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Fundamental study on sputter deposition of ceramic film
by large-area electron beam irradiation

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Abstract

The sputter deposition of ceramic film on metal mold steel surface by large-area electron beam (EB) irradiation was discussed. The large-area EB has high energy density enough to generate plasma above the workpiece surface during the surface smoothing process, which causes the sputtering of target material set near the workpiece surface. The sputter deposition of target material with simultaneous surface melting and resolidification of workpiece surface by large-area EB would improve the adhesion between the deposited film and the workpiece. Short ceramic tube made of alumina or zirconia as a target was put on the substrate surface of steel, and large-area EB was irradiated to the surface. The workpiece surface component and structure after the irradiation were investigated using EDX and XRD analysis, in order to discuss the possibility of large-area EB irradiation as a new coating method.

Keywords: Large-area EB, Sputter deposition, alumina, zirconia, hardness

1. Introduction

Recently, many surfacing processes, such as coating, surface modifying, and surface texturing, have been widely applied to the industrial products. By these surface processes, the surface functions including hardness, wear resistance, corrosion resistance, friction coefficient, or repellency can be improved, which leads to high value-added productions, the lifetime extension of products, and resource saving.

One of the practical surfacing processes is a sputter deposition \cite{1}, in which the sputtered target material is deposited on the substrate surface. Differently from electroplating and ion coating used widely, alloys and insulating materials also can be deposited on the substrate surface. Furthermore, the substrate material can be metals, alloys, insulators, and plastics because of its relatively low process temperature. However, the adhesion of film to the substrate surface is not so strong, and there remains the problem of the film peeling.

In order to solve the problem, the possibility of large-area electron beam (EB) irradiation as a sputter deposition was discussed in this study. In large-area EB irradiation method, EB with very high energy density can be obtained without focusing the beam \cite{2}, \cite{3}. Therefore, large-area EB of 60mm in diameter can be used for instant melting and evaporation of the material surface. Then, our previous studies \cite{2}, \cite{4} clarified that high efficient surface smoothing of metal mold made of steel, or cemented carbide is possible by the large-area EB irradiation. Also this method can be applied to the surface finishing of such biomaterials as stainless steel \cite{5} and titanium alloy \cite{6}.

During the large-area EB irradiation, plasma generates above the substrate surface because of its high energy density of EB. This phenomenon would cause the sputtering of target material set near the substrate surface. If the target material deposits on the substrate surface simultaneously with the surface melting and resolidification of substrate material by large-area EB, the adhesion between the deposited film and the substrate surface would be very strong.
Short ceramic tube made of alumina or zirconia as a target was put on the substrate surface of metal mold steel, and large-area EB was irradiated to the surface from above. The substrate surface component and structure after the irradiation were investigated using EDX and XRD analysis in order to discuss the possibility of large-area EB irradiation as a new coating method. Furthermore, the effect of EB conditions was discussed.

2. Experimental Procedure

2.1. Large-area EB irradiation apparatus

Fig.1 shows schematic diagram of large-area EB apparatus (Sodick PF-00A) used in this study [3], [7], [8]. The operating chamber is filled with an argon gas of about 10⁻³Pa. At first, a magnetic field is generated by the solenoid coil mounted on the outer side of the chamber. When the magnetic field reaches maximum intensity, a pulse voltage is applied to the ring anode placed in the middle of chamber. In the chamber, electrons are generated by the Penning effect, and move towards the anode. Simultaneously, a Lorentz force is applied to the electrons, which causes the electrons to move spirally, and so plasma generates near the ring anode. When the plasma intensity reaches maximum, a pulse voltage is applied to the cathode set on the top. The electrons are accelerated by high electric field due to electric double layer formed near the cathode, and an explosive electron emission [9] occurs.

By this mechanism, high energy density EB can be generated without focusing the beam. Then, large-area EB of 60mm in diameter can be used for instant melting and evaporation of the workpiece surface. In this system, the EB irradiation is carried out in a series of pulses, and the pulse duration is only a few microseconds.

2.2. Experimental set-up

Fig.2 shows the experimental set-up for examining the possibility of ceramic coating by large-area EB irradiation. The workpiece material is alloy tool steel SKD11 (in JIS) used widely as a metal mold. Ceramic tube of 20mm in diameter was used as target, and put on the steel surface. The inner diameter of the tube is 16mm. When the possibility of ceramic film formation was investigated with varying the inner diameter of the tube, the diameter of 16mm was better to form the ceramic film with uniform thickness under these EB conditions. When the diameter was wider, it was impossible to obtain uniformly thick films. Thus, this tube shape is applied in this work. A Jig holder block made of SKD11 was fixed to the workpiece plate with small screws in order to keep the ceramic tube from moving with the impact of EB irradiation. Large-area EB is irradiated from above, as shown in the figure. In this study, two types of ceramics tube target were used. One is alumina Al₂O₃ and another is zirconia ZrO₂. In Table 1, the mechanical and thermal properties of these ceramics tubes are listed. Alumina has high hardness and high wear-resistance. Zirconia (yttria stabilized zirconia, YTZ) has high wear-resistance and high heat-resistance.

The workpiece surface before EB irradiation was ground, and its surface roughness was controlled in 2.0±0.5μmRz. The pulsed EB was irradiated to the workpiece with varying the energy density of EB and the number of pulse. Large-area EB irradiating conditions are shown in Table 2.

![Fig.1 Large-area EB irradiation apparatus](image1)

![Fig.2 Experimental set-up](image2)

<table>
<thead>
<tr>
<th>Ceramics</th>
<th>Alumina</th>
<th>Zirconia (YTZ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition formula</td>
<td>Al₂O₃:99.6%</td>
<td>ZrO₂:95%</td>
</tr>
<tr>
<td>Hardness Hv</td>
<td>2,200</td>
<td>1,300</td>
</tr>
<tr>
<td>Thermal expansion coefficient 1/K</td>
<td>8.1×10⁻⁶</td>
<td>10.4×10⁻⁶</td>
</tr>
</tbody>
</table>

| Pulse duration \(D_p\) μs | 2 |
| Pulse frequency \(F_p\) Hz | 0.125 |
| Energy density \(E_d\) J/cm² | 2.0 -15.0 |
| Number of pulse \(N\) shot | 5 -30 |
3. Deposition Mechanism

As shown below, alumina and zirconia coating film could be successfully formed by the large-area EB irradiation. The expected coating mechanism in this method is shown in Fig. 3. Considering the fact that the composition and structure of the ceramic can almost be kept even in the coating layer, sputter deposition phenomenon probably occur in the following way.

First, when the large-area EB is irradiated to the substrate surface from above, the surface is rapidly heated up with high energy density of EB, and the surface material rapidly evaporates. Furthermore, the electrons in the beam collide with the generated vapour molecules. Consequently, the plasma is generated from the vapour. Or, the plasma is directly generated from the substrate material by ionization due to high energy of beam when the energy density of EB is sufficiently high.

Next, some of ions in the generated plasma collide with the internal wall surface of ceramic tube, and the ceramic is sputtered. The plasma generates inside the pipe which restricts the plasma expansion and leads to efficient sputtering.

Then the sputtered ceramic deposits to the substrate surface. At this time, it is guessed that the substrate surface is melting by large-area EB irradiation. Therefore, some of sputtered ceramic may be mixed with melted substrate material on the surface. Due to this mechanism, strong adhesion of the deposited film with the substrate surface is highly expected.

4. Results and Discussion

4.1. Surface element and structure

In order to investigate the surface structure, SEM observation and energy dispersive X-ray spectroscopy (EDX) analysis were firstly undertaken. Fig. 4 shows the EDX mapping analysis of the substrate surface after EB irradiation. The EB conditions are 7J/cm² and 30 shots, which are optimum condition for surface smoothing of SKD11 surface. As can be seen from the figure (a), large amount of aluminium and oxygen are detected and they are uniformly distributed on the surface after EB irradiation. Similarly, when zirconia tube is used as a target, zirconium and oxygen are uniformly distributed on the surface as shown in (b).

Next, the elemental content of the treated surface and the effects of EB irradiating condition were discussed. Fig. 5 show the elemental contents by EDX analysis with the number of EB irradiation for various energy densities when alumina tube is used as a target. At least 3 samples under each EB condition were analyzed here, and the small dispersions of values were confirmed. When the ceramic target tube is used, the energy density of EB and the number of irradiation are expressed with $E_d$ and $N$, respectively in the following figures. $E_d$ and $N$ show those in the case of normal EB irradiation without ceramic target tube.

In the case of lower energy densities of EB or smaller number of irradiation, aluminium and oxygen contents are small. On the other hand, they become larger with the number of irradiation in the case of higher energy densities. Then, it is considered that larger EB energy condition promotes the vaporization of substrate material, the sputtering of alumina, and the deposition to the surface. Also, under any EB irradiating conditions, the elemental ratio of aluminium and oxygen is almost 2:3, which is the same ratio as alumina $\text{Al}_2\text{O}_3$. Therefore, alumina film deposition by the large-area EB irradiation is highly expected without decomposition of alumina.

Fig. 6 shows the elemental contents when zirconia tube is used as a target. Also in the case of zirconia tube.
zirconium and oxygen contents on the surface become larger with the number of irradiation in the case of higher energy densities. The ratio of zirconium to oxygen is close to 1:2 of the ratio of zirconium $\text{ZrO}_2$. However, amount of zirconia content (zirconium and oxygen content) deposited on the substrate surface is a little smaller than that in the case of alumina under each EB condition.

In order to verify the surface structure of deposited layer, X-ray diffraction analysis was carried out. Fig.7
shows XRD spectra of EB irradiated substrate surface using alumina target tube. Before EB irradiation, detected peaks indicate structure of SKD11 as substrate. On the other hand, alumina peak could be obviously detected besides the peaks resulting from SKD11. Fig.8 shows the XRD spectra using zirconia tube. Similar to the case using alumina tube, zirconia peak can be confirmed clearly.

From these results, it was made clear that alumina or zirconia film could be readily formed on the metal mold steel surface by using the large-are EB irradiation with ceramic target tube.

4.2. Surface roughness and hardness

Small surface roughness of deposited ceramic surface will be needed for practical application of this technique. Then, the surface roughness was discussed. Fig.9 shows the surface roughness curves of zirconia deposited surface under various EB conditions. The surface undulation seems to increase with increasing number of pulse under low energy density condition of 2J/cm². Under high energy density of 10 and 15J/cm², the surfaces are rough, regardless of number of pulse.

The variations of surface roughness of zirconia deposited surface for various EB conditions are shown in Fig.10. As shown in the graph, the surface roughness in the case of 2J/cm² is slightly larger than the substrate surface before EB irradiation. In the cases of large energy densities 7 and 12J/cm², the surface roughness becomes larger. When alumina deposited surface is made using alumina target tube, a similar tendency in surface roughness variation was confirmed. For practical use of this method, further discussion to reduce the surface roughness should be done.

Ceramics is one of the hard materials, and so improvement in the surface hardness is expected. The surface hardness was tested using a micro Vickers hardness tester. Fig.11 shows variations of surface hardness with the number of pulse for various energy densities. In our previous works, it was clarified that the surface hardness of alloy tool steel SKD11 decreases by
large-area EB irradiation.

In the graph, open marks indicates the surface hardness of EB irradiated SKD11 surface without ceramics target tubes. As shown in the graph (A), the drop in surface hardness of SKD11 by about 100 Hv is again confirmed by EB irradiation without alumina target tube. This is because the SKD11 surface is subjected to high temperature during EB irradiation. On the other hand, the surface hardness values of alumina deposited surfaces using alumina target tube are higher than those of EB irradiated SKD11 surface. Also, they are almost the same as that of ground surface before EB irradiation in the case of 2 and 7 J/cm². In the case of 12 J/cm², the surface hardness of alumina deposited surface is higher than that of ground SKD11 surface. For zirconia deposited surface shown in (B), similar variations of surface hardness can be obtained. Since thin ceramics layer must be deposited on the SKD11 surface by large-area EB irradiation, the surface hardness could be kept or improved.

However, the thickness of deposited layer seems to be very thin, and it is generally difficult to accurately measure the real surface hardness by the Vickers hardness tester. Then, the estimation of real surface hardness was tried by investigating the variation of hardness with changing the indentation load. Fig.12 shows the variation of surface hardness of ceramics deposited surface with indentation load. As the load becomes smaller, the surface hardness increases in both cases of alumina and zirconia target tubes. The real surface hardness values can be expected from the variation, and they are about 1950 Hv and 1500 Hv respectively. These hardness values almost agree with the original hardness of alumina and zirconia. This result also indicates that the surface is certainly coated with alumina or zirconia thin layer.

5. Conclusions

In this study, sputter deposition of ceramic film by large-area EB irradiation was tried. The experimental results showed that sputter deposition of ceramic on the metal mold steel surface with uniform thickness was possible by large-area EB irradiation with ceramic target. The amount of ceramics deposition layer can be controlled with EB conditions. Also, the surface hardness could be increased.

References