Study on Improvement of Wear Resistance for Zirconia by Large-area Electron Beam Irradiation

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Abstract

Zirconia has been widely applied for cutting tools and biomaterials, since it has superior mechanical properties such as high fracture toughness, bending strength and biocompatibility in ceramics. In order to maintain its surface functions for long-term, further improvement of wear resistance for zirconia has been required. In this study, improvement of wear resistance for zirconia is proposed by large-area electron beam (EB) irradiation. Experimental results show that mean width in roughness curve of zirconia surface increases with increasing the energy density of EB, although the maximum height in surface roughness is almost same as the ground surface. In friction and wear test, coefficient of friction reduces with increasing the energy density of EB since ball material smoothly slides on the EB irradiated zirconia surface. Furthermore, it is made clear that wear resistance of zirconia significantly improves by the EB irradiation under appropriate energy density.

Key words: large-area electron beam, zirconia, coefficient of friction, wear resistance

1. INTRODUCTION

Ceramics has high wear resistance, corrosion resistance and heat resistance, compared with metal materials. In particular, zirconia has been widely applied for cutting tools, manufacture parts, and biomaterials in dental treatment, since it has superior mechanical properties such as high fracture toughness, bending strength and biocompatibility in ceramics1, 2. In order to maintain its surface functions for long-term, further improvement of wear resistance for zirconia has been required.

On the other hand, in a large-area electron beam (EB) irradiation method developed recently, high energy density of EB can be obtained without focusing the beam3, 4. Then, the large-area EB with uniform energy density distribution of about 60mm in diameter can be used for melting and evaporating material surface instantly. Our previous study showed that surface roughness of metal molds made of steel decreased from several μmRz to less than 1.0μmRz in a few minutes under appropriate EB conditions5, 6. Thus, highly efficient surface finishing of metal molds was possible by using the large-area EB. This technique was also applied for titanium alloy7, 8, aluminum9 and cemented carbide10. Furthermore, surface functions, such as wear resistance, water repellency and corrosion resistance of metal molds were improved by the EB irradiation, since the material surface was instantly melted and thin re-solidified layer with fine microstructures was formed on the workpiece surface11. Therefore, it is highly expected that wear resistance of zirconia will be also improved by the large-area EB irradiation.

In this study, improvement of wear resistance for zirconia was proposed by large-area EB irradiation. Surface topography and crystal structure of EB irradiated zirconia surface were evaluated in order to discuss change of wear resistance for zirconia.

2. EXPERIMENTAL PROCEDURE

2.1 Large-area EB Irradiation Method and Workpiece

In the experiments, 3mol% yttria partially stabilized zirconia was used as a workpiece. It had crystal structures of tetragonal and monoclinic phases as major and minor ones at room temperature. Workpiece size was 10×10×0.5mm, and material properties of zirconia were shown in Table1. In this experiment, initial surface roughness of ground zirconia surface was fixed at about 5.8μmRz.

Schematic illustration of a large-area EB irradiation equipment is shown in Fig.1. The large-area EB irradiation is performed in an argon (Ar) gas ambience of about 10^{-2} Pa. At first, a magnetic field is generated by the solenoid coils set on the outer side of chamber. When the magnetic field takes a maximum intensity, pulse voltage is loaded to the anode. Then, Ar plasma is generated in the operating chamber by rapid changes in magnetic and electric fields. Next, a pulse voltage is applied to the cathode, and the electrons are explosively emitted from the cathode by high
electric field near the cathode. Therefore, large-area EB with uniformly high energy density enough to melt and evaporate the workpiece surface can be obtained.

The large-area EB was irradiated upper side of zirconia surface. EB irradiating conditions were shown in Table 2. Energy density $E_d$ was varied from 2.5 to 12.5 J/cm$^2$, while shot number $N$ and pulse duration $t_p$ were fixed at 1 shot and 2 μs. The EB irradiated surface was observed by using a scanning electron microscope (SEM), and surface roughness of zirconia surface was measured by using a surface profilometer in order to evaluate change of surface topography after the EB irradiation.

### 2.2 Measurement of Wear Resistance

The coefficient of friction and wear resistance of zirconia surface before and after the large-area EB irradiation were evaluated by using a friction and wear tester. Schematic illustration of friction and wear test was shown in Fig. 2. Reciprocating friction and wear test machine was used in the experiment. Experimental conditions of friction and wear test were shown in Table 3. SiC was used as ball material, since hardness of SiC was higher than that of zirconia. The SiC ball repeatedly slid on the zirconia surface for 100 min. The load was set at 7.84 N. Sliding speed and stroke were fixed to 720 mm/min and 3.0 mm. Sliding direction was perpendicular to the grinding trace direction of surface. After friction and wear test, the SiC ball and zirconia surfaces were observed by using an optical microscope, and worn amount of zirconia was measured by the surface profile of wear track.

### 3. RESULTS AND DISCUSSION

#### 3.1 Surface Topography

SEM images of zirconia surface after the large-area EB irradiation are shown in Fig. 3. The image of non-EB irradiated surface (ground surface) is also shown. As shown in the figure, grinding traces are clearly observed on the non-EB irradiated surface, while the small convex parts of grinding traces are removed and the width of grinding traces seems to increase after the EB irradiation at energy density of 5.0 J/cm$^2$. Moreover, the grinding traces seem to be more removed with increasing energy density, and the grinding traces are not clearly observed on the EB irradiated surface at energy density of more than 7.5 J/cm$^2$. Then, micro-cracks are generated at the energy density of more than 7.5 J/cm$^2$. In order to evaluate the surface topography in detail, roughness curves

### Table 1 Properties of zirconia

| Property           | Value |
|--------------------|-------|
| Density $r$ [g/cm$^3$] | 6.0   |
| Specific heat $c$ [J/(g·K)] | 0.46  |
| Thermal conductivity $k$ [W/(m·K)] | 3.0   |
| Melting point $T_m$ [K] | 2,998 |

### Table 2 EB irradiating conditions

| Condition         | Value |
|-------------------|-------|
| Energy density $E_d$ [J/cm$^2$] | 2.5-12.5 |
| Shot number $N$ [shots] | 1     |
| Pulse duration $t_p$ [μs] | 2     |

### Table 3 Friction and wear test conditions

| Condition         | Value |
|-------------------|-------|
| Ball material     | SiC   |
| Load $L_f$ [N]    | 7.84  |
| Stroke $L_s$ [mm] | 3.0   |
| Time $t_s$ [min]  | 100   |
| Sliding speed $v_s$ [mm/min] | 720   |
were measured by using a surface profilometer. The roughness curve at each energy density condition is shown in Fig.3. As shown in the figure, the small convex parts of grinding traces are preferentially removed after the EB irradiation, while large ones still remain regardless of increase of energy density.

In order to evaluate the surface topography of zirconia after the EB irradiation quantitatively, surface roughness and mean width in roughness curve of EB irradiated surface were measured. Figure 4 shows variations of surface roughness and mean width of zirconia surface with various energy densities. As shown in the figure, surface roughness of EB irradiated surface is almost same as the ground one. On the other hand, the mean width significantly increases after the EB irradiation, compared with that of ground surface. Moreover, the mean width lineally increases from 80µm to more than 150µm with increasing energy density from 2.5 to 12.5J/cm². The mean width of EB irradiated surface at $E_d=12.5$J/cm² is 5 times higher than that of ground one.

Therefore, it is made clear that mean width in surface roughness increases after the EB irradiation, although maximum height in surface roughness is almost same as the ground surface. It is probably caused that the small convex parts of ground surface can be preferentially evaporated or melted in large-area EB irradiation, while it is difficult to remove the large convex parts of ground surface.

**3.2 Surface Element**

Surface element of EB irradiated zirconia surface was examined by using an energy dispersion X-ray spectroscopy (EDX) in order to investigate chemical composition of zirconia surface after the EB irradiation. Figure 5 shows the elemental contents of EB irradiated surface for various energy densities. As shown in the figure, large amount of zirconium and oxygen contents which are main contents of zirconia are clearly detected on the non-EB zirconia surface. Zirconium and oxygen

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**Fig.3** SEM images and roughness curve of zirconia surface

**Fig.4** Variations of surface roughness and mean width with energy density

**Fig.5** Element analysis results of EB irradiated zirconia surface
contents of EB irradiated surface are almost same as the non-EB one under each energy density condition. In addition, under any EB irradiating conditions, the elemental ratio of zirconium and oxygen is almost 1:2, which agrees with that of zirconia (ZrO$_2$). On the other hand, yttrium, aluminium and hafnium contents which are slightly contained in the 3mol% yttria partially stabilized zirconia hardly change after the EB irradiation. These results indicate that surface element of zirconia surface maintains after the EB irradiation.

3.3 Improvement of Wear Resistance

The coefficient of friction and worn amount of zirconia surface after the EB irradiation were investigated. Figure 6 shows variations of coefficient of friction with time at various energy densities. In the cases of non-EB and the energy density of 2.5J/cm$^2$, the coefficient of friction increases with increasing time and it becomes constant over 2000s, while it becomes constant over 3000s in the cases of energy density of more than 5.0J/cm$^2$.

Figure 7 shows variations of coefficient of friction with various energy densities. As shown in the figure, the coefficient of friction decreases with increasing the energy density of EB. Moreover, the coefficient of friction in the cases of zirconia surfaces at energy density of more than 5.0J/cm$^2$ becomes lower than that on the ground one. These results suggest that the SiC ball smoothly slides on the zirconia surface after the EB irradiation under appropriate energy density, since the mean width of zirconia surface increases at higher energy density of EB.

Figure 8 shows optical images of SiC ball surface and surface profiles of wear track on the
zirconia surface. As shown in the optical images, grooves along the sliding direction are clearly observed on the ball surface in the cases of sliding on the ground surface and the EB irradiated zirconia surface at $E_d=5.0\text{J/cm}^2$. On the other hand, the grooves are not clearly observed on the ball surface in the case of sliding on the EB irradiated zirconia surface at energy density of more than 7.5J/cm². The results imply that the wear behavior on the zirconia surface is changed after the EB irradiation at high energy density condition, since the ball smoothly slides on the EB irradiated surface at higher energy density.

Meanwhile, as shown in the surface profiles of wear track on zirconia surface, width and depth of wear track become smaller on the EB irradiated surface at energy density of less than 7.5J/cm², compared with that on the ground surface. However, the width and depth of wear track increase as the energy density increases from 7.5 to 12.5J/cm². Then, the worn amount $S_w$ was measured by calculating the cross sectional area of wear track as shown in Fig. 9.

Figure 10 shows variations of worn amount on the zirconia surface with various energy densities. The worn amount significantly decreases on the EB irradiated surface at energy density of less than 7.5J/cm², compared with the ground surface. Then, the worn amount of EB irradiated surface at $E_d=5.0\text{J/cm}^2$ becomes smallest and almost half of ground surface. On the other hand, the worn amount again increases at high energy density of more than 7.5 J/cm².

It is concluded that the wear resistance of zirconia surface significantly improves by the large-area EB irradiation under appropriate energy density. One of the reasons for improvement of wear resistance is the increment of mean width and reduction of coefficient of friction for zirconia surface by the EB irradiation under appropriate energy density.

3.4 Transformation of Crystal Structure

Experimental results shown above indicate that the wear resistance of zirconia surface improves at appropriate energy density of EB, while it decreases at higher energy density. It is considered that the excessive energy density of EB leads to transformation of crystal structure of zirconia surface due to thermal effect. It may also lead to surface deterioration. Therefore, the crystal structure of zirconia surface was analyzed by thin film X-ray diffraction (XRD) method.

Figure 11 shows XRD spectra of zirconia surface before and after the large-area EB irradiation with various energy densities. As shown in the figure, the non-EB irradiated surface has tetragonal and monoclinic phases, and it does not change after the EB irradiation at the energy density of less than 5.0J/cm². On the other hand, only tetragonal phase can be detected at the energy density of more than 7.5J/cm². In general, 3mol% yttria partially stabilized zirconia has tetragonal and monoclinic
phases. Existence of monoclinic phase prevents generation of micro-cracks into the zirconia surface, and high wear resistance can be realized for the zirconia. Then, it is reported that transformation of crystal structure from monoclinic phase to tetragonal one is caused by raising the temperature of zirconia at about 1443K.

Therefore, it is considered that the micro-crack generation and decrease of wear resistance on the EB irradiated zirconia surface at higher energy density are caused by transformation of crystal structure from monoclinic phase to tetragonal one due to the thermal effect of excessive energy density of EB. In other words, the crystal structure of zirconia can be maintained by the EB irradiation under appropriate energy density, and improvement of wear resistance for zirconia can be realized by the EB irradiation.

4. CONCLUSIONS

In this study, improvement of wear resistance for zirconia was proposed by large-area EB irradiation. Surface topography and crystal structure of EB irradiated zirconia surface were evaluated in order to discuss change of wear resistance for the zirconia. Main conclusions obtained in this study are as follows;

1) Mean width in roughness curve of EB irradiated zirconia surface increases with increasing energy density of EB, although maximum height in surface roughness is almost same as the ground surface before EB irradiation.

2) Coefficient of friction decreases with increasing energy density, since SiC ball smoothly slides on the EB irradiated zirconia surface due to increment of mean width in roughness curve at higher energy density.

3) Wear resistance of zirconia significantly improves by large-area EB irradiation under appropriate energy density.

4) Excessive energy density of EB leads to decrease of wear resistance for zirconia, since crystal structure of zirconia surface is changed from monoclinic phase to tetragonal one due to the thermal effect of EB irradiation.

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REFERENCES

[1] C. Piconi, G. Maccario: Zirconia as a ceramic biomaterial, Biomaterials, 20 (1999) 1-25.
[2] M.S. Suh, Y. H. Chae, S.S. Kim: Friction and wear behavior of structural ceramics sliding against zirconia, Wear, 264 (2008) 800-806.
[3] Y. Uno, A. Okada, K. Uemura, P. Raharjo, T. Furukawa, K. Karato: High efficiency surface finishing process for metal mold by large-area electron beam irradiation, Precision Engineering, 29 (2005) 449-455.
[4] D.I. Proskurovsky, V.P. Rotshtein, G.E. Ozur: Use of low-energy, high-current electron beams for surface treatment of materials, Surface and Coatings Technology, 96 (1997) 117-122.
[5] Y. Daichi, S. Sano, Y. Uno, A. Okada: Surface finishing of SKD11 tool steel via plasma-based electron beam irradiation, Key Engineering Materials, 364/366 (2007) 302-307.
[6] J.W. Murray, P.K. Kinell, A.H. Cannon, B. Bailey, A.T. Clare: Surface finishing of intricate metal mould structures by large-area electron beam irradiation, Precision Engineering, 37 (2013) 443-450.
[7] A. Okada, Y. Uno, N. Yabushita, K. Uemura, P. Raharjo: High efficient surface finishing of bio-titanium alloy by large-area electron beam irradiation, Journal of Materials Processing Technology, 149 (2004) 506-511.
[8] J.C. Walker, J.W. Murray, M. Nie, R.B. Cook, A.T. Clare: The effect of large-area pulsed electron beam melting on the corrosion and microstructure of a Ti6Al4V alloy, Applied Surface Science, 311 (2014) 534-540.
[9] T. Shionaga, A. Okada, H. Liu, M. Kimura: Magnetic fixtures for enhancement of smoothing effect by electron beam melting, Journal of Materials Processing Technology, 254 (2018) 229-237.
[10] A. Okada, R. Kitada, Y. Okamoto, Y. Uno: Surface modification of cemented carbide by EB polishing, CIRP Annals, 60/1 (2011) 575-578.
[11] A. Okada, Y. Okamoto, Y. Uno, K. Uemura: Improvement of surface characteristics for long life of metal molds by large-area EB irradiation, Journal of Materials Processing Technology, 214 (2014) 1740-1748.
[12] I. Nettleship, R. Stevens: Tetragonal zirconia polycrystal (TZP) - A review, International Journal of High Technology Ceramics, 3/1 (1987) 1-32.
[13] R.N. Patil, E. C. Subbarao: Monoclinic-tetragonal phase transition in zirconia: mechanism, pretransformation and coexistence, Acta Crystallographica Section A, 26/5 (1970) 535-542.