irradiation at dosages of 0.22 to 0.43 MGy clearly decreases the impact values. The impact values of samples irradiated at 0.43 MGy are slightly higher than those before irradiation. Consequently, EB-irradiation at 0.04 to 0.22 MGy appears to enhance the a_{uc} value at each P_f value of borosilicate glass.

3.2 Dangling-bond formation by EB-irradiation

No marked differences are found in the X-ray diffraction patterns of the borosilicate glasses recorded before and after

Fig. 2 Change in the impact value versus EB irradiation dosages at different fracture probabilities of borosilicate glass, together with a_0 from eq. (6) at $P_f = 0.632$.

Fig. 3 ESR signals of borosilicate and silica glasses before and after EB irradiation.

EB irradiation. On the other hand, EB irradiation produces detectable dangling bonds. To clarify the effects of EB irradiation on the Charpy impact values, ESR signals related to dangling bonds are recorded.

Figure 3 depicts the ESR signals of borosilicate and silica glasses before and after EB irradiation. Although no ESR signals of the untreated sample can be detected, a sharp ESR signal is observed in the irradiated silica glasses, corresponding to dangling bonds of an E-prime center consisting of a Si–O pair.^{22,23)} In silica glass, each silicon atom is generally coordinated to four atoms of oxygen, whereas a silicon atom with a dangling bond is coordinated to three atoms of oxygen: A silicon atom site with a dangling bond in silica glass is defined as an E-prime center. As illustrated in Fig. 3, EB irradiation at 0.22 MGy enhances the intensity of the ESR signal, demonstrating that dangling bonds are formed in the silica glass.^{17,18)} Furthermore, additional irradiation from

0.22 to 0.43 MGy enhances the intensity of the ESR signal. The densities of dangling bonds in silica glass samples irradiated at 0.22 and 0.43 MGy are 2.43×10^{16} and 3.23×10^{16} spinsm $^{-3}$, respectively.

Although a sharp ESR signal, corresponding to dangling bonds of an E-prime center consisting of a Si–O pair,^{17,18)} cannot be observed in the irradiated borosilicate glasses, the irradiated borosilicate glass exhibits many ESR signals at different magnetic field values of the top peak, as indicated in Fig. 3. Since the ionic bonding energy between sodium and oxygen (252 kJmol^{-1})¹⁸⁾ is smaller than covalent bonding energy of silica glass (794 kJmol^{-1})¹⁸⁾ EB irradiation with small dose easily cuts the ionic bonding between terminated sodium ions and its chained oxygen in silica network structure. Namely, apparent dangling bonds constructed with the sodium atoms with high density of outer-shell electrons and terminated oxygen atom of silica network probably exist in the borosilicate glass.

Since the intensity of ESR signals of borosilicate glass is approximately equal to that of silica after 0.22 MGy-irradiation, the density of apparent dangling bonds in borosilicate glass (1.83×10^{16} spinsm $^{-3}$) is approximately equal to that of dangling bonds of silica glass.

Furthermore, additional irradiation (0.43 MGy) to borosilicate glass enhances the intensity of the ESR signal, which is higher than that at 0.22 MGy and is also apparently higher than that of silica. Thus, the density of dangling bonds in borosilicate glass is 1.28×10^{16} spinsm $^{-3}$, which is higher than that (2.21×10^{14} spinsm $^{-3}$) of silica glass at 0.43 MGy of additional irradiation.

4. Discussion

4.1 Effect of EB irradiation on the Weibull coefficient

In order to evaluate the reproducibility (reliability) in comparison with other structural materials, Weibull coefficient (n) is a standard indicator.¹⁹⁾ If the statistical equation is assumed to apply to the measured Charpy impact value (a_{uc}), the probability of fracture (P_f) depends on the risk of rupture (a_{uc}/a_o).²⁴⁾

$$P_f = 1 - \exp[-(a_{uc}/a_o)^n] \quad (5)$$

Here, a_o and n are a_{uc} at $P_f = 0.63$ and Weibull coefficient (n), respectively.

Figure 4 presents Weibull plots of borosilicate glass irradiated at various dosages. The slopes (n) for the Weibull plots are obtained.

Figure 5 depicts changes in the n values plotted against the EB irradiation dosage. The n value from 0.043 MGy to 0.13 MGy is larger than that in untreated samples. High n values for borosilicate glass are obtained by EB irradiation at 0.13 MGy. Thus, EB irradiation from 0.04 to 0.13 MGy apparently enhances the Weibull coefficient (n) of impact value related to the reproducibility (reliability) of borosilicate glass.

4.2 Effects of EB-irradiation on the lowest impact value

Although n value is a standard indicator to evaluate the reproducibility, the Weibull plots at low P_f values apparently deviate from the linear relationship, as shown in Fig. 4. In

Fig. 4 Weibull plots (n) of borosilicate glass irradiated by an electron beam at each dose.

Fig. 5 Changes in Weibull coefficient (n) versus EB irradiation dosages.

order to estimate the impact value at extremely low P_f value, precisely, the lowest impact value (a_s) for safety design in the three parameter Weibull equation is assumed to get the adaptable relationship with the high correlation coefficient (F). The fracture probability (P_f) depends on the risk of rupture ($[a_{uc} - a_s]/a_{III}$).^{25,26)}

$$P_f = 1 - \exp[-([a_{uc} - a_s]/a_{III})^m] \quad (6)$$

In predicting the required impact value (a_{uc}) of the new structural materials, coefficient (m), and constant (a_{III}) are the key parameters. The a_{III} value is the a_{uc} value at a P_f of 0.632, when the term $\ln[-\ln(1 - P_f)]$ is zero. The changes in a_{III} value in relation to the EB irradiation dose are plotted in Fig. 2. The a_{III} values of borosilicate glasses irradiated from 0.04 to 0.43 MGy are higher than those before EB irradiation.

When P_f is equal to zero, the a_{uc} value is defined as the lowest impact value (a_s). Figure 6 plots changes in the

Fig. 6 Changes in correlation coefficient (F) versus the potential a_s value ($^e a_s$). The lowest impact value (a_s) was determined at maximum F .

Fig. 7 Linear relationships between $(a_{uc} - a_s)$ and $\ln[-\ln(1 - P_f)]$ for borosilicate glass irradiated by electron beams at each dosage.

correlation coefficient (F) with respect to the potential a_s value ($^e a_s$) estimated from eq. (6). The a_s value is the $^e a_s$ value at the maximum F value.

Figure 7 illustrates the linear relationships for borosilicate glass irradiated at each dosage. The values of a_{III} and m are determined by the least-squares method. The m value is estimated by the slope of the relationship when the a_s value is first decided.

Figure 8 presents variations in the a_s value of borosilicate glass versus the EB irradiation dose, together with the low experimental a_{uc} value at $P_f = 0.02$. Here, a_s is always lower than the experimental a_{uc} value. The a_s of borosilicate glass irradiated from 0.04 to 0.22 MGy is 1.3 ± 0.1 times higher than that before irradiation.

Therefore, EB irradiation from 0.04 to 0.22 MGy apparently enhances the a_s value of impact value related to reliability of borosilicate glass.

Fig. 8 Change in the impact value against EB irradiation dosages at different fracture probabilities of borosilicate glass.

Fig. 9 Variations of the lowest impact value (a_s) for silica (Ref. 15) and borosilicate glasses versus EB irradiation dose.

4.3 a_s enhancement of borosilicate glass by irradiation with small dose

Based on the covalent bonding energies (805 and 794 kJ mol⁻¹)¹⁸⁾ between oxygen and positive (B and Si) elements, both strengthening the a_s value by boron addition and shortening the start dose to the a_s enhancement can be expected for borosilicate glass. Figure 9 depicts changes in the a_s value for silica and borosilicate glasses versus EB irradiation dose. The a_s value of borosilicate glass is always higher than that of silica glass. Since the bonding energy between boron and oxygen is higher than that of silicon and oxygen, the boron addition probably enhances the a_s value.

On the other hand, the start point of irradiation dose to strengthening the a_s value of borosilicate is shorter than that of silica glass (see Fig. 9). Since the bonding energy

between sodium and oxygen (252 kJmol^{-1})¹⁸⁾ is smaller than that of silica glass (794 kJmol^{-1}),¹⁸⁾ EB irradiation with small dose easily cuts the ionic bonding between terminated sodium ions and its chained oxygen in silica network structure. Thus, the repulsive force probably occurs between the sodium atoms with high density of outer-shell electrons and terminated oxygen atom of silica network. As illustrated in Fig. 3, the complex ESR signals are found in the borosilicate glass initially irradiated at 0.04 MGy. When the repulsive force generates the stress relaxation with compressive stress in silica network structure, it is possible that EB-irradiation with small dose easily enhances the a_{uc} value of borosilicate glass.

4.4 High resistance to irradiation damage of borosilicate glass

Additional EB irradiation at 0.43 MGy remarkably decreases the a_s value of the glasses, because the additional dangling bonds (high density of dangling bonds) act as a crack origins and crack pass in the borosilicate glass. Although the large start point of irradiation dose to decrease the a_s value is 0.08 MGy for silica glass, it is 0.22 MGy for borosilicate glass. Consequently, the strong resistance to irradiation damage of borosilicate glass is qualitatively confirmed.

On the other hand, this influence can be explained by complex ESR signals in Fig. 3. Additional irradiation (0.43 MGy) to borosilicate glass enhances the intensity of the ESR signal, which is remarkably higher than that of silica. The density of dangling bonds in borosilicate glass is higher than that of silica glass after additional irradiation at 0.43 MGy. Based on the covalent bonding energies (805 and 794 kJmol^{-1})¹⁸⁾ between oxygen and positive (B and Si) elements, the dangling bond formation at boron-oxygen is not easier than that at silicon-oxygen. Thus, the ESR signals of borosilicate glass is the dangling bonds of silicon-oxygen pairs, as well as the apparent dangling bonds constructed with free sodium atoms with high density of outer-shell electrons and terminated oxygen atoms of polarized silica network. The strong resistance to irradiation damage of borosilicate glass is explained, when the boron addition probably reinforces the resistivity to irradiation damage of silica network structure.

4.5 Influence of nanostructure change on impact value of borosilicate glass

Annealed borosilicate glass is brittle because of the sharp potential curve of the tight network structure with high atomic density. The sharp potential curve probably exhibits a strong inter-atomic force of chemical bonding at the minimum value of the curve of annealed borosilicate glass.

EB irradiation provides the 796 , 805 , 252 , 507 kJmol^{-1} (here, based on the atomic mass (19.56 gmol^{-1}) of borosilicate glass. One kJmol^{-1} irradiation energy corresponds to $5.11 \times 10^{-2} \text{ MGy}$ ($= 51.1 \text{ Jg}^{-1}$)-irradiation dose.) of energy necessary to break chemical bonds between Si-O, B-O, Na-O, and Al-O pairs.¹⁸⁾

Based on the height enhancement of electron spin resonance (ESR) spectra, EB irradiation formed apparent and real dangling bonds in a silica glass network structure.

If EB irradiation results in the formation of apparent dangling bonds from Na-O pairs (see Fig. 3), this should result in a partial relaxation of residual molecular strains and compressive stress in the silica glass network structure.

Since the outer-shell electron at terminated atoms of the relaxation sites (dangling bonds) between terminated oxygen and positive atoms exhibit the repulsive force dangling bonds act as atomic scale cushions against applied stress. Generating both compressive stress and relaxation of residual stress in front of crack tip prevents to the crack generation and propagation. Thus, EB-irradiation enhances both a_{uc} and a_s values of the borosilicate glass.

When the interatomic distances of the bonded Si-O pairs are optimal in terms of the interatomic potential curve, relaxation increases the bonding energy of the network structure, possibly allowing an enhancement of compressive stress in its surface. Therefore, we conclude that both enhancement of the compressive stress in the surface of borosilicate glass and relaxation of the silica network contribute to increasing the impact value of the borosilicate glass (Figs. 2 and 8). Namely, to improve the a_{uc} value, EB-irradiation from 0.04 to 0.22 MGy probably introduces both compressive zone and relaxation sites at mostly apparent (Na-O) dangling bonds, which density is $1.83 \times 10^{16} \text{ spinsm}^{-3}$ at 0.22 MGy (see Fig. 3).

On the other hand, an additional (excessive) EB irradiation dose of more than 0.43 MGy (kJg^{-1}) apparently decreases the impact value (Figs. 2 and 8). Because irradiation mainly breaks bonds between Si-O pairs, additional irradiation from 0.22 to 0.43 MGy increases the density of real dangling bonds from 1.83×10^{16} to $3.76 \times 10^{16} \text{ spinsm}^{-3}$ (see Fig. 3) in the glass network structure. The high density of dangling bonds probably results in linking of cracks and acceleration of crack propagation; this may explain the deterioration in the a_{uc} values of samples irradiated from 0.22 to 0.43 MGy.

Therefore, the optimum density of apparent dangling bonds with the high impact value induced by 0.22 MGy-EB irradiation is $1.83 \times 10^{16} \text{ spinsm}^{-3}$.

4.6 Penetration depth of electron beam in borosilicate glass

Christenhusz and Reimer evaluated the depth of EB irradiation penetration of less than 200 kV electrical potential by measuring the Joule heat generated in copper films.²⁷⁾ Based on density (ρ : kg/m^3) and potential drop (ΔV : kV), penetration depth (D_{th} : m) was given by

$$D_{th} = 66.7 \times \Delta V^{5/3} / \rho. \quad (7)$$

The potential at the surface sample (V_s) was expressed by the following equation.²⁷⁾

$$V_s = V_o - \Delta V \quad (8)$$

Based on the assumption of Christenhusz and Reimer, the potential drop (ΔV) was caused by the irradiation energy loss of the electron beam from the initial potential at the filament surface of the electron beam gun (V_o) to the potential at the surface sample (V_s). The potential drop (ΔV) was expressed by the following equation.²⁷⁾

$$\Delta V = \tau \cdot V_o / S \quad (9)$$

Here, τ is thickness, and S is the mass thickness of the Ti sheet and nitrogen gas.

The electrical potential (128 keV) was estimated from the initial electrical potential (170 keV), the thickness [1.0×10^{-5} m (10 μ m)] of the titanium window [$\rho = 4540$ kg/m³ (4.54 g/cm³)], and the distance (30 mm) in the nitrogen gas atmosphere ($\rho = 1.13$ kg/m³) between the surface of the sample and the window. Since the electrical potential was 128 keV, eq. (7) estimated by Christenhusz and Reimer predicts that the penetration depth (D_{th} : m) of borosilicate glass, which density (ρ) was 2230 kg/m³, should be 99.8 μ m.

The penetration depth (Libby assumption²⁸) of EB irradiation related to mass thickness (S : mg/cm²) and irradiation voltage (V_s /kV) is expressed by

$$S = 1/150 \times \Delta V^{5/3}. \quad (10)$$

The estimated mass thickness was 34.8 mg/cm² when the initial irradiation voltage was 170 keV. Since the mass thickness of the Ti foil (1.78 mg/cm²) and N₂ gas (0.15 mg/cm²) reduced the penetration depth of EB irradiation, the mass thickness (S) of the glass sample was 32.9 mg/cm². In addition, the electrical potential of the sample surface was expressed by

$$\Delta V = (150 \times S)^{3/5}. \quad (11)$$

Based on the Libby assumption,²⁸ the penetration depth of borosilicate glass was 145.1 μ m.

Since the mean value of penetration (irradiated) depth at both broad surface sides of borosilicate glass is 122 ± 23 μ m, the irradiated thickness from surface is $24 \pm 5\%$ of the sample thickness (1.0 mm).

5. Conclusion

The effect of homogeneous electron-beam (EB) irradiation with low voltage on the Charpy impact value (a_{uc}) of borosilicate glass was studied.

- (1) EB irradiation of less than 0.216 MGy enhanced the a_{uc} value.
- (2) EB irradiation of less than 0.216 MGy enhanced the Weibull coefficient (n).
- (3) The lowest impact value (a_s), estimated by the modified Weibull equation with three parameter, was defined to be the a_{uc} value at zero of fracture probability (P_f). EB irradiation from 0.043 to 0.216 MGy apparently enhanced the a_s value of borosilicate glass. The a_s of borosilicate glass irradiated from 0.043 to 0.216 MGy was 1.3 ± 0.1 times higher than that before irradiation.
- (4) The a_s value of borosilicate glass was higher than the a_s value of silica glass.
- (5) The effective EB irradiation dose for generating the high a_s value of borosilicate glass was smaller than that of silica glass.
- (6) Based on the increasing height of the electron-spin resonance (ESR) spectra, the initial EB-irradiation with small dose formed the apparent dangling bonds con-

structed with the sodium atoms with high density of outer-shell electrons and terminated oxygen atom of silica net work in borosilicate glass. If both partial relaxation of the deformation strain and compressive stress in front of crack tip mainly occurred, the initial enhancement of a_{uc} value by the initial EB-irradiation could be explained.

- (7) Furthermore, the strong resistance to irradiation damage of borosilicate glass was qualitatively confirmed. Although the large start point of irradiation dose to decrease the a_s value was 0.08 MGy for silica glass, it was 0.22 MGy for borosilicate glass. Consequently, the boron addition enhanced the resistivity to irradiation damage.

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REFERENCES

- 1) K. Maeda: J. Jpn. Soc. Precision Eng. **70** (2004) 466–469.
- 2) S. Miwa: New Glass. **18** (2003) 7–11.
- 3) K. Niihara: Ceramics Jpn. **21** (1986) 581–589.
- 4) M. Sakai: Ceramics Jpn. **27** (1992) 281–287.
- 5) A. A. Griffith: Phil. Trans. Roy. Soc. A **221** (1920) 163–198.
- 6) S. Inoue, T. Uchiyama and K. Niihara: Ceramics Jpn. **21** (1986) 621–629.
- 7) T. Sato and M. Shimada: Ceramics Jpn. **21** (1986) 613–619.
- 8) A. L. Zijlstra and A. J. Burggraaf: J. Non-Cryst. Solids **1** (1968) 49–68.
- 9) Y. Nishi, H. Harano, T. Fukunaga and K. Suzuki: Phys. Rev. B **37** (1988) 2855–2860.
- 10) Y. Nishi and H. Harano: J. Appl. Phys. **63** (1988) 1141–1143.
- 11) Y. Nishi, T. Kai and N. Inoue: J. Mater. Sci. Lett. **5** (1986) 1135–1136.
- 12) N. Yamaguchi, K. Oguri, A. Tonegawa and Y. Nishi: J. Japan Inst. Metals **68** (2004) 198–201.
- 13) Y. Nishi, A. Kadowaki and T. Shinoda: Mater. Trans. **45** (2004) 3314–3317.
- 14) K. Iwata and Y. Nishi: Mater. Trans. **50** (2009) in press.
- 15) K. Iwata and Y. Nishi: Mater. Trans. **49** (2008) 2058–2062.
- 16) Y. Taira, K. Iwata and Y. Nishi: J. Japan Inst. Metals **73** (2009) 52–57.
- 17) Y. Nishi and K. Iwata: Mater. Trans. **46** (2005) 2241–2245.
- 18) J. B. Pedley and E. M. Marshall: J. Phys. Chem. Ref. Data **12** (1983) 967–1031.
- 19) Y. Nishi and K. Iwata: Mater. Trans. **47** (2006) 1810–1814.
- 20) N. Tsoufianidis: Measurement and Detection of Radiation, (Houshasen Keisoku no riron to enshu), (Gendai Kougaku sha, 1983) pp. 543–552. (in Japanese)
- 21) T. Nishida and E. Yasuda: Evaluation of dynamic properties of ceramics, (Ceramics no rikigaku tokusei hyouka), (Nikkan Kogyo Shimbun Sha, Tokyo, 1986) pp. 50–51. (in Japanese)
- 22) D. L. Griscom and E. J. Friebele: Radiat. Eff. **65** (1982) 303–312.
- 23) D. L. Griscom: The Centennial Memorial Issue of the Ceramic Soc. Jpn. **99** (1991) 923–942.
- 24) W. Weibull: *Ingeniörs vetenskaps akademien*, nr. 151 (Generalstabens litografiska anstalts förlag, Stockholm, 1939) pp. 12–14.
- 25) Y. Nishi, H. Kobayashi and M. Salvia: Mater. Trans. **48** (2007) 1924–1927.
- 26) W. Weibull: *Ingeniörs vetenskaps akademien*, nr. 153 (Generalstabens litografiska anstalts förlag, Stockholm, 1939) pp. 16–22.
- 27) R. Christenhusz and L. Reimer: Z. Angew. Phys. **23** (1967) 396–404.
- 28) W. F. Libby: Anal. Chem. **19** (1947) 2–6.