Plasma Anodic Oxidation Technology and Coating Properties

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Light metals such as aluminum are widely used as part materials for the purpose of weight reduction. Because of the increasingly severe environment in which such parts are used, requirements have increased for materials and surface treatments to improve wear resistance. This report introduces an anodic oxidation technology essential to improving light metal properties, an advanced surface treatment technology called plasma anodic oxide coating and its basic properties. The coating on aluminum alloys obtained by the plasma anodic oxidation is smooth and possesses high hardness of Hv 1 000 and high wear resistance.

***Key Words**: aluminum, anodic oxidation, plasma anodic oxidation, friction, wear*

1. Introduction

From the viewpoint of global environmental conservation such as CO_2 emission reduction, environmental protection, natural resources saving, energy saving and new energy development, technology development has been actively promoted. The current main targets are low fuel consumption, reduction of friction loss, high durability, compactness and light weight. For example, in case of automobiles (petrol engines) of which weight ranges from 1 to 1.5 tons, weight reduction by 100 kg is reported to improve fuel consumption by about 1 km/L[1]. It is well known that this brings a significant benefit to the environment. From this point of view, adoption of light metal materials like aluminum is a very useful means for improvement of product characteristics and the global environmental conservation, which is now widely applied in the various industry sectors including automotive industry[2].

Aluminum is so light as one third of the specific gravity of iron and has a high specific tensile strength. Alloying aluminum with silicon (Si), magnesium (Mg), copper (Cu) and so on can improve its characteristics. Various types of surface treatment are often applied for further improvement of the characteristics[3]. When aluminum is used for mechanical applications, an anodizing may be applied in order to ensure high durability. Recently, particular attention has been given to a technology that can add multiple functions to an anodic oxide coating. One of them, for example, is that the coating can be made capable of self-lubrication by applying treatment of solid lubricants such as molybdenum disulfide or polytetrafluoroethylene (PTFE) after the anodizing. Thus a variety of technological developments are now under way[4].

As the application of light metal materials is expanding and the operating conditions become more severe, the necessity arises for a surface treatment technology that can provide high hardness and high wear resistance. High Si-containing aluminum alloys are superior in wear resistance, but they have difficulty in accepting an anodizing because crystals of Si inside the base material prevent an anodic oxide coating from being formed[5]. Therefore, it is now necessary to develop a new technology of surface treatment in which even the alloys mentioned above can be treated without difficulty.

One of the recent developments is an anodizing using plasma technology (a plasma anodic oxidation)[6]. The plasma anodic oxidation is capable of forming a ceramic surface coating with hardness higher than that of the anodic oxide coatings and is compatible with high Si-containing aluminum alloys that make the anodizing difficult. This report covers the evaluation results of the basic properties and tribological characteristics regarding the plasma anodic oxide coatings as well as the details of the plasma anodic oxidation.

2. Anodic Oxide Coating

The anodizing is a method for using electrolysis in an electrolytic solution such as aqueous sulphuric acid solution with a metal as an anode to form a coating (**Fig. 1**)[7]. At the surface of the aluminum (anode), the aluminum itself reacts with the oxygen generated in the solution by electrolization, which forms an oxide coating on the surface. It forms first a thin coating of 100 nm in thickness called the barrier layer. Secondly, it causes dissolution of the aluminum in some areas. Thirdly it builds an oxide on the barrier layer and finally it forms an anodic oxide coating having a porous membrane of several tens of μm thick. As a result, the coating finally formed has high adhesiveness and superior hardness to the base material. The new coating is inferior in corrosion resistance and smoothness because of the porous anodic oxide coating. As a general practice, to rectify this inferiority, sealing (a treatment which exposes the coating to boiling water or hot vapor and then generates hydrates to seal the coating) and smoothing treatments are applied. The anodizing is also applicable to ceramics as well as other light metals such as titanium, magnesium, and zirconium.

The main component of the aluminum anodic oxide coatings formed through anodizing is alumina (Al_2O_3), which is chemically stable having a hardness of Hv 300 to 600 and is durable against abrasive wear. However, its capability for lubrication is poor and it is weak in shock and repeated stress.

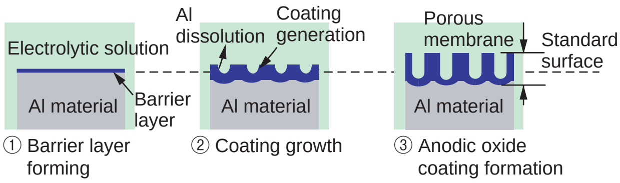

Fig. 1 Process of anodic oxide coating formation

3. Plasma Anodic Oxide Coating

3. 1 Plasma Anodic Oxidation

Plasma anodic oxidation is used for light metals including such metals that cannot be treated well by anodizing, and it has a feature of forming smooth surface coating with high hardness of Hv 1 000[6]. This treatment also uses metal as an anode, applies high voltage in the electrolytic solution containing zirconium and then forms coating in a state of arc discharge (**Fig. 2**). In the process of this treatment, a ceramic coating is also formed from zirconium salt contained in the solution, resulting in a hard and smooth coating. Changing the conditions of treatment allows this treatment to adjust the coating thickness and surface roughness.

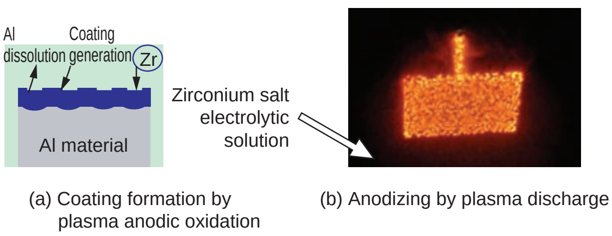

Fig. 2 Formation of plasma anodic oxide coating

3. 2 Formation of Plasma Anodic Oxide Coating and Coating Properties

Six different types of the plasma anodic oxide coatings were formed under different conditions by the use of high Si-containing aluminum casting (equivalent to ADC14 material). The coatings obtained were measured for thickness by an eddy current thicknessmeter, hardness by a micro hardness tester and surface roughness by a roughness gauge. In addition, the coating structure was analyzed by X-ray diffraction and the structures of both its surface and cross-section were visually observed and analyzed by SEM.

3. 2. 1 Coating Thickness, Surface Roughness and Hardness

As shown in **Fig. 3**, there is correlation between the coating thickness and surface roughness regarding the sample coatings, which shows that as the coating thickness increases, the surface roughness tends to be larger. On the other hand, the coating hardness is consistent at Hv 800 to 1 000 regardless of the treatment conditions. No hardness measurements were made for the thin coatings of 8 μm or less in consideration of influence by the base material during the measurement. These results indicate that it is possible to control the coating thickness and surface roughness by changing the treatment conditions with high hardness being maintained.

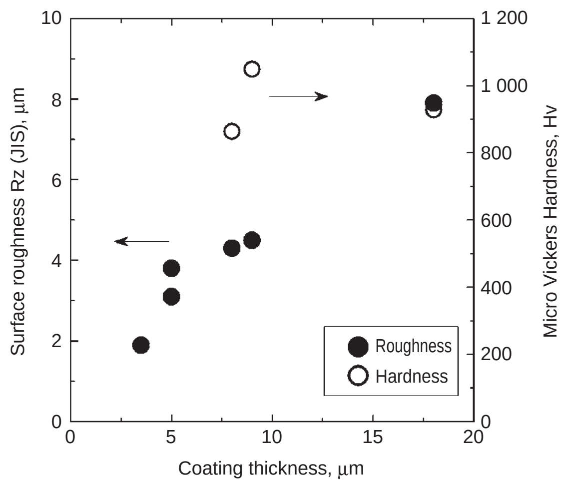

Fig. 3 Relation of surface roughness and hardness with thickness in plasma anodic oxide coating

3. 2. 2 Coating Properties

Figure 4 shows XRD patterns of the plasma anodic oxide coating and a metallic untreated material. Peaks of ZrO_2 as well as Si and Al (base material) are seen on the plasma anodic oxide coating. It is considered that high hardness can be secured through forming a ceramic type coating from ZrO_2 which is a main component of the coating. With regard to the thin coatings which are difficult to measure by XRD analysis, a surface was analyzed by EPMA. This confirmed that Zr is evenly distributed on all over the surface and the coatings are the same no matter how thick each of them may be. The SEM observation results of the plasma anodic oxide coatings are shown in **Fig. 5**. Although micro porosities were found on the surface, there were no voids spanning the entire section from the surface to the base. This is proof of super-micro coatings having been completely formed. The coatings formed by the plasma anodic oxidation are of very smooth and super-micro structures unlike porous anodic oxide coatings.

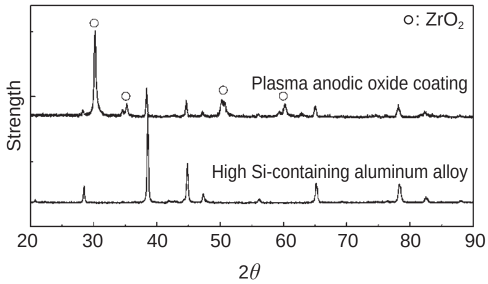

Fig. 4 XRD pattern of plasma anodic oxide coating

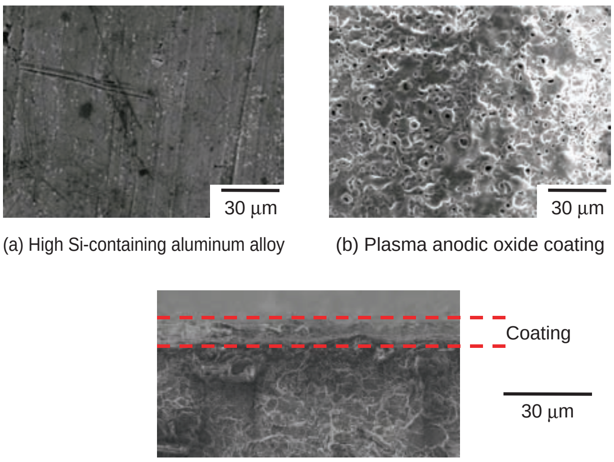

Fig. 5 Observations of plasma anodic oxide coating surface and cross-section

3. 3 Evaluation of Tribological Characteristics of Plasma Anodic Oxide Coating

A tribological characteristics test was carried out on a Ball-on-Disk type friction test machine with the specimens being immersed in mineral oil (viscosity 9.1 × 10^{-7} Pa・s). The sample coatings and the untreated base material (for a comparison purpose) were used for disk specimens (25 × 25mm, 5mm thick). Balls made of SUJ2 (r = 2.2mm, HRC 62 to 66) were used as a mating material. Before the test, these specimens were subjected to ultrasonic cleaning in acetone for 5 minutes and then dried. The test conditions were set up as 30 minutes (total sliding distance: 470 m) at the uniform speed of 250 min^{-1} (rotation radius: 10mm) and under the load of 5 N. After the test, traces of wear on the friction surface were observed by an optical microscope.

Figure 6 shows friction behavior of each coating. The plasma anodic oxide coatings showed constant coefficient of friction in the initial period of friction. Surface observation after the test confirmed very little buckling or wear of the coatings even under the condition of point contact at 5 N, which made it clear that these coatings are superior in wear resistance (**Fig. 7**). On the other hand, in the untreated material, there was a large friction fluctuation, so that it showed inconsistent friction behavior. In addition, the specific wear rate obtained from the cross-sectional shape was so large as 10^{-6} mm^3/N・m. As far as the mating material is concerned, traces of wear were observed on both the plasma anodic oxide coatings and the untreated material, and the specific wear rate tends to be larger in proportion to the surface roughness.

Under the test conditions mentioned above, the plasma anodic oxide coatings showed low and stable friction behavior and have been proved to be superior in wear resistance. On the contrary, aggressiveness against the mating material is found to be in relation to roughness of the coating surfaces and as shown in **Fig. 8**, the relation pattern is very different at Rz 4 μm as a borderline.

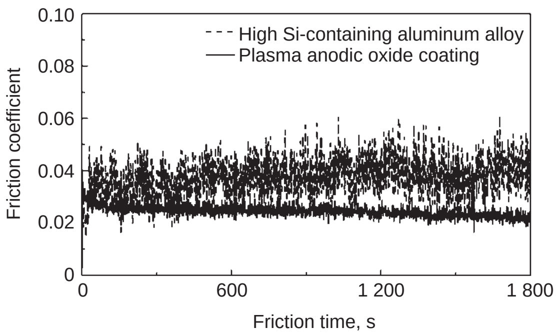

Fig. 6 Friction behavior of plasma anodic oxide coating

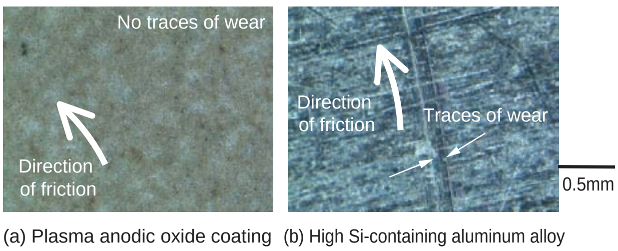

Fig. 7 Observation of wear trace on plasma anodic oxide coating

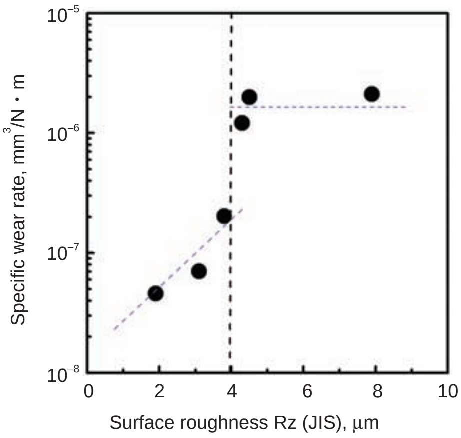

Fig. 8 Relation between roughness of plasma anodic oxide coating and specific wear rate of mating material

In the area under Rz 4 µm, the aggressiveness against the mating material is low, and as the roughness becomes larger, the specific wear rate increases. In the area above Rz 4 µm, the specific wear rate stays at a certain level although the aggressiveness is high. It is considered that with small roughness, the mating material wears in proportion to the roughness as the surface pressure gradually changes and that the roughness being above Rz 4 µm leads to a large amount of wear at an early stage due to the large roughness itself and no additional wear progress exists while the surface pressure decreases. These results indicate the necessity for selecting optimum treatment conditions depending on applications when using the plasma anodic oxidation.

4. Conclusion

The plasma anodic oxidation method makes it possible to provide very hard and smooth coatings to light metal materials. The tribological characteristics of the plasma anodic oxide coatings show a low and constant coefficient of friction in oil lubrication, and a superiority in wear resistance that is useful for improvement in wear resistance of sliding components. The operating requirements for all kinds of products will become increasingly severe. In order to make the products more compact and lighter while maintaining the characteristics, the importance of further improvement in the surface treatment technology as well as material development technology will be increased. The need is arising also for improvement of the base material characteristics and for new functions to be added. It appears that the surface treatment technology such as the plasma anodic oxidation will be widely used.

5. Acknowledgment

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