Electron Beam Processed Silica Glass with Multi-Property

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This paper mainly describes that surface density changes in dangling bond and charging and impurity atom adsorption caused the multi-properties of silica glass irradiated by electron beam (EB). The irradiated silica glass with high wettability, misting free, sterilization, and high strength has been successfully obtained. Dangling bond formation and charging generally attract the poling water molecules. Thus, EB irradiation decreased the water contact angle of silica glass. Scattering of light reflection of fine sessile drops of water usually causes the misting. When the water wettability is caused by EB irradiation, the water thin film is formed. Thus, the electron beam irradiation prevents the misting. On the other hand, the strengthening, generated by EB irradiation, was mainly induced by the stress relaxation induced by dangling bond in network structure of silica glass irradiated.

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1. Introduction

In order to obtain multi-properties, such as misting free, sterilization, wettability and high strength, the surface physical properties should be controlled by high power treatments with atom activation. EB irradiation is an excellent tool to control surface physical properties related to dangling bond, charging, and absorption impurity atoms.

On the other hand, it is a serious problem that the lens of the endoscope used in many medical operations is often misted. In order to reduce the medical doctor’s fatigue and to improve diagnostic accuracy, a procedure to ensure a blur-free endoscope lens is developed. One of the proposed countermeasures to the present difficulties caused by misting borrows from the ability of the human eye to recover from blurring. The eye’s tears are a key factor in achieving clear vision. Thus, we have tried to enhance wettability via commercially achievable, safe, and convenient irradiations. Plasma irradiation increases wettability. However, the effect may not be reproducible, since plasma irradiation generally retains residual impurities in samples. In contrast, sheet electron beam irradiation increases wettability, while eliminating residual impurity atoms. The mist free dentist’s mirror, sapphire lens, and diamond window have been made possible by a sheet electron beam irradiation [SEBI] treatment with sterilization, in which the effective exposure time varies from a few minutes to a few hours. Namely, EB irradiation has been applicable to misting free treatment with sterilization.

In addition, EB irradiation is also useful to enhance surface strength of glassy ceramics because of network structure relaxation related to dangling bond. Brittleness was often found in as quenched glasses. Heating is a useful tool often employed to homogenize residual stress in liquid-quenched metallic glasses. However, heating is often required at high temperature and long heating time. Furthermore, it is difficult to improve fracture toughness, that is, to improve both ductility and also fracture stress simultaneously after solidification. In order to homogenize and improve the mechanical properties of liquid-quenched metallic glass after solidification, a solid-randomization process was developed using shot peening. However it is not suitable for brittle ceramics. Although glassy ceramics are widely used because of their high heat resistance combined with good optical transparency, brittleness is a serious problem. From an engineering point of view, homogeneous reinforcement of silica glass is also required to produce precisely formed articles after casting. To control smart properties such as sterilization, wettability, misting free and strength for silica glass; electron beam (EB) irradiation is presently being developed. EB irradiation is also a homogenizing process. Namely, EB irradiation homogeneously activates surface atoms, breaks chemical bonds and migrates mobile atoms in a glass surface layer up to 0.1 mm in depth (see eq. 2 in Methods). EB irradiation provides the 799.6 kJ/mol of energy necessary to break the chemical bond between silicon and oxygen (Si-O) atoms pair. It may relax the loading and residual stress in the tightly bonded network structure of silica glass, possibly allowing us to control the fracture toughness.

The surface property changes in dangling bond density and charging should simultaneously cause the multi-properties, such as high wettability, high resistance to misting, sterilization and high strength of silica glass irradiated by electron beam. Therefore, we have undertaken the present study to investigate the possible beneficial effects of electron beam irradiation on the multi-properties of the surface layer in silica glass.

2. Experimental

The silica glassy samples (99.97%SiO$_2$; Asahi Glass Ltd., Tokyo) were 30.05 mm × 30.05 mm squares sheets with a thickness of 3 mm. The sheets were homogeneously irradiated using an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co. Ltd., Tokyo). The specimen was irradiated by the electron beam through a titanium thin film window attached to the vacuum chamber (240 mm in diameter). A tungsten filament in the vacuum chamber generated the
electron beam using an acceleration potential of 170 kV and an irradiating current of 4.0 mA. In order to prevent oxidation, samples were kept under the protection of one atmosphere of nitrogen gas having a residual concentration of oxygen below 400 ppm. Each dose of EB irradiation was only applied for a short time (0.23 s) to avoid excessive heating of the sample. The temperature of the surface of the sample was below 323 K just after irradiation. The sample was transported on a conveyor at a speed of 9.56 m/min. The dosage was proportional to the yield value determined from the irradiation current \( I, mA \), the conveyor speed \( S, m/min \), and number of irradiations \( N \) according to the following equation:

\[
\text{Dose}(\text{MGy}) = 0.216(I/S)N
\]  

(1)

Irradiation dose was corrected by RCD nylon radiometer film (Far West Technology, Inc., CA, USA). The distance between sample and window was 35 mm. The average irradiation depth \( D_{h} \), calculated by sample density \( \rho, kg/m^3 \) and irradiation potential \( V, kV \), was expressed by the following equation:

\[
D_{h} \cdot \rho = 66.7 \cdot V^{5/3}
\]  

(2)

Here the measured density was 2220 kg/m^3 for the silica glass. Thus, the EB-irradiation depth should be 0.1 mm for this material. The energy of the incident electrons was reduced from 170 to 128 keV due to the nitrogen atmosphere and the titanium window of 13 \( \mu m \) in thickness.

To obtain more precise information on structural changes in the glass at the atomic scale, the density of dangling bonds in a sample was obtained using an electron spin resonance spectrometer (ESR, JES-FA100, JEOL Ltd., Tokyo). The microwave frequency range used in the ESR analysis was the X-band of 9.45 ± 0.05 GHz, with a field modulation of 100 kHz. The spin density was calculated using a Mn\(^{2+}\) standard sample. ESR signals attributable to dangling bonds were observed. The charging was measured by using Faraday cup and electrometer.

To measure the rate of mist removal, droplets were blown onto the surface at an approximate rate of \( 6 \times 10^{-4} \) m\(^2\)/s at 310 K under atmospheric pressure. The distribution of the radii of the fine drops on the diamond surface immediately after completion of the blowing was determined by means of a microscope and a videotape recorder. The time to clear vision \( \tau_c \) was measured using a videotape recorder. The starting point for measuring mist removal was considered to be just after the completion of blowing for 3 s under saturated vapor pressure. The minimum detectable time to clear vision was 0.2 s.

3. Results and Discussion

3.1 Electron beam processed physical properties

Based on the X-ray diffraction patterns of the silica glass before and after EB treatment, remarkable structure changes could not be observed. On the other hand, it was possible to detect dangling bonds generated by the EB irradiation, resulting in EB-reinforcement. ESR signals were observed for silica glasses irradiated by electron beam.\(^{14}\) A sharp ESR signal was observed in irradiated pure silica glass corresponding to dangling bonds of an E-prime center,\(^{15}\) with a chemical bonding energy of 627 kJ/mol per Si-O pair.\(^{12}\) The EB irradiation enhanced density of dangling bonds, as shown in Fig. 1. Since the dangling bond strongly attracts poling molecules, the electron beam irradiation probably affects the wettability. Furthermore, high ductility is also expected. In doing so, it should relax the loading stress in the tightly bonded network structure of silica glass, probably allowing us to control the fracture toughness.

Remarkable charging was found on silica glass surface irradiated by electron beam, as shown in Fig. 2. The slight EB irradiation tremendously charged. If the electron charging strongly affected one of multi-properties, the effect of slight irradiation on the property should be large. If water molecules show poling, the water contact angle should be small on surface of irradiated silica glass.

3.2 Wettability

Dangling bond formation\(^{14,16}\) and charging\(^{3}\) caused adsorption\(^{17}\) of poled molecules. Since water molecules show poling, the water contact angle should be small on surface of silica glass irradiated by electron beam.
The EB irradiation decreased the contact angle of water sessile drop on apatite ceramics applied for artificial bone.\textsuperscript{5} The high wettability with sterilization was lower the activation energy of the reaction to form artificial bone, resulting in the short cure period. The Ar ion beam irradiation enhanced the wettability of silica glass.\textsuperscript{5} The EB irradiation should decrease the contact angle of water sessile drop on silica glass. Fig. 3(a) shows relationship between EB irradiation dose and water-contact angle. The EB irradiation enhanced the wettability of silicon wafer.\textsuperscript{15} Based on results of effective dose of electron beam, dangling bond formation mainly caused the EB effects, although effects of charging and atom adsorption were not so small.

3.3 Misting

The misting is serious problems especially in the field of medical engineering. Scattering of light reflection of fine sessile drops of water usually causes the misting. When the water wettability is caused by EB irradiation, the water thin film is formed. Thus, the effects of electron beam irradiation should prevent the misting. The EB treatment of misting free for ceramics was successively developed. The dentist mirror,\textsuperscript{11} endoscope’s sapphire lens,\textsuperscript{21} diamond,\textsuperscript{6} Quartz,\textsuperscript{6} silica glass,\textsuperscript{16} ITO\textsuperscript{7} and TiO\textsubscript{2}\textsuperscript{18,19} were performed by EB irradiation. Fig. 3(b) shows change in time to clear vision against EB irradiation dose of silica glass. The EB irradiation also decreased the time to clear vision of silica glass, as predicted by water wettability (see Fig. 3(a)).

3.4 Strengthening

The EB treatment strengthened inorganic materials, such as hydroxyapatite ceramics applied for soda glass\textsuperscript{20} and glass fiber.\textsuperscript{21} Furthermore, to evaluate the micro-fracture toughness related to the critical energy release rate (\(G_c\)),\textsuperscript{22} the experimental values of the critical indentation diameter (\(d_i\)) and the critical fracture load (\(P_f\)) was obtained. These values were measured using a micro-Vickers’ indentation tester.\textsuperscript{22} The relationship between the load (\(P\)) and the diagonal distance (\(d\)) of the indentation was obtained. The maximum values (\(d_i^{\text{max}}\) and \(P_f^{\text{max}}\)) of \(d\) and \(P\) were determined from indentations that were free of cracks. On the other hand, the minimum values of \(d\) and \(P\) (\(d_i^{\text{min}}\) and \(P_f^{\text{min}}\)) were determined from indentations that were observed to be cracked. The critical indentation diameter (\(d_i\)) on fracture and the critical fracture load (\(P_f\)) were expressed by the following equations:\textsuperscript{22}

\[
d_i = \frac{(d_i^{\text{min}} + d_i^{\text{max}})}{2} \quad (3)
\]

\[
P_f = \frac{(P_f^{\text{min}} + P_f^{\text{max}})}{2} \quad (4)
\]

EB irradiation also enhanced the fracture stress and fracture strain as represented by \(P_f\) and \(d_i\). Figs. 3(c) and (d) show the changes in fracture load \(P_f\) and the fracture strain \(d_i\) of silica glass as a function of EB irradiation dose. EB irradiation doses below \(0.864\) MGy enhanced these properties as hoped. Annealed glass generally shows network tight structure. Free volume formation relaxed the residual stress, the EB irradiation should enhanced the ductility and then enlarged the fracture toughness. Namely, the strengthening by the EB irradiation was mainly induced by the stress relaxation generated by dangling bond in network structure of silica glass.

3.5 Sterilization

The sterilization was also observed in dentist mirror\textsuperscript{7} and endoscope’s lens. The colonies of bacillus were observed on the ceramics aged after one weak. The electron beam irradiation sterilized the ceramics. Since the EB irradiation broke the weak bonding pairs in proteins of bacillus, the EB induced sterilization should be also effective for silica glass.

4. Conclusion

Based on surface physical properties of electron charging and dangling bond, silica glass with multi-properties of wettability, misting free, sterilization and high strength have been successfully developed by the EB irradiation. The electron beam irradiation decreases the contact angle of water and prevents the misting. On the other hand, the electron beam irradiation also strengthens the silica glass. We conclude that it is mainly induced by the stress relaxation generated by dangling bond in network structure of silica glass.

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