Metallization of Oxide /Hydroxide Film of Aluminum:  the Palladium Activation Techniques

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Palladium-activation-based techniques for area-selective microscale metallization on porous oxide film of aluminum and complete metallization of the oxide/hydroxide surface of aluminum are demonstrated. For area-selective metallization, a porous anodic oxide film of aluminum was colored in an organic dye solution containing small amounts of palladium acetate. It was then hydrothermally sealed, thereby trapping the palladium acetate underneath the newly formed crystalline hydroxide layer. Removal of the surface hydroxide layer using a laser beam, exposes the palladium acetate, which also undergoes photothermal decomposition and reduction to metallic palladium and acts as a catalytic center for subsequent electroless plating. Similarly, complete metallization of the porous oxide and hydroxide of aluminum were performed by adsorbing palladium acetate onto the surface, followed by electroless nickel plating of the specimen. Here, palladium acetate (on the surface) was first reduced to metallic palladium by the hypophosphite that is present in electroless plating solution, providing a catalytic center subsequent electroless nickel deposition.

**Keywords:** Aluminum Anodizing, Laser-micromachining, Palladium Activation, Electroless Plating, Metallization

1. Introduction

Surface of the aluminum is always covered with oxide film, which is a very good insulator, and isolates the aluminum surface from the outer environment quite effectively. The oxide film on aluminum can also be grown by anodizing of aluminum with thickness up to hundreds of micrometer. Besides the insulation property, such films are highly temperature and chemical resistant as well as it has very good mechanical strength. Taking advantage of such characteristics, various applications of the anodic alumina are reported for past several years, such as in electronic packaging purposes, in fabrication of micro-devices and its components, for hybrid integrated circuit fabrication

Emerging applications of aluminum/ alloy-oxide films and anodic oxide film in various fields of technologies are continuously attracting investigations on its surface finishing, coatings, metal deposition. As most of the processing needs electrochemically active surface, it is often difficult to perform such actions on aluminum surface because of the formation of highly stable, non-conducting oxide film at the surface. In this context, metallic coating on the aluminum surface insulated by natural or synthetic oxide/hydroxide film is worthwhile for the promotion of its application towards more flexible and wide application range.

Electroless plating is one of the extensively used techniques for the deposition of metals/ alloys on variety of surfaces. However, such plating over the insulator surface is limited because of the lack of catalytically active surface that required for the initiation of the electroless deposition. Usually, the catalytic centres on the insulator surface is created by sensitization/ activation in suitable solutions, which finally results in catalytically active sites on the surface for further electroless plating. A number of other methods for the formation of catalytic sites on the insulator surface like polymers, ceramics are reported. However, depending on the substrate material, one activation technique may or may not be effective for others. Accordingly, the authors have reported a novel technique for the micro-scale, area selective metallization on porous anodic oxide film of aluminum, and laser beam is used to selectively expose the active site for the subsequent electroless plating. In that process first the palladium ions impregnated inside the pores and then hydrothermally-sealed, which forms a uniform hydroxide layer on the surface of the film, trapping the palladium ion impregnated zone underneath the surface. Such hydroxide layer, then, selectively removed from the surface by using laser beam exposing palladium on the surface.

This paper describes the palladium activation techniques for the area-selective as well as complete metallization of porous anodic oxide film of aluminum; and the complete metallization of the boiled aluminum specimen surface (i.e. hydroxide film on the surface). In these techniques, first the surface is completely or selectively activated by palladium and then subjected for electroless nickel plating.

2. Experimental

2.1 Area-selective micro-scale metal deposition on porous anodic alumina

Porous anodic alumina was obtained by anodizing electropolished 99.99% pure aluminum sheet in 0.22 mol/dm³ oxalic acid solution at constant current of 100 Am⁻² and temperature 293K for 2h. In the mentioned condition, about 32µm thick, porous type anodic oxide of aluminum was formed, which then coloured with a solution containing 25 vol% of 8.9×10⁻³ mol/dm³ Pd(CH₂COO)₂ solution in CH₃COOH and 75 vol% of 0.029 mol/dm³ Alizarin red-S solution at 333K for 5min. After coloring, the specimens were subjected for hydrothermal pore-sealing in boiling doubly-distilled water for 20 min. Then, the specimens were subjected...
were machined by Q-switched, second harmonic (λ=532nm), 8ns pulsed width, 50Hz frequency, Nd:YAG laser (Spectra Physics; GCR-100). For the micromachining the power of the laser beam was fixed to 2mW. The machining was carried out inside a plastic cell fitted with quartz window and contained electroless nickel plating solution with composition 0.13 mol/dm³ NiSO₄, 0.27 mol/dm³ CH₃COONa, 0.19 mol/dm³ NaH₂PO₄, 0.6ppm Pb²⁺ at pH 4.5 adjusted by H₂SO₄. In order to make different structures (such as mesh and lines) during the laser machining, the cell was switched, second harmonic was used. As-received aluminum sheet were boiled in doubly-distilled water for 15 min to get “boiled aluminum” specimen. Similarly, “anodized aluminum” specimen was obtained after electropolishing as-received aluminum sheet followed by anodizing in 0.22 mol/dm³ oxalic acid solution at 293K for 2h. Both the specimens were first immersed in 8.9 × 10⁻⁴ mol/dm³ Pd(CH₃COO)₂ in 10% CH₃COOH, at 328K for 10 min. After then, the specimens were lightly washed and transferred to electroless nickel plating bath with composition mentioned in section 2.1. The steps for the complete metallization on aluminum oxide/hydroxide surface are schematically presented in Fig. 1.

2. 2 Complete metallization on aluminum oxide/hydroxide surface

Two types of aluminum specimens, “boiled aluminum” and “anodized aluminum” were used. As-received aluminum sheet was removed completely.

2. 3 Analysis

The specimens were characterized by using confocal scanning laser microscope, CSLM (Lasertec, 1LM21D), field emission scanning electron microscope, FE-SEM (JSM-6500F, JEOL), and scanning electron microscope (Miniscope, TM-1000, Hitachi). Similarly, elemental analysis was carried out by electron probe micro-analysis, EPMA (JXA8900, JEOL).

3. Results and Discussion

3.1 Area-selective micro-scale metal deposition on porous anodic alumina

Anodizing of aluminum in oxalic acid solution leads to the formation of porous type anodic oxide film of aluminum. During the coloring of such porous oxide film with alizarin red solution, the dye-stuff adsorb on the surface as well as, to some extent, on the walls of the pores near surface. In the similar fashion, the palladium acetate, which mixed with the dye solution, also adsorbed on the surface as well as inside the pores. When the specimens were boiled in water, crystalline hydroxide of aluminum i.e. boehmite or pseudo-boehmite, formed on the surface and also inside the pores, known as pore-sealing[20,12]. This process leads to the

![Fig. 1](image1.png) Schematics of the techniques for palladium activated area-selective and complete metallization of aluminum oxide/ hydroxide surface. (Not to scale)
Ladium is also occurring due to the presence of hypophosphite about face hydroxide layer in electroless solution, electrochemical reduction to metallic palladium acetate photo-thermally decompose to metallic palladium, at the same time, as the laser micromachining was carried out in nickel electroless plating solution is presented in Fig. 1. Then the deposition was vigorously starts over the specimen surface, as shown in Fig. 2. It can be seen that the metal is deposited continuously and uniformly over the machined area. Since the laser, we used, has Gaussian type energy distribution, it may be possible that the edge of the beam does not have sufficient energy to completely remove the hydroxide layer to expose the palladium. In such cases, the deposition of nickel only takes place at the centre of the machined area, as shown in the right part portion of Fig. 2(a) and magnified view in Fig. 2(b). These results demonstrate the extent of selectiveness of the present metallization technique. However, increasing deposition time all the machined area covered with Ni-P due to lateral expansion during deposition.

Using this method, various types of metallic micro-patterns or structures can be fabricated on the porous anodic alumina, for example, mesh like structure, and parallel lines as shown in Fig. 3. The deposition is uniform and continuous without any observable selectiveness, in the case of complex shaped specimens as shown in Fig. 4. These results demonstrate the extent of selectiveness of the present metallization technique. Laser micromachining of the colored and pore-sealed, porous anodic oxide film is capable of removing the surface hydroxide layer selectively from porous oxide layer. Laser micromachining of the specimen, in the mentioned experimental conditions, found about 1–1.2 μm deep groove on the surface by removing the surface hydroxide layer. When the palladium trapped specimen is subjected for the laser micromachining, the trapped palladium can be exposed by removing the hydroxide layer selectively from the surface. During the laser micromachining, the palladium acetate photo-thermally decompose to metallic palladium, at the same time, as the laser micromachining was carried out in nickel electroless solution, electrochemical reduction to metallic palladium is also occurring due to the presence of hypophosphite.

The details of the phenomena during the laser mechanising inside the electroless plating solution is presented in Fig. 1. Then the micromachined specimens were transferred to the electroless nickel plating bath for the further metallization. Observation shows that, after 5 min of immersion in electroless solution, several nickel domes were formed randomly over the laser machined surface, and gas (hydrogen) evolution can be seen at this stage. After 10 min of immersion in plating bath, the laser machined part is uniformly covered by Ni-P, as shown in Fig. 2. It can be seen that the metal is deposited continuously and uniformly over the machined area. Since the laser, we used, has Gaussian type energy distribution, it may be possible that the edge of the beam does not have sufficient energy to completely remove the hydroxide layer to expose the palladium. In such cases, the deposition of nickel only takes place at the centre of the machined area, as shown in the right part portion of Fig. 2(a) and magnified view in Fig. 2(b). These results demonstrate the extent of selectiveness of the present metallization technique. However, increasing deposition time all the machined area covered with Ni-P due to lateral expansion during deposition.
able defects. On the other hand, such deposition on the anodized aluminum (after electropolishing) appears shiny due to smooth deposited surface, as shown in Fig. 4(c). This is because of the anodizing of electropolished aluminum specimen, which results in the formation of oxide film with smooth surface. Here, also, the deposited Ni-P layer has uniform thickness of about 6 μm, as shown in Fig. 4(d). The deposition is uniform and continuous throughout the porous anodic alumina surface.

Our observation shows that, when a porous oxide film immersed in palladium acetate solution followed by immersion in 0.19 mol/dm$^3$ sodium hypophosphite solution (which present in the nickel electroless solution as a reducing agent) for about 5 min, very fine palladium nanoparticles were found over the oxide film surface, as shown in Fig. 5. The magnified view (in inset) shows that numerous fine palladium particles with comparable size are formed on the surface. Since the observed nanoparticles were very small, measuring about few tens of nanometer, it is very difficult for the mapping or analysis of such nanoparticles by EPMA. Hence, an anodized aluminum specimen with prolonged immersion in palladium activation solution, 30 min at 333K, followed by immersion in hypophosphite solution was prepared, where few big (about 2μm) palladium deposition were observed over the surface as shown in Fig. 6(a). The EPMA elemental mapping of the Al, O, and Pd are shown in Fig. 6(b), (c) and (d) respectively, where it confirm about the palladium particle on the surface.

Based on the above experiments and observations, the palladium activation mechanisms for the metallization process are proposed as describe in Fig. 7. In the case of area-selective metallization, Fig. 7(a), irradiation of laser beam results in the exposure of palladium trapped zone as well as photothermal decomposition and chemical reduction of the palladium acetate to palladium at the laser irradiated part, which acts as a catalytic centre for the subsequent electroless plating. Similarly, in the case of complete metallization, Fig. 7(b), the oxide or hydroxide surface

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Fig. 5 FE-SEM image of the porous anodic oxide film surface after immersion in palladium acetate solution followed by reduction in hypophosphite solution, and magnified view of a portion of the film is shown in inset figure. Fine palladium nanoparticles were clearly seen on the film surface.

Fig. 6 EPMA elemental analysis of anodic oxide film surface of aluminium after prolonged immersion in palladium acetate solution, 30 min., followed by reduction in hypophosphite solution. [a] SEM image of the elemental mapping area (dark zone); [b] elemental mapping for Aluminium; [c] elemental mapping of oxygen; and [d] elemental mapping of palladium.

Fig. 7 Surface activation processes for area-selective and complete metallization of the porous oxide film of aluminium. [a] During the laser micromachining of the palladium acetate impregnated, hydrothermally sealed porous oxide film in the presence of electroless nickel solution, palladium is formed by photothermal decomposition as well as by the reduction. [b] Immersion of palladium acetate adsorbed surface in the electroless nickel plating solution, where palladium nanoparticles were formed on the surface after the reduction of palladium acetate by the hypophosphite. (The diagrams are not to scale)
when immersed in palladium acetate solution, the later adsorbs or traps in the acicular hydroxide layer of the boiled specimen or in the pores of the anodized specimen. Transferring the specimen in the electroless plating bath, the palladium acetate reduced to metallic palladium by the sodium hypophosphite present in the nickel electroless solution, and deposited in the form of fine nanoparticles. Such nanoparticles, then, act as catalytic centres for the subsequent electroless deposition of nickel over the surface. In complete metallization technique, the nanoparticles and the deposited Ni-P layer are weakly anchored to the surface; the adhesion of the deposited Ni-P layer is weak. Consequently, the Ni-P layer on the both types of the surfaces, i.e. on porous oxide and acicular hydroxide, do not pass the Scotch-tape test. However, such metallization over the surface is ideal for the applications that need low adhesion metallic coating or for re-cycling and re-use of the substrate.

4. Conclusion

Successful techniques, based on palladium activation, for the microscale metallization on anodic alumina as well as for the complete metallization on the aluminum oxide/hydroxide are demonstrated. The area-selective, micro-scale metallic patterns formed by the present technique shows uniform deposition of metal (Ni-P) over laser irradiated area and have thickness about 2μm without any defects. Similarly, uniform deposition of metal (Ni-P) obtained on aluminum oxide/hydroxide surface by activating it in palladium acetate solution followed by electroless nickel plating, where palladium nanoparticles were first formed on the surface facilitating the subsequent deposition of metal.

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