Effect of 100 keV Class Electron Beam Irradiation on Impact Fatigue Behavior of PZT Ceramics

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INTRODUCTION

PZT(lead zirconate titanate: Pb(ZrₓTi₁₋ₓ)O₃) is a complex perovskite structure of a mixed crystal constructed with lead titanate tetragonal (x < 0.52) and lead zirconate rhombohedral (x > 0.52) crystals.¹ When x is 0.525 (Morphotropic phase boundary: MPB), the marvelous performances of permittivity, piezoelectric effect, ferroelectricity can be broadly utilized for supersonic generator, flint, infrared sensor, energy absorber and electrical power generator.²

On the other hand, a fatigue fracture is one of serious problems in applying material systems and structures. Thus, it is important to know the collision fracture toughness, its fatigue life and its fatigue limit of the materials. However the fatigue test is usually quite time consuming. Therefore, a determination test, by which the collision fatigue limit can be precisely obtained, has been expected. If a nondestructive method of collision fatigue limit can be developed, it should be applied broadly in the fields of aerospace, civil, mechanical, electronic, and biomedical engineering, as well as in emerging technologies.

To evaluate the fatigue resistance for the piezoelectric ceramics, a nondestructive method has been suggested to evaluate the collision fatigue limit of PZT, since the materials show large changes in electrical potential induced by pressure on the collision.³ Since a relationship between the maximum value of electrical potential and supplied collision energy below the collision fatigue limit has been expressed, the collision fatigue limit was nondestructively determined for PZT materials.

Both transformation of ZrO₂ ceramics⁵ and surface compressive stress by potassium chemical penetration for alkali silicate glass⁶ have been recently developed as the new methods to strengthen ceramics. However, effective conditions to each material are not easily determined. On the other hand, shot-peening is convenient to activate and randomize surface of metallic glass with enhancement of mean atomic distance and free volume as well as decreasing coordination number.⁶ It improves the permeability of soft magnetic Fe-Si-B alloys glasses⁷ and the corrosion resistance of Fr-Cr stainless steel glass⁸, as well as the Vickers hardness of Pd-Cu-Si glassy alloys.⁹ However, it is easy to generate cracks in brittle materials, simultaneously. In order to randomize the brittle glass except crack generation, electron with extremely fine mass is used without (accompanying) crack formation.

The electron beam irradiation (EBI) with homogeneous low potential of 100 keV class has been suggested and developed to draw the marvelous properties of strengthening and ductility enhancement for silica and silicate glass without crack generation.¹⁰⁻¹² Active terminated atoms with dangling bonds¹³,¹⁴ have been formed in silica¹⁰ and silicate glasses¹¹ treated by EBI. On the other hand, additional dose of 0.43 MGy-EBI reduces the bending strength, its strain and its fracture energy, to approximately 1/2, 1/3 and 1/6 of that untreated because of radiation damages.¹⁵ According to the results, EBI should be useful to strengthen ceramics. Therefore, the purpose of the present work is to investigate effects of electron beam irradiation on fatigue resistance by number of impact force of PZT (Pb(Nb₂/₃Ni₁/₃)O₃-Pb(Zr₁/₃Ti₂/₃)O₃) ceramics.

EXPERIMENTAL PROCEDURE

2.1 PZT sample preparation

Oxide compounds of PbO, ZrO₂:TiO₂:NiO, and Nb₂O₅ (all from High Purity Chemicals, purity > 99%, Sakado and Higashi-matsuyama, Japan) were mixed for 24 h in a nylon jar with zirconia balls and then dried. The dried powders were calcined at 1153 K for 4 h. After that, the powders were dried and pressed into discs under a pressure of 1000 Pa, and sintered at 1473 K for 4 h. To obtain reproducible results of fracture test PZT samples (2 mm × 2 mm × 5 mm), commercially used as a flint produced by TOKAI...
CORNORPATION with high quality control, were prepared by sintering under high pressure. Although the original oxide composition of lead titanate zirconate was Pb(Zr,Ti)Oₓ (x = 0.525), the standard composition of PZT was currently Pb(Nb₂/₃Ni₁/₃)O₃-Pb(Zr₁/₃Ti₂/₃)O₃ utilized for practical applications. The metal atomic ratios of chemical composition measured by using EPMA (EPMA-1610, Electron Micro Pro Analysis, Shimazu, Kyoto) were 0.3775 +/-0.0115 for lead, 0.2915 +/-0.0065 for zirconium, 0.159 +/-0.002 for titanium, 0.08765 +/-0.00005 for niobium, 0.0841 +/-0.0072 for nickel, 0.050 for aluminum and 0.033 for strontium. Although crystal structure was perovskite confirmed by using XRD (MiniFlex-2, Rigaku, Tokyo),3 angles of complex XRD peaks with high intensity were observed using a scanning electron microscopy (SEM(SG-8000 type1, Hitachi high tec., Tokyo) and optical profile projection.

2.2 Condition of EBI

Figure 1 is a schematic of the electron beam processor (Type CB250/30/20 mA, Energy Science Inc., Woburn, MA, Iwasaki Electric Group Co. Ltd. Tokyo).16–25) The sheet-like electron beam was generated by a tungsten (W) filament in a vacuum chamber. The homogeneous irradiation was achieved by optical observation. The process zone kept under protective N₂(g) at atmospheric pressure with an O₂(g) residual rate of the sample. The N₂(g) flow rate was 1.5 L·s⁻¹ at 0.1 MPa N₂(g) pressure. The distance between sample and Ti window was 25 mm. The PZT samples in the aluminum plate holder (0.15 m x 0.15 m) carrying on a conveyor was irradiated through the homogeneous electron beam.

Since the density (ρ) of present PZT samples was 7140 kg·m⁻³, the penetration depth (D₀ = 32.2 μm) was estimated by assumptions of Christenhusz & Reimer.26) The penetration depth (D₀ = μm) of EBI was expressed by the following equation and was obtained by using the density (ρ: kg·m⁻³) and irradiation voltage at the specimen surface (V: kV).

\[ D₀ = 66.7V^{5/3}/ρ \]  

The electrical potential (V) of specimen surface was mainly reduced due to the penetration of electrons going through the Ti window (ΔV₁) and N₂(g) gas atmosphere (ΔV₄). This condition leads to the potential dropping estimated by the following equations.

\[ V = 170 keV - ΔV₁ - ΔV₄ \]  

Using eq. (1), the dropped potential values, ΔV₁, and ΔV₄ are estimated from the acceleration potential (170 keV), the 10 μm thickness (T₁) of the titanium window (density: 4540 kg·m⁻³), and the 25 mm distance between the sample and the window (T₄) in the N₂(g) gas atmosphere (density: ρN₂ = 1.13 kg·m⁻³).

Since the dropped potential values were 22.2 keV and 15.2 keV, the mean electrical potential of specimen surface, V was obtained to be 132.6 keV as follows.

\[ V = 170 keV - 22.2 keV - 15.2 keV = 132.6 keV \]  

Using the eq. (1), the penetration depth (D₀ = μm) was 32 and 80 μm for PZT and soda cover glass samples with densities of 7140 and 2760 kg·m⁻³, respectively.

Although the experimental D₀ obtained by using electron spin resonance (ESR) signals (more than 300 μm) was higher than estimated values (220 +/-40 μm) for the PEEK polymer,25) the experimentally obtained depth D₀ of the soda glass was 80 +/-20 μm determined by changes in the Vickers hardness, that was, indicator of the micro-plastic deformation. Thus, the estimation was assumed to be adaptable for ceramics.

2.3 Impact fatigue test

The fatigue test, as shown in Fig. 2, was repeatedly performed by the collision of a stainless steel stick. The mass (m), length and diameter of the stick were 1.463 g, 5 mm and 4 mm, respectively. The sample size of the PZT sample was 2 mm x 2 mm x 5 mm. To load homogeneously, a hemispheric shock absorber made of 18-8 stainless steel was set between PZT sample and stick (see Fig. 2). The sample was apparently fractured by optical observation.

\[ E_c = mgh = 143.9 (mJ · m⁻¹) h (m) \]  

Figure 3 shows optical micrographs of PZT surface before and after fracture with crack just below hemisphere. The supplied collision energy (E_c: J) was total energy of collisions, as the energy of one collision was equal to static energy, which was determined by sample mass, gravity accel-
eration speed \((g: \text{m·s}^{-2})\) and the height \((h: \text{m})\) from the sample top surface to the iron stick bottom. \(^3\)

On the other hand, the accumulative probability \((P)\) of the median rank method\(^{19-25,28,29}\), which was useful for statistical evaluation often used in quality control (QC), was one of the convenient ways to analyze mechanical probability. Here, the accumulative probability of the critical number of collision fracture was expressed by the following equation:

\[
P_f = \frac{(i - 0.3)}{(n + 0.4)}
\]  

(5)

Here, \(n\) and \(i\) were the total number of samples \((n = 3)\) and the median rank of the critical collision number of fracture \((N_c)\) for each sample from the weakest \((i = 1)\) to the strongest \((i = 3)\), respectively. \(P_f\) values were 0.21, 0.5 and 0.79, respectively, when \(i\) values are 1, 2, and 3.

3. Results

3.1 Collision fatigue test of PZT without EBI

The fatigue test is repeatedly performed by the stick collision against the three PZT samples at different collision energies, until the samples are apparently fractured by optical observation, as shown in Fig. 3. Figure 4 shows changes in critical collision number \((N_c)\) against its supplied constant energy of collision \((E_{Ci})\) of PZT untreated. When \(N_c\) is one, that is, fracture occurs by one collision, the maximum \(E_{Ci}\) value obtained should be 25 mJ. Decreasing the \(E_{Ci}\) value from 25 to 3.6 mJ increases the \(N_c\) value from one to 21. When the collision energy becomes small enough, the total number of collisions to fracture should become infinite long.

On the other hand, when the \(E_{Ci}\) was below 3.6 mJ, the collision fracture could not be easily determined by the collision test. Since micro-cracks cannot be observed below the collision fatigue limit by SEM observation, the collision fatigue limit can be defined for the PZT sample. The long lifetime on collision fatigue of the material lies below the limit, as shown in Fig. 4.

3.2 Influence of EBI on collision fatigue life of PZT

Figure 5 illustrates changes in critical collision number of fracture of PZT without EBI and with EBI of dosage varying from 0.043 to 0.13 MGy against the accumulative probability of fracture, when one collision energy is 3.6 mJ. EBI dose of 0.086 MGy apparently improves the \(N_c\) from 18 \(+/−3\) to 37 \(+/−11\) at all \(P_f\), from 0.21 to 0.79, that is, it prolongs the fatigue life.

EBI dose of 0.065 to 0.13 MGy remarkably improves the \(N_c\) at the high \(P_f\) value of 0.79, whereas additional EBI dose of 0.13 MGy apparently decreases the \(N_c\) values at the low and medium \(P_f\) values of 0.21 and 0.50. The minimum \(N_c\) value at the low \(P_f\) of 0.21 is found in 0.13 MGy-irradiated...
PZT because of general radiation damage. On the other hand, slight dose of 0.043 Mgy-EBI apparently decreases the \( N_c \) values at all \( P_f \) values.

4. Discussion

4.1 Prolonging fatigue life of PZT by optimum dose EBI

Figure 6 illustrates EBI-dose dependence of the critical collision number (\( N_c \)) of impact fracture of PZT at the medium \( P_f \). As usual radiation damages occur, the additional dose of 0.13 Mgy-EBI apparently decreases the \( N_c \) value at the low \( P_f \) values of 0.21, as shown in Figs. 5 and 6. On the other hand, the optimal dose of 0.086 Mgy-EBI apparently improves the \( N_c \) and \( E_c \) of PZT. One of the possible reasons is that the annihilation of sharp crack tips is probably induced by the migration of surface atoms, since it has been often observed by using electron microscopy. Furthermore, since active terminated atoms with dangling bonds without crack generation have been formed by EBI for silica and silicate glasses,\(^ {13,14} \) both strengthening and ductility enhancement are drawn.\(^ {10-12} \) Using the radial distribution function of \( \text{SO}_2 \) glass, optimal dose of EBI has decreased its mean atomic distance\(^ {10} \). The compressive strain generally occurs at surface of the ceramics with similar chemical bonds.

4.2 Discussion of XRD results of untreated PZT

To explain the results of the collision test, the crystallographic analysis has been performed. Figure 7 illustrates both (101) and (110) XRD peaks of PZT (\( \text{Pb(Nb}_{2/3}\text{Ni}_{1/3})\text{O}_{3-\delta}\text{Pb(Zr}_{1/3}\text{Ti}_{2/3})\text{O}_3 \)) samples treated by the perovskite structure\(^ {3} \) just before the first collision (see broken lines) and just after the collisions to fracture (see solid lines). Since the collisions to fracture decreases the peak angle and peak height \((\text{see Fig. 7(a)})\), it increases the distance of crystal plain, strongly related to the lattice constant, and disorders the crystal lattice sites with lattice defects. The residual strain is stored and relaxed simultaneously by the collisions to fracture. The collision stores the residual strain by the formation of lattice defects, whereas the collisions to fracture also relaxes the stored strain because of cutting the chemical bonds between metal and oxygen ions at micro-crack interface. According to the XRD results of untreated PZT in Fig. 6(a), the irreversible stored strain is probably relaxed by the defects formation and crack.

4.3 Discussion of long life of PZT irradiated by optimal dose

Figure 7(b) also shows XRD peaks of PZT (\( \text{Pb(Nb}_{2/3}\text{Ni}_{1/3})\text{O}_{3-\delta}\text{Pb(Zr}_{1/3}\text{Ti}_{2/3})\text{O}_3 \)) samples treated by the optimal dose of 0.086 Mgy-EBI just before the first collision (broken line) and just after the collisions to fracture (solid line). Since the optimal dose of EBI decreases the peak angle of XRD results, as shown in Fig. 7(a) and (b) (broken lines), it decreases the peak angle which indicates the increase of lattice constant.

When the volume expansion is assumed to be induced by the oxygen enrichment and/or the annihilation of oxygen defects by the optimal dose of 0.086 Mgy-EBI, it can be explained.

Since the collision after EBI with the optimal dose shortens the lattice constant of PZT, it probably prevents the crack generation and propagation.

Therefore, the optimal dose of 0.086 Mgy-EBI apparently increases the fatigue life, that is, it also improves the critical collision number of fracture (\( N_c \)) of PZT at all accumulative probabilities (\( P_f \)), as shown in Figs. 5 and 6.

4.4 Radiation damage of PZT irradiated by additional dose

Although the XRD peak angle \((\text{see broken line in Fig. 7(c)})\) of radiation damaged PZT with an additional dose of 0.13 Mgy-EBI prior to the collision test is lower than that of untreated PZT \((\text{see broken line in Fig. 7(a)})\), it is slightly higher than that of PZT with the optimal dose of 0.086 Mgy-EBI prior to the collision test \((\text{see broken line in Fig. 7(b)})\).
Fig. 6(b)). Namely, the lattice constant at additional dose prior to the collision test is larger than that untreated, whereas it is slightly lower than that with the optimal dose. When the slight volume reduction by the additional dose EBI is assumed to be induced by oxygen desorption and formation of oxygen defects, it can be explained.

As shown in Fig. 7(c) with XRD peaks of radiation damaged PZT samples treated by the additional dose of 0.13 MGy-EBI just before the first collision (broken lines) and just after collisions to fracture (solid lines), the collisions to the radiation damaged PZT slightly decreases the XRD-peak angle. It increases the lattice constant because of cutting the chemical bonds between metals and oxygen ions at micro-crack interface.

Thus, the additional dose of 0.13 MGy-EBI decreases the critical collision number to fracture (Nc) of PZT, as shown in Fig. 6. Namely, the additional dose apparently decreases the fatigue life,

\[ \text{4.5 Relationship between log} N_c \text{ and log} E_{C}^{i} \text{ of untreated PZT} \]

Figure 8 illustrates the linear relationship between logNc and logEc of untreated PZT, when a collision is 3.6 mJ. When the hemispheric stick homogenizes the distribution of impact force on the collisions on the PZT surface, the linear relationship of untreated PZT can be obtained and expressed by the following equation.

\[ \log E_{C}^{i} = -1/2 \log N_c \text{ (untreated)} + 1.3 \quad (6) \]

Namely, the integrated impact energy (Ec) of untreated PZT can be inversely proportional to root Nc (Nc/2) can be expressed by the following equations.

\[ E_{C}^{i} \times N_c^{1/2} = 3.6 \text{ mJ} \times (18+/-3)^{1/2} \]
\[ = 15.3 \text{ mJ} \text{ (untreated)} \quad (7) \]

\[ E_{C}^{i} = 15.3 \text{ mJ (untreated)} / N_c^{1/2} \quad (8) \]

4.6 Prediction of collision fatigue life of PZT with optimal dose

When the critical collision number to fracture (Nc) is 10⁵ (10⁶), the Ec is deduced to be 48.4 (15.3) μJ. Using eq. (4), the height of the stick just before falling should be 0.3 (0.1) mm.

When the linear relationship is assumed to be applied to the PZT samples with optimal dose of 0.086 MGy-EBI, it is
possible that the intercept strongly depended on HLEBI dose should be obtained, as the following equation.

\[
E_C^1 \times N_c^{1/2} = 3.6 \text{ mJ} \times (37^{+/-11})^{1/2} = 21.9 \text{ mJ} (0.086 \text{ MGy})
\]

\[
E_C^1 = 21.9 \text{ mJ (0.086 MGy)} / N_c^{1/2}
\]

When the critical collision number to fracture \((N_c)\) is 10^5 and 10^6, the \(E_C^1\) can be estimated to be 69.3 and 21.9 \(\mu\)J, respectively. Using eq. (4), the height of the stainless steel stick should be 0.48 and 15.2 mm, respectively.

Therefore, optimal dose of 0.086 MGy-EBI can be predicted to improve the resistance to fatigue fracture from 48.4 and 15.3 to 69.3 and 21.9 \(\mu\)J at practical high \(P_f\) values of 10^5 and 10^6, respectively.

5. Conclusion

The homogeneous and quick treatment of electron beam irradiation with low potential (EBI) improved the critical collision number \((N_c)\) and its integrated collision energy \((E_C^1)\) of impact fracture of PZT \((\text{Pb}(\text{Nb}_{2/3}\text{Ti}_{1/3})_2\text{O}_5-\text{Pb}(\text{Zr}_{1/3}\text{Ti}_{2/3})_3\text{O}_3)\) ceramics, although additional dose decayed them.

1) The optimal dose of 0.086 MGy-EBI apparently improved the \(N_c\) of PZT.

2) Since the collision after EBI with the optimal dose shortened the lattice constant of PZT, it probably prevented the crack generation and propagation. Therefore, the long life of impact fatigue could be explained for the PZT irradiated with the optimal dose.

3) Decreasing the \(E_C^1\) value from 25 to 3.6 mJ increased the \(N_c\) value from one to 21 for PZT untreated. The linear relationship between the log \(N_c\) and log \(E_C^1\) of untreated PZT was obtained, when one impact collision energy was 3.6 mJ.

4) Using the linear relationship between log \(E_C^1\) and log \(N_c\), the estimated values of PZT samples assumed to be predicted. The optimal dose of 0.086 MGy-EBI probably improved the resistance to fatigue fracture from 48.4 (15.3) to 69.3 (21.9) \(\mu\)J at high practical \(P_f\) values of 10^5 (10^6).

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