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Role of Electron Beam Irradiation-Induced Surface Nanostructure Changes on the Multi-functional Properties of Ceramics

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This paper describes the recent development of irradiated inorganic materials with 'intelligent' properties for medical use. The creation of these 'smart' properties depended upon such causative factors as charging, dangling bond formation and terminal atom conversion. Through nanotechnologies that take advantage of these agents, we have been able to use electron beam (EB) irradiation to develop multi-functional medical inorganic materials that are transparent, mist resistant, wettable, and strong. We also have utilized EB irradiation to obtain a highly wettable and sterilizable apatite ceramic, a material, which was recently used for artificial bone, as well as other mist resistant, sterilizable and strong inorganic materials.

Key words: misting, electron beam, sterilization, wettability, strength,

1. INTRODUCTION

Multi-functional ceramics, transparent, mist-free, sterilizable, and wettable, are a long-desired goal of scientists and engineers. At the moment, however, although glassy ceramics are widely used because of their high heat resistance combined with good optical transparency, ceramic brittleness remains a serious problem. From an engineering point of view, glassy ceramics require homogeneous reinforcement to produce precisely formed articles after casting. Heating is often employed to homogenize residual stress in liquid-quenched metallic glasses; however, high temperatures and long time periods are often required. In addition, after solidification, it is difficult to improve fracture toughness, that is, to improve both ductility and fracture stress simultaneously. To address these problems in liquid-quenched metallic glass after solidification, researchers have developed a solid-randomization process using shot peening.[1-3] Unfortunately, it is not suitable for brittle ceramics.

To control properties such as sterilization, wettability, mist resistance, hardness, ductility, and strength, without fracturing the material, a new technique, electron beam (EB) irradiation, is now under development. In the present study, we investigate the possible beneficial effects of EB irradiation on the fracture toughness of the surface layer in glassy ceramics.

2. EXPERIMENTAL

The mass composition of the glassy ceramics sample used in this work was 73%SiO_2, 13%Na_2O, 8%CaO, 4%MgO and 2%Al_2O_3. The samples were 30.05 x 30.05 mm square sheets 3 mm thick, homogeneously irradiated using an electron-curtain processor (Type CB175/15/180L, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co. Ltd. Tokyo)[5-19], as shown in Fig. 2. The electron beam irradiated the specimen through a titanium thin film window attached to ~~the~~ a vacuum chamber (240 mm in diameter). A tungsten filament in vacuum generated the electron beam using an acceleration potential of 170kV and an irradiating current of 4.0 mA. To prevent oxidation, the samples were kept under the protection of one atmosphere of nitrogen gas having a residual oxygen concentration below 400ppm. Each dose of EB irradiation was ~~only~~ applied for only 0.23s to avoid excessive heating of the sample. Just after irradiation, the temperature of the surface of the sample was below 323 K. The sample was transported on a conveyor at a speed of 9.56m/min. Repeated applications increased the total dose of radiation. 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:

$$\text{Dosage(MGy)}=0.216(I/S)N \quad (1)$$

To calibrate the yield value, we employed FWT nylon dosimeters (Far West Technology, Inc. 330-D South Kellogg Goleta, California 93117,USA). We estimated the surface electrical potential (128 kV) from the electrical potential (170 kV) and the titanium window thickness (13μm). The distance between the sample and window was 35 mm. Based on the density (ρ: g/cm^3) and irradiation voltage (V: kV), the EB-irradiation depth (D_{th}: μm) was expressed by the following equation.[4]

$$D_{th}=0.0667V^{5/3}/\rho \quad (2)$$

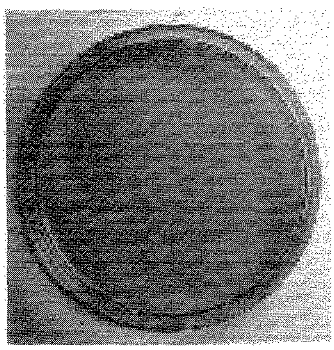
Here, the glassy ceramic's measured density was 2.22 g/ cm^3. Thus, the EB-irradiation depth should be 0.1 mm for this material.

To obtain more precise information on structural changes in the glass at the atomic scale, we observed electron spin resonance (ESR) signals attributable to dangling bonds using an, SA2000 spectrometer (Nippon Dennshi Ltd., Tokyo). The microwave frequency range used in the ESR analysis was the X-band of 9.45 $\pm$ 0.05 GHz, with a field modulation of 100 kHz. The spin density was calculated using a Mn^{2+} standard.

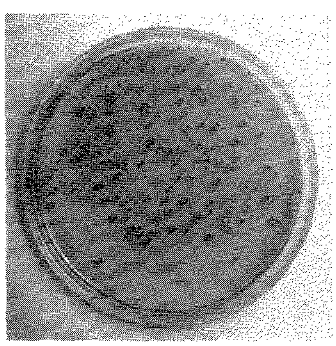
3. RESULTS AND DISCUSSION

3.1.Sterilization

To test for sterilization, we employed a dentist's mirror (Ref.5) and an endoscope lens (Ref.6). Figure 1(a) shows the colonies of bacillus formed on the ceramics after one week's incubation. The electron beam irradiation sterilized the ceramics, as Fig.1-(b) demonstrates. Evidently, the EB irradiation induced sterilization by breaking the weak bonding pairs in the bacillus' proteins.



(a)



(b)

Fig. 1. Colonies of bacillus on the ceramics aged after one weak. (a) and (b) are for samples before and after EB irradiation.

3.2 Wettability

Figure 2 shows the relationship between the EB irradiation time and the water contact angle. The ~~EB~~ irradiation decreased the contact angle of a sessile water drop on apatite ceramics used to build artificial bone.[7] A high wettability of sterilized material should be lower the activation energy of the reaction needed to form artificial bone, resulting in a shorter curing period.

Argon ion beam irradiation enhances the wettability of silica glass.[8] Furthermore, EB irradiation raises the wettability of silicon wafers[9], sapphire lenses[10], TiO_2[11] and diamond.[12] Charging[10], dangling bond formation[9] and terminal atom conversion and absorption[12] were the respective main causes of the EB effects in the sapphire, silica glass and diamond.

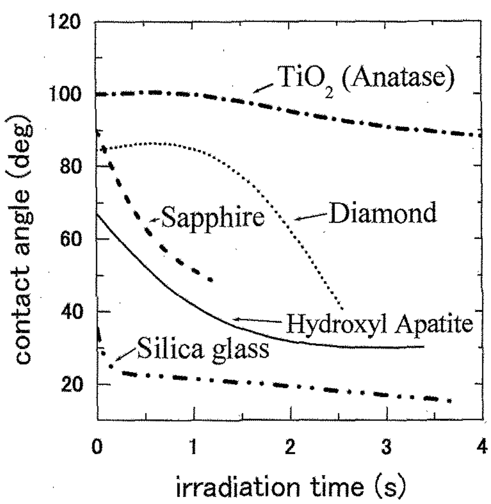


Fig.2 Relationship between EB irradiation time and water-contact angle.

3.3. Misting

Misting is a serious problem in the field of medical engineering. The developments of EB treatments yielding mist-free ceramics have a long history. Investigators have applied EB irradiation to dental mirrors[13], sapphire endoscopic lenses[14], diamond[15], quartz[16], silica glass[17], ITO and TiO_2[18,19]. In our experiments, to measure the rate of mist removal, we sprayed droplets onto the sample surface at an approximate rate of 6 x 10^{-4} m^3/s at 310 K under atmospheric pressure. We then immediately determined, with a microscope, the distribution of the radii of the fine drops on the diamond surface, and used a videotape recorder to measure the time to clear vision (τ_c). Our starting point for measuring the mist removal was just after the completion of blowing for 3 s under saturated vapor pressure. The minimum detectable time to clear vision was 0.2 s.

Figure 3 shows a plot of the change in time to clear vision against the level of EB irradiation; EB irradiation decreased this time. Charging[14], dangling bond formation[13,16-18] and terminal atom conversion and absorption[15,19] were the main factors involved in these EB effects.

In summary, because of nanotechnologies taking advantage of the factors mentioned above, electron charging, etc., electron beam irradiation has been a key factor in producing mist-free medical inorganic materials.

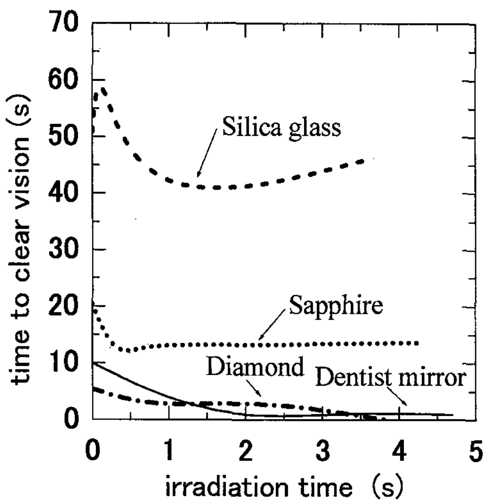


Fig.3 Change in time to clear vision of inorganic materials against EB irradiation.

3.4 Transparency

The sheet electron beam slightly enhanced the transparency of silica glass[20], as shown in Fig.4. The EB irradiation's slight relaxation of the residual stress of the glassy structure of the silicon-oxygen pairs in the glass may explain this increased transparency. In any case, the rise in transparency that EB irradiation brings about is evidently an important step toward the overall goal of augmenting ceramic functionality.

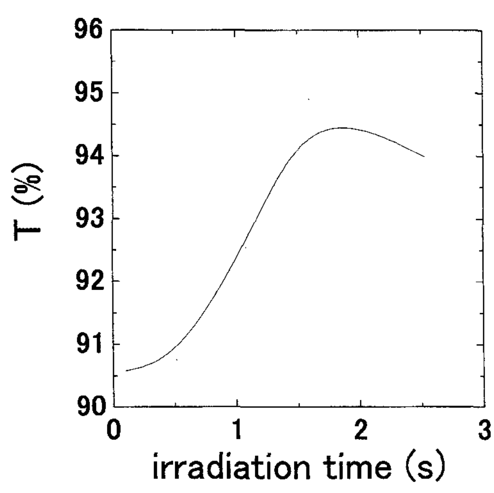


Fig. 4. Transparency of silica glass at different EB irradiation dose.

3.5 Strengthening

Previous reports state that EB treatment strengthened inorganic materials, such as a polycrystalline α-Al_2O_3 [21], soda glass[16,22] and glass fiber.[21] EB irradiation homogeneously activates surface atoms, breaks chemical bonds and facilitates the migration of mobile atoms in a glass surface layer up to 0.1mm in depth (see eq. 2).[4] It provides the various quantities of energy, 799.6, 256.1, 402.1, 363.2, and 511 $kJ.mol^{-1}$ [11] necessary to break the chemical bonds between the Si, Na, Ca, Mg and Al-O pairs. In doing so, it relaxes the loading and residual stress in the tightly bonded network structure of these glassy ceramics, possibly allowing us to control their fracture toughness.

Figure 5-(a) shows the change in fracture stress of a glass fiber plotted against the EB irradiation dose at a fracture probability level of 0.5. Evidently, the EB irradiation enhanced the fracture stress resistance of the glass fiber.[21]

To evaluate the fracture toughness, we obtained the critical fracture energy of micro-plastic deformation (E_f), related to K_{Ic}[22], using the experimental values of the critical indentation diameter (d_f) and the critical fracture load (P_f). We measured these quantities with a micro-Vickers' indentation tester, and obtained the relationship between the load (P) and the diagonal distance (d) of the indentation; we chose indentations that were free of cracks to determine the maximum values (d_f^{max} and P_f^{max}) of d and P. On the other hand, to calculate the minimum values (d_f^{min} and P_f^{min}) of d and P, we selected indentations that were obviously cracked. The following equations express the critical indentation diameter (d_f) on fracture and the critical fracture load (P_f): [22]

$$d_f = (d_f^{min} + d_f^{max}) / 2 \quad (3)$$

$$P_f = (P_f^{min} + P_f^{max}) / 2 \quad (4)$$

Furthermore, to evaluate the effects of EB on the fracture toughness in ceramics sheets, we obtained the fracture toughness values of $\underline{K_{Ic}}$. Figure 5-(b) illustrates the change in the fracture toughness, E_f, of hydroxyapatite and soda glassy ceramics as a function of the EB irradiation dose. The EB irradiation enhanced the fracture toughness, related to K_{Ic}.[22] Annealed glass generally exhibits a tight network structure. Perhaps the elevated free volume formation relaxed the residual stress, an effect that could explain the observed effects of the EB irradiation.

Vickers' hardness is a useful tool to evaluate resistance to plastic deformation. Figure 5-(c) demonstrates the change in Vickers' hardness (Hv) of silica and soda glasses as a function of the EB irradiation dose.[22] Although the hardness of silica glass didn't depend on the EB irradiation, it enhanced the hardness of soda glass. The hardening was probably caused by a reinforcement of the bonding force of silicon-oxygen atoms pairs (Si-O) in the soda glass; the dangling bonds resulting from the annihilation of the weak Na-O atomic bonding may have induced the Si-O reinforcement.

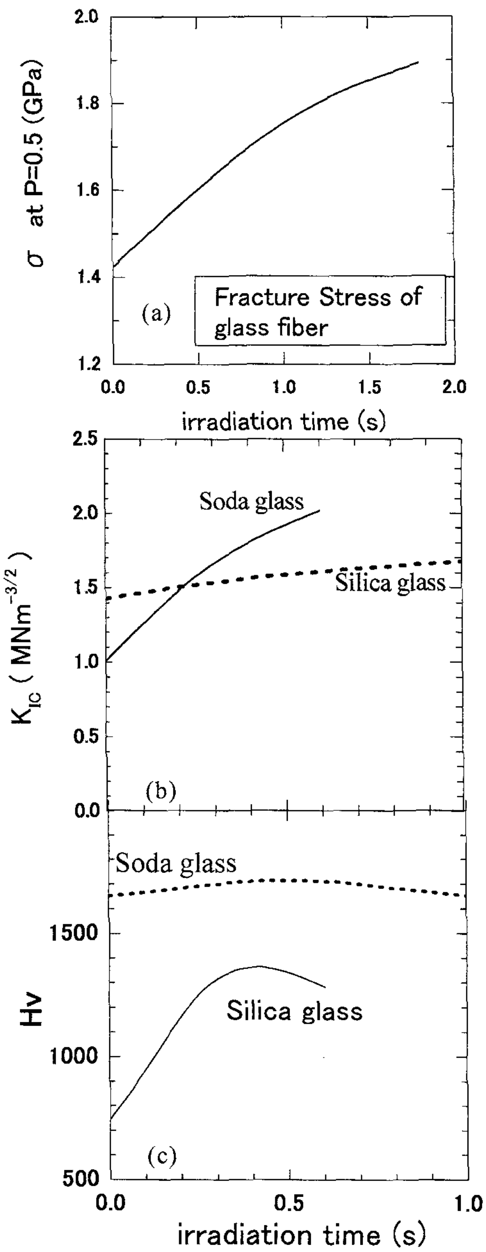


Figure 5. Change in mechanical properties plotted against EB irradiation dose. (a) change in fracture stress at 0.5 fracture probability of the glass fiber; (b) change in fracture toughness K_{1c} of silica and soda glasses; (c) change in Vickers' hardness (Hv) of silica and soda glasses.

5.CONCLUSION

Nanotechnological techniques taking advantage of such factors as electron charging, dangling bonds, point defects and atomic distance now permit the development of improved medical inorganic materials. An example discussed here, EB irradiation-treated silica glass, possesses valuable enhancements in transparency, mist resistance, sterilizability, wettability and strength.

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