Study on Metal Film Formation by Large-area Electron Beam Irradiation

Togo Shinonaga*, Masashi Takata*, Akira Okada*, Sadao Sano**
(Received Dec.24, 2015)
* Graduate School of Natural Science & Technology, Okayama University, Okayama 7008530, Japan
** Machining Center Division, Sodick Co., Ltd, Yokohama 2248522, Japan

Abstract

Recently, many surfacing processes, such as coating have been widely applied to the industrial products in order to improve the surface functions. One of the practical surfacing processes is a sputter deposition, in which the sputtered target material is deposited on the substrate surface. This method can be used not only for metals but also for insulators and plastics materials as substrate surface. In this study, the possibility of sputter deposition by using a large-area electron beam was discussed. 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 strong. Alloy tool steel SKD11 was used as a substrate material, and pure metal tube made of nickel or titanium were used as a target material. Then, the substrate surface after EB irradiation was analyzed and the surface characteristics were investigated.

Key words: Large-area electron beam, Film formation, Sputter deposition, Pure metal

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 1), in which the sputtered target material is deposited on the substrate surface. This method can be used not only for metals, alloys, insulators, but also for plastics substrate materials because of its relatively low process temperature.

On the other hand, in large-area electron beam (EB) irradiation method, EB with very high energy density can be obtained without focusing the beam 2), 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 2), 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 5) and titanium alloy 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, compared with the conventional methods. In this study, the possibility of sputter deposition by using large-area electron beam irradiation using target material was experimentally discussed.

Short metal tubes made of nickel and titanium as a target were 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, TEM and XRD analysis in order to discuss the possibility of large-area EB irradiation as a new coating method. Moreover, corrosion resistance and water contact angle were examined to investigate the surface function of the film.

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). The operating chamber is filled with an argon gas of about 10⁻² Pa. 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 of 100mm in diameter consisting of the titanium wire aggregate. The electrons are accelerated by high electric field due to electric double layer formed near the cathode, and an explosive electron emission occurs.

By this mechanism, high energy density of EB can be generated without focusing the beam. Then, large-area EB of 60mm in effective 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. The large-area EB irradiating conditions in this experiment are shown in Table 1.

| 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 | 2 -50 |

2.2 Experimental Set-up

Fig. 2 shows the experimental set-up for examining the possibility of metal film coating by large-area EB irradiation. The workpiece material is alloy tool steel SKD11 (in JIS specifications) used widely as a metal mold. Metal tube was used as target, and put on the steel surface. The inner diameter of the tube is 16mm, and the outer 18mm, since the primary experiments showed that the inner diameter of about 15-20mm was optimal to form the film with uniform thickness. The tube target is intended to limit the plasma generating on the workpiece surface and the sputtered metal in only the tube inside. A jig holder block made of SKD11 was put on the workpiece plate to keep the target metal tube from moving with the impact of EB irradiation. Large-area EB is irradiated from above, as shown in the figure. In this study, pure Ni and Ti were used as the metal tube.

3. DEPOSITION MECHANISM

As shown below, titanium and nickel films 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 plasma generates just on the substrate surface during large-area EB irradiation, sputter deposition phenomenon probably occurs in the following way.

First, when the large-area EB is irradiated to the substrate surface from above, the substrate 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 vapor molecules. Consequently, the plasma is generated from the vapor. Next, some of ions in the generated plasma collide with the internal wall surface of target metal tube, and the metal is sputtered. The plasma generates inside the tube, which restricts the plasma expansion only to the inside and leads to efficient sputtering. Then, the sputtered metal deposits to the substrate surface. At this time, it is guessed that the substrate surface is still melting by the large-area EB irradiation. Therefore, some of sputtered metal may be mixed with melted substrate material on the surface. Due to this mechanism, a strong adhesion of the deposited film with the substrate surface is highly expected.

4. NICKEL FILM COATING

4.1 Surface Element and Structure

In order to check the possibility of nickel coating by large-area EB, SEM observation and energy dispersive X-ray spectroscopy (EDX) analysis of the substrate surface were firstly undertaken. Fig. 4 shows the EDX mapping analysis of the substrate surface after EB irradiation. The EB conditions were 71/cm² and 30shots, which are optimum condition for surface
smoothing of SKD11 substrate surface. As shown in the figure, the substrate surface seems to be smooth. It was confirmed that the surface roughness after the large-area EB irradiation was almost same or a little smaller, compared with that of ground surface before irradiation. Furthermore, nickel element can be newly detected and it is uniformly distributed on the surface after EB irradiation.

Next, the elemental content of substrate surface and the effects of EB irradiating condition were discussed. Fig. 5 shows the variations of elemental contents by EDX analysis with the number of EB irradiation when a nickel tube was used as a target. The nickel content increases with number of EB irradiation. When the number of EB irradiation is 40 shots under 15 J/cm², the nickel content reaches 30%. On the other hand, the ratio of chromium to iron hardly changes with the number of irradiation, and keeps the original ratio of substrate material. In addition, it was confirmed that the nickel content increased also with the energy density of large-area EB. Therefore, it is considered that the film thickness would be controlled by these large-area EB conditions and large amount of nickel film can be formed on the substrate surface with high number of EB irradiation or high energy density.

Fig. 6 shows TEM and each element images of the cross-section of nickel coated film on the substrate surface by large-area EB with nickel target. The border just below carbon layer deposited for the preparation of TEM observation is the film surface. Almost uniform nickel film of about 500 nm in thickness can be formed by EB irradiation. Also, the coated film surface is very smooth. In addition, at the interface between nickel film and substrate, nickel element seems to diffuse into the substrate. Furthermore, large grain of chromium carbide cannot be detected near the surface, which indicates that substrate surface was melted by EB irradiation and resolidified. The thickness of resolidified layer below nickel surface layer is about 1.0 micron or thicker. From these results,
In order to verify the crystal structure of deposited layer, X-ray diffraction analysis was carried out. Fig. 7 is the XRD spectra of the surface before and after large-area EB irradiation. In the case before EB irradiation, the material structure of SKD11 can be detected clearly. On the other hand, nickel and some nickel alloys are detected on the surface after irradiation. The formation of nickel alloy indicates that the substrate surface material and nickel sputtered from the target somewhat mixed at atomic-level when the substrate material resolidified. This agrees well with the TEM observation and element image analysis results of cross section shown above.

4.2 Corrosion Resistance

In order to investigate the corrosion resistance of the nickel coated surface, anode polarization current densities were measured using an electrochemical analysis system. Anodic polarization current is measured when the voltage between the workpiece surface and counter electrode increases from natural potential to maximum potential of 1.5V at a constant potential scan rate of 1mV/s. As an electrolyte, 3% sodium chloride solution was used. Fig. 8 shows the anodic polarization current density curves of the substrate surfaces. For comparison, the current density for pure nickel is also shown. The equilibrium potential for pure nickel is larger than those of other surfaces, which well indicate its high corrosion resistance. The current density for EB irradiated surfaces are smaller than non EB surface at any potentials. Therefore, the corrosion resistance of metal mold surface can be improved by nickel coating with large-area EB. It is also noticed that the equilibrium potential becomes larger with the energy density of EB. This is probably because the nickel content and the nickel coated film thickness increases with the energy density.

4.3 Water Repellency

In order to investigate the water repellency of the nickel coated surface, contact angle of water on the surface was measured. Fig. 9 shows variations of contact angle with the number of EB irradiation when a nickel tube was used as a target. For comparison, the contact angle for pure nickel is also shown. Under any EB conditions, the high contact angle could be obtained as compared with the before EB irradiation. When the energy density was changed from 2 to 7J/cm², the contact angle becomes larger. In the case of 7J/cm², it was confirmed that a large quantity of nickel component was coated uniformly on the substrate surface as compared with the low energy density.

On the other hand, when the energy density was 15J/cm², the contact angle becomes smaller in comparison with other conditions. When the energy density was high, a crater and crack were generated, and surface roughness slightly increased. Therefore, it is expected that the contact angle becomes smaller with increasing the surface roughness, following Wenzel equation (10). From these results, the water repellency can be improved by the nickel film coating.

5. TITANIUM FILM COATING

5.1 Surface Element and Structure

The possibility of titanium film coating was also investigated. Fig. 10 shows SEM and EDX mapping images of the substrate surface after large-area EB with using a titanium target tube. Similarly to the
nickel coating shown above, the substrate surface after EB irradiation is smooth and titanium element is distributed uniformly on the surface.

Fig. 11 shows the variations of elemental contents by EDX analysis with the number of EB irradiation when a titanium tube was used as a target. The titanium ratio on the surface increases with the number of EB irradiation. When the number of EB irradiation is sufficiently large, the ratio exceed 40%. Therefore, thick titanium film could be formed on the substrate surface by large number of EB irradiation or high energy of EB.

Fig. 12 shows TEM and each element images of the cross-section of titanium coated film on the substrate surface by large-area EB. As shown in the figure, the titanium was coated on the workpiece, and the maximum thickness was about 1.0μm. However, titanium content distribution in the resolidified layer is not so uniform, although a very thin surface layer with high titanium content can be observed on the surface. In addition, at the interface between the resolidified layer and substrate, titanium element seems to diffuse into the substrate. Furthermore, large grain of chromium carbide cannot be detected near the surface, which indicates that substrate surface was melted by EB irradiation and resolidified. Therefore, it is considered that the substrate surface material and titanium sputtered from the target somewhat mixed at atomic-level when the substrate material resolidified. Then, the strong adhesion of the film to substrate surface can be expected.

XRD spectra of the surface before and after large-area EB irradiation with titanium target tube is shown in Fig. 13. As shown in the figure titanium and some titanium alloys are detected on the surface after EB irradiation, apart from the original substrate structures.

5.2 Corrosion Resistance

Fig. 14 shows the anodic polarization current density curves of the titanium coated surface. For comparison, the current density for pure titanium is also shown. The equilibrium potential for pure titanium is larger than those of other surfaces, which indicate its high corrosion resistance. The current density for EB irradiated surfaces are smaller than non
EB surface at any potentials. From these results, it was made clear that the corrosion resistance of metal mold surface can be improved by this coating method with large-area EB.

Furthermore, when the energy density was 7J/cm², the equilibrium potential is the largest in comparison with other conditions. This is probably because the uniform coated surface is obtained as compared with the high energy density.

6. CONCLUSIONS

In this study, metal film coating is conducted by large-area EB irradiation. Then, substrate surface component and structure are investigated with EDX, TEM and XRD analysis. Furthermore, surface function such as corrosion resistance and water repellency were examined. Main conclusions obtained in this study are as follows.

(1) Ni and Ti film coatings on the metal mold steel surface are possible by large-area EB irradiation, using target tube.

(2) Ni and Ti components on the coated surface increases with number of irradiation and energy density of EB.

(3) Ni and Ti elements seem to diffuse into the substrate. Large grains of chromium carbide cannot be detected near the substrate surface, which indicates that substrate surface is melted and resolidified, when the target materials are deposited.

(4) The formation of metal alloys indicates that the substrate surface and metal sputtered from the target somewhat mix at atomic-level when the substrate material is resolidified.

(5) The corrosion resistance and water repellency of substrate surface can be improved by metal film coating with large-area EB irradiation.

REFERENCES

1) Wasa, K., Hayakawa, S., 1992, Handbook of sputter deposition technology, Noyes Publications, Park Ridge.

2) Uno, Y., Okada, A., Uemura, K., Raharjo, P., 2005, High Efficiency Finishing Process for Metal Mold by Large-area Electron Beam Irradiation, Precision Engineering 29/4, pp.449-455.

3) Uno, Y., Okada, A., Uemura, K., Raharjo, P., 2006, Method for Surface Treating a Die by Electron Beam Irradiation and a Die Treated Thereby, United States Patent, 2006, US 7,049,539 B2.

4) Okada, A., Kitada, R., Okamoto, Y., Uno Y., 2011, Surface modification of cemented carbide by EB polishing, CIRP Annals Manufacturing Technology 60/1, pp.575-578.

5) Okada, A., Uno, Y., McGeeough, J.A., Fujiwara, K., Doi, K., Uemura, K., Sano, S., 2008, Surface Finishing of Stainless Steels for Orthopedic Surgical Tools by Large-area Electron Beam Irradiation, CIRP Annals 57, pp.223-226.

6) Okada, A., Uno, Y., Uemura, K., Raharjo, P., McGeeough, J.A., 2007, Surface Modification for Orthopaedic Titanium Alloy by Wide-area Electron Beam, IMechE J. of Engineering Manufacture 221, pp.173-178.

7) Proskurovsky, D.I., Rotshtein, V.P., Ozur, G.E., 1997, Use of Low-energy High-current Electron Beams for Surface Treatment of Materials, Surface and Coating Technology, 96/1, pp.117-122.

8) Proskurovsky, D.I., Rotshtein, V.P., Ozur, G.E., Ivanov, Yu.F., Markov, A.B., 2000, Physical Foundations for Surface Treatment of Materials with Low Energy High Current Electron Beams, Surface and Coating Technology, 125/1-3, pp.49-56.

9) Mesyats, G.A., 1998, Explosive Electron Emission, URO-Press, Ekaterinburg, p.248.

10) Wenzel, R.N., 1936, Resistance of Solid Surfaces to Wetting by water, Ind. Eng. Chem., 28/8, pp. 988-994.