Effect of Electron-Beam Irradiation on Impact Value of Silica Glass

Keisuke Iwata* and Yoshitake Nishi

Department of Science and Technology, Graduate School of Science and Engineering, Tokai University, Hiratsuka 259-1292, Japan

The effect of electron-beam (EB) irradiation on the impact value of silica glass was studied by means of a standard Charpy impact test. When it performed in short bursts to maintain a low temperature, EB irradiation at a dosage of less than 0.216 MGy increased the impact value of the glass. Because the EB irradiation generated dangling bonds in the silica glass, partial relaxation of residual strain probably occurred around these dangling bonds in the network structure. If this relaxation resulted in optimization of the interatomic distance of the silicon–oxygen pairs to minimize the potential energy, it would increase the bonding energy of the network structure. The increased impact value was therefore mainly due to an increase in the bonding energy for the silicon–oxygen atomic pairs in the network structure, as well as to the relaxation of the network structure.

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1. Introduction

Strengthening of transparent thin sheet glass is an important technique in the manufacture of large-area liquid-crystal displays for televisions. Transparent silica glass consists of silicon and oxygen, and does not contain any alkali metals that are soluble in water or organic solvents. Thus, silica glass can be used as an electronic insulator and biological knife. However, the weak fracture toughness of silica glass is a serious problem when it is used in the form of sheets or fine needles.

Low-energy electron-beam (EB) irradiation is widely used as an industrial surface treatment, for example, in accelerating crosslinking and polymerization of polymers to improve their wettability and to increase hardness and luster. EB irradiation has been shown to increase hardness by eliminating dangling bonds in the case of carbon fiber, carbon-deposited carbon fiber composite materials, and carbon fiber-reinforced polymers.1–5 EB irradiation techniques are also being developed to assist in the production of ceramic products, such as dentists’ mirrors and sapphire lenses and diamond windows for endoscopes, that are free from misting and can be rapidly sterilized.6–8) Thus, EB irradiation is a useful tool for generating a range of attractive multifunctional properties.

Another effect of EB irradiation is the homogeneous activation of surface atoms and the breaking of chemical bonds between Si–O pairs to form dangling bonds.9,10) Silica glass with dangling bonds is highly resistant to fracture under a static strain loads.10) EB irradiation is a useful tool for reducing the brittleness of glass, because of the high rate at which it forms dangling bonds. For this reason, the effects of EB irradiation on the static micromechanical properties of silica glass have been studied.11) EB irradiation increases the microfracture resistance and enhances the rigidity of silica glass, as shown by measurements of the micro-Vickers hardness. When EB irradiation generates dangling bonds at Si–O atomic pairs in the silica network, a partial relaxation of residual strains in the network structure occurs. The increase in rigidity is mainly due to an increase in the bonding energy of Si–O atomic pairs in the network structure.11)

The Charpy impact value of a material is an important property in terms of practical applications. When EB irradiation generates dangling bonds at Si–O pairs and thus relaxes the network structure of silica glass,11) it also enhances its impact value. To confirm that it is possible to strengthen transparent thin sheets of glass, we have investigated the possible beneficial effects of EB irradiation on the impact value of silica glass. Furthermore, to clarify our results, we have confirmed the existence of dangling bonds by means of electron spin resonance (ESR) spectroscopy.

2. Experimental Procedure

2.1 Electron beam irradiation

The silica glass sheets (Matsuda Silica Glass, Co. Ltd., Japan) were homogeneously irradiated by using an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co. Ltd., Tokyo).1–9,11) 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 under 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 L s⁻¹.

Christenhusz and Reimer12) evaluated the penetration depth of EB irradiation of less than 200 kV electrical potential by measuring the Joule heat generated in copper films.12) Based on the density (ρ: kg/m³) and electrical potential (V: kV), the penetration depth (Dₜₘ: m) is given by the following equation:

\[ Dₜₘ = 66.7 \sqrt[3]{V/\rho}. \]  

(1)

The electrical potential (128 kV) was estimated from the electrical potential (170 kV), the thickness [10.0 × 10⁻⁵ mm (10 μm)] of the titanium window [ρ = 4540 kg/m³ (4.54 g/cm³)], and the distance (30 mm) in the nitrogen gas
atmosphere \((\rho = 1.13 \text{ kg/m}^3)\) between the surface of the sample and the window.

On the basis that the electrical potential was 128 keV, equation (1) predicts that the penetration depth \((D_{\text{pen}} \text{ m})\) should be 100 \(\mu\text{m}\) in the case of the silica glass \((\rho = 2220 \text{ kg/m}^3)\).

The sample, positioned in an aluminum plate holder \((0.15 \times 0.15 \text{ m})\), was transported on a conveyor at a speed of 9.56 m/min. Because the minimum dose of EB irradiation was 0.0432 MJ/kg (0.0432 MGY), each burst of irradiation was performed for a short time \((0.23 \text{ s})\) at 0.0432 MJ/kg to avoid excessive heating of the sample: 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 value determined from the irradiation current, the conveyor speed, and number of irradiations. The yield value was calibrated by means of FWT nylon dosimeters (Far West Technology, Inc., Goleta, CA, USA).

### 2.2 Samples preparation and impact test

The silica glass samples measured 20 \(\times\) 10 \(\times\) 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 was expressed by the following equation:

\[
E = WgR[\cos \beta - \cos \alpha - (\cos \alpha' - \cos \alpha)(\alpha + \beta)/(\alpha - \alpha')]
\]

where, \(E\), \(W\), \(g\), \(R\), \(\beta\), \(\alpha\) and \(\alpha'\) are, respectively, the impact fracture energy (kJ), the hammer mass (kg), acceleration of gravity (\(\text{m s}^{-2}\)), 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 \((\text{kJ m}^{-2})\) was given by the following equation:

\[
a_{\text{uc}} = E/(b \times t).
\]

Here, \(E\) (= 10 mm), and \(t\) (= 1.00 \(\pm\) 0.005 mm) were the impact fracture energy \((I)\), sample width (mm), and span distance (sample thickness, mm), respectively. The distance between the supporting points was 11.45 mm.

### 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-FAX2000, Nippon Densi Ltd., Tokyo). The microwave frequency range used in the ESR analysis was the X-band at 9.45 \(\pm\) 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 a Mn\(^{2+}\) standard sample. Only ESR spectra, instead of spin densities, were given. Based on the standard calibration material \([4\text{-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL, 089-04191, Wako Pure Chemical Industries Ltd., Tokyo]}\] and Mn\(^{2+}\) in the MnO, the density of dangling bonds was estimated by double integration of the intensity of ESR signal.

### 3. Results

#### 3.1 Impact value of silica glass before and after EB irradiation

Evaluation of the probability of fracture \((P_f)\) is a convenient method for quantitative analysis of experimental values relating to fracture. It is expressed by the following equation, which is a generalized form of the median rank method: \(^{(13)}\)

\[
P_f = (I - 0.3)/(n + 0.4)
\]

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 shows the relationships between the \(P_f\) values and the experimental Charpy impact values \((a_{\text{uc}})\) for silica glass irradiated at each dosage. The \(a_{\text{uc}}\) values at both a high \(P_f\) value of more than 0.949 and a low \(P_f\) value of less than 0.051 for silica glass irradiated at 0.216 MJ/kg (MGy) are apparently larger than the corresponding values before irradiation. In other words, irradiation at 0.216 MJ/kg appears to enhance the impact value \((a_{\text{uc}})\) at the higher and lower \(P_f\) values of silica glass.

Figure 2 shows the experimental impact values \((a_{\text{uc}})\) of the silica glass for various electron beam (EB) irradiation dosages at each \(P_f\) value. The \(a_{\text{uc}}\) value at \(P_f\) value of 0.020 and 0.979 of silica glass irradiated at a dosage of 0.216 MJ/kg (MGy) is about 1.4 times larger than that before irradiation. The impact values of samples irradiated at 0.0432 and 0.432 MJ/kg (MGy) are approximately equal to those before irradiation. Excess EB irradiation at dosages of 0.216 to 0.432 MJ/kg (MGy) clearly decreases the impact value of silica glass.

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**Fig. 1** Relationships between Charpy impact value and fracture probability at each EB irradiation dose.
values. Thus, EB irradiation at 0.216 MJ/kg (MGy) probably enhances the impact value (a_{uc}) of silica glass.

3.2 Dangling bond formation

No marked differences are found in the X-ray diffraction patterns of the silica glass recorded before and after EB irradiation. On the other hand, EB irradiation produces detectable dangling bonds.\(^{11}\) To elucidate the effects of EB irradiation on the Charpy impact values, ESR signals related to dangling bonds are recorded.

Figure 3 shows the ESR signals of silica glasses before and after EB irradiation. Although no ESR signals can be detected from the untreated sample, a sharp ESR signal is observed in the irradiated silica glass, corresponding to dangling bonds of an E-prime center consisting of a Si–O pair.\(^{9,10}\) 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 is defined as an E-prime center.

As shown in Fig. 3, EB irradiation at 0–0.216 MJ/kg (MGy) enhances the intensity of the ESR signal, showing that dangling bonds are formed in the silica glass.\(^{14}\) Furthermore, additional irradiation from 0.216 to 0.432 MJ/kg (MGy) enhances the intensity of the ESR signal. The densities of dangling bonds in silica glass samples irradiated at 0.216 and 0.432 MJ/kg (MGy) are \(2.43 \times 10^{16}\) and \(3.23 \times 10^{16}\) spins/m\(^3\), respectively.

4. Discussion

4.1 Effects of EB-irradiation on the lowest impact value

If the statistical equation is assumed to be applicable to the measured Charpy impact value (a_{uc}), the probability of fracture (P_f) depends on the risk of rupture (\([a_{uc} - a_i]/a_o\))\(^{15,16}\)

\[
P_f = 1 - \exp\left[-\left([a_{uc} - a_i]/a_o\right)^m\right] \quad (5)
\]

In predicting the required impact value of the new structural materials, the lowest impact value (a_i), coefficient (m), and constant (a_o) are the key parameters: a_i is the a_{uc} value at a P_f of 0.632 when the term \(\ln[-\ln(1 - P_f)]\) is zero. Figure 2 shows that the a_o value changes in relation to the EB irradiation dose. The a_o values of EB-irradiated silica glass are slightly less than the value before EB irradiation.

When the P_f value is equal to zero, the a_{uc} value is defined as the lowest impact value (a_i). Figure 4 shows changes in the correlation coefficient (F) with respect to the potential a_i value (\('a_i'\). The lowest value of the impact value (a_i), estimated from eq. (5), is determined. When the correlation coefficient F is maximal, the lowest impact value (a_i) can be obtained, as shown in Fig. 4.

Figure 5 shows variations in the lowest impact value (a_i) against the EB irradiation dose, together with the low experimental a_{uc} value at P_f = 0.020 for each sample. Here, the value of a_i is always lower than the experimental a_{uc} value. The a_i of silica glass irradiated at 0.086 MJ/kg (MGy) is 2.7 times that before irradiation. High a_i values, which are related to a higher impact strength for silica glass, appear to be obtained by EB irradiation doses between 0.086 and 0.216 MJ/kg (MGy).

Figure 6 shows linear relationships for silica glass irradiated by EB at each dosage. The values of a_o, a_{uc}, and m were determined by the least-squares method. The slope (m) of the relationship is obtained when the lowest estimated impact value (a_i) is first reached. Thus, the a_i values rather than the m contribute markedly to the reliability. Whereas EB irradiation at 0.0432 MJ/kg (MGy) slightly increases the m value (Fig. 7), EB irradiation from 0.086 to 0.216 MJ/kg
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4.2 Effect of EB irradiation on the Weibull coefficient

Although the $a_s$ value is the most important factor in the evaluations of reliability related to the fracture of materials, the Weibull coefficient ($n$) is a standard and customary measurement that can be used in comparisons with other structural materials. If the $a_s$ value in eq. (5) becomes zero, the $m$ value is defined as the Weibull coefficient ($n$).\(^{17}\) The fracture probability ($P_f$), which depends on the risk of rupture ($a_{uc}/a_s$), is expressed by the following equation:\(^{17}\)

$$P_f = \exp[-(a_{uc}/a_s)^n]. \quad (6)$$

Figure 7 shows Weibull plots of silica glass irradiated by electron beam at each dose. Figure 8 shows changes in the $n$ and $n_i$ values plotted against the EB irradiation dosage. With 0.0432 MJ/kg (MGy) of EB irradiation, the $n$ and $n_i$ values, as well as the $m$ value, are enhanced. High $n$ and $n_i$ values for silica glass were obtained by EB irradiation at 0.0432 to 0.0864 MJ/kg (MGy). Thus, EB irradiation from 0.0432 to 0.0864 MJ/kg (MGy) apparently enhances the reliability related to the impact value of silica glass.
4.3 Formation of dangling bonds in silica glass

Because the annealed structure of silica glass is a tightly bonded network, the glass is brittle. EB irradiation provides the 794 kJ/mol of energy that is necessary to break chemical bonds between Si–O pairs. 

If EB irradiation results in the formation of dangling bonds from Si–O pairs (Fig. 3), this should result in a partial relaxation of residual molecular strains in the silica glass network structure; as a result, EB irradiation enhances the impact values of silica glass.

ESR spectra of irradiated silica glass (Fig. 3) show a sharp signal corresponding to dangling bonds of E-prime centers consisting of Si–O pairs, proving that EB irradiation does, in fact, generate dangling bonds from Si–O pairs in the glass network structure. When the EB irradiation dose is less than 0.216 MGy, it generates dangling bonds from Si–O atomic pairs in the surface layer of the glass, resulting in partial relaxation of strains in the glassy network of Si–O pairs near the dangling bonds. 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 its rigidity. Therefore, we conclude that both the enhancement of the rigidity and the relaxation of the Si–O network contribute to an increase in the impact value of the glass (Figs. 2 and 5).

On the other hand, an excessive EB irradiation dose of more than 0.4 MJ/kg causes an apparent decreases in the impact value (Figs. 2 and 5). Because irradiation breaks bonds between Si–O pairs, excess irradiation increases the density of dangling bonds (Fig. 3) in the Si–O network structure. The high density of dangling bonds may result in linking of cracks and acceleration of crack growth; this may explain the deterioration in the impact values of samples irradiated at 0.22–0.43 MJ/kg (MGy). Because the densities of dangling bonds in silica glass samples irradiated at 0.216 and 0.432 MJ/kg (MGy) are $2.43 \times 10^{16}$ and $3.23 \times 10^{16}$ spins/m$^2$, respectively, the critical density for dangling bonds for maximal impact strengthening by EB irradiation is more than $2.43 \times 10^{16}$ spins/m$^2$.

5. Conclusion

EB irradiation up to a certain level increases the impact value of silica glass. ESR observations showed that this enhancement can be explained in terms of relaxation of stress as a result of an increase in the density of dangling bonds. The number of dangling bonds can be evaluated from the ESR signals associated with Si–O pairs.

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