BATCH AND SPOT REPAIRS FOR COLOR-ANODIZED PANELS

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This paper discusses repair methods for the damaged electrolytic-colored anodized panels. For surface damages (scratches and chipped oxide) without any dents, there are two approaches to repair them. The first is a full panel repair, stripping off the oxide coating, then re-growing and re-coloring the anodic oxide using a regular color-anodization process to match thickness and color. This method has been successfully demonstrated in our laboratory and is a good means of repairing damaged panels within a large anodizing facility. The second approach is a spot repair method, which can repair damaged panels without disassembly. After numerous attempts, some very challenging technical issues were identified: (1) noticeable borderline between the original and repaired anodized surfaces, and (2) lack of an electrolytic method available in the market for spot coloring the repaired area.

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Aluminum is one of the most abundant elements on earth and its alloys are widely used in many engineering applications due to its high strength to weight ratio and good formability. Currently, automotive manufacturers are considering higher aluminum content to reduce weight for better fuel economy. Traditionally, the aluminum parts are painted to match other surfaces on the vehicle. The paint operation involves many complicated process steps and environmental safeguards, and it is expensive to build and operate. Alternatively, color anodizing has been proposed to finish aluminum automotive parts since it is already widely used for architectural applications and it is a simple, environmentally friendlier process.

Anodizing is an electrochemical process in which the aluminum part is made to be the positive electrode (anode) in a suitable electrolyte (e.g., sulfuric acid); a sufficiently high voltage is applied to establish the desired polarization to generate oxygen at the surface [1-3]. The formation of oxide takes place by the migration of Al^{3+} ions from the metal towards the electrolyte interface, and the O^{2-} ions in the opposite direction. The anodic half-cell reaction for the oxide formation is shown as follows:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^- \uparrow$$

In the sulfuric acid anodizing process, the oxide formed is slowly dissolved by the electrolyte. Thus, a porous oxide coating is produced (see Fig. 1). The net coating growth rate and its porosity depend on the equilibrium set up between the film growth and dissolution [4].

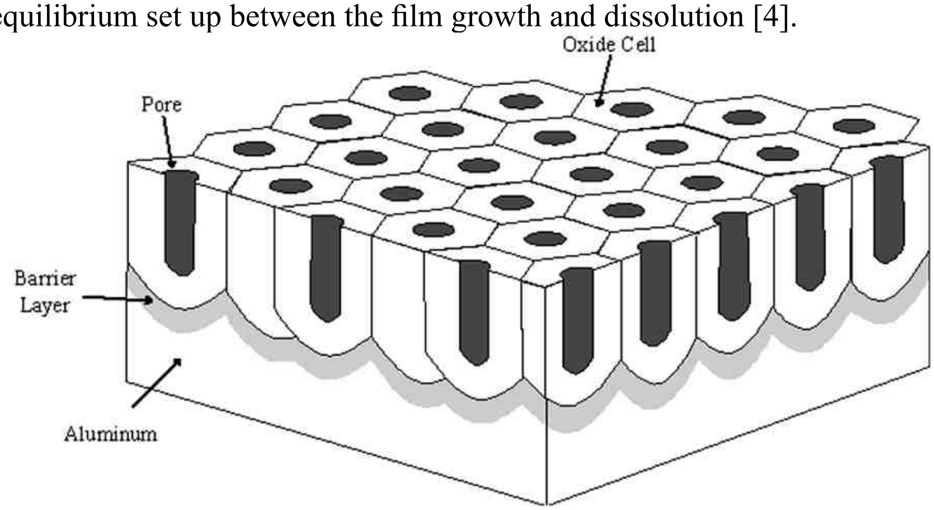

Figure 1. Schematic illustration of anodic oxide structure; typical oxide thickness, 10 to 30 µm; pore diameter, 20 nm.

The properties of the anodic film are highly dependent upon factors such as electrolyte type, concentration and temperature as well as anodizing voltage (current density) and time. Anodizing starts with the formation of a barrier (i.e., non-porous) film. Although this film is barely soluble in the electrolyte, with increasing anodizing time the oxide film will grow inward and the outer surface will be slowly dissolved in the electrolyte at the same time. The precise balance of these two actions is needed during anodization in order to produce the desired porous film. This porous film can be electrolytically colored by depositing metal in the pores of the anodic oxide film.

Generally, the oxide film is hard and durable and it can be colored for automotive use. However, a good repair technology needs to be developed before color anodizing becomes a viable alternative method for finishing automotive exteriors. This technology preferably can do the color-anodized repair without disassembling, which includes stripping the damaged anodic coat, re-anodizing and re-coloring to match the original substrate texture, coating thickness and color. Extensive work has been conducted to develop this technology but we have not found a comprehensive and viable solution.

EXPERIMENTAL

Batch Color Anodized Panel Repair

This method is targeted to repair the entire damaged color anodized panel with no noticeable dents. The following method has been successfully developed to carry out this type of panel repair.

1. Stripping the old anodic coat
   All the anodic coats on the aluminum parts including both good and damaged surfaces are being removed by strong sodium hydroxide solutions with additives.

2. Rinsing between chemical steps
   There is a rinsing step or multiple rinses after each process step. The rinse water is normally flowing from the tank with the cleanest water to the tank with the dirtiest water (counter-flow rinse). Tap water is normally being used, but the last rinsing step before sealing should use de-ionized water. The temperature of the water should be the same as in the process tanks, and the rinsing time is usually a few minutes. Good agitation of the water is very important to achieve clean surfaces.

3. Mechanical surface modification
   The bare aluminum surfaces are sanded to reproduce original surface textures.

4. Degreasing
   In the degreasing tank, oil, grease, and other surface contaminants are removed from the profile surface. In this stage, alkaline cleaning is mostly used. Since aluminum is readily attacked by strong alkaline solutions, solutions at relatively low alkalinity are used to prevent attack of

the metal during cleaning. Degreasing or acid cleaning by solutions containing sulfuric acid is also used. Temperatures from 20°C to 70°C are normal. The cleaning time is between 5 to 15 minutes.

5. Etching
   Aluminum has a thin natural oxide coating on the surface, which has to be removed before anodizing. This oxide coating is removed by sodium hydroxide solutions with additives. The purpose of this step is not only to remove a thin natural oxide coating on the surface but also to produce a matte appearance.

6. Brightening
   The parts are either brightened by an electropolishing or a chemical brightening process whichever is more suitable to convert the surface back to the original part surface appearance.

   - Electropolishing is a process by which metal is removed from a work piece by passage of electric current while the work is submerged in a specially formulated solution. It literally dissects the metal crystal atom by atom, with rapid attack on the high current density areas and lesser attack on the low current density areas. The result is an overall reduction of the surface profile with simultaneous smoothing and brightening of the metal surface.

   - Chemical brightening is a process to brighten the aluminum surface by immersing the part in various acids (e.g., phosphoric and nitric acids mixture) to chemically smooth the surface – creating a brighter, more reflective appearance.

7. Desmutting
   During the etching operation, a black smut layer may be left on the aluminum surface. This smut tends to be heavier with more highly alloyed aluminum, and is particularly heavy on copper-based aluminum alloys. It may consist of particles of oxide, secondary metals, etc., which are insoluble in the alkaline solution, and in general are quite loosely held on the surface. Smut is usually removed by a dip in an acid solution, most commonly 25 to 50 volume % nitric acid, at ambient temperature. This desmutting step is also called deoxidization step, or neutralization step due to neutralization of the caustic soda by the nitric or sulfuric acid. Such a step does not attack the aluminum substrate.

8. Re-anodizing
   During re-anodizing the aluminum parts are electrically connected as the anode; the cathode is made of a flat bar of stainless steel. The electrolyte and processing conditions used are similar to the original production settings. The electrolyte used for anodizing is sulfuric acid. The concentration is between 160 and 200 g/l, the temperature is between 18 and 22°C, and the

current density is from 1.4 to 1.8 A/dm^2. The anodic oxide typically grows at a rate of about 0.3 to 0.5 µm per minute. Dependent on the desired coating thickness, it will take approximately 30 minutes to build up an anodizing layer of 15 µm.

9. Electrolytic Coloring
   After anodizing, the metal is immersed in a bath containing an inorganic metal salt. Current is applied to deposit the metal in the base of the pores. The resulting color ranging from light bronze to black is dependent on the metal salt used and the specific processing conditions. Commonly used metals include tin, cobalt, nickel, and copper. This process offers color versatility and is the most technically advanced coloring method for architectural applications.

10. Sealing
    Sealing is one of the most important steps in the anodizing process. It closes the pores in the anodic film, which in turn will influence color stability, abrasion and corrosion resistance. The sealing operation is usually carried out in boiling hot water. During the sealing process, the aluminum oxide is converted to aluminum hydrate (boehmite, $Al_2O_3.H_2O$). The conversion is accompanied by an increase in volume, which bridges over and closes up the porous structure. It is important that the water in the sealing tank is very clean. De-ionized water has to be used since impurities in the sealing bath could have serious effect on the sealing quality of the anodic oxide layer.

Spot Anodizing Repair

This repair approach is designed to do the repair of damaged color-anodized parts without disassembling. The repair steps are:

1. Masking the area to be repaired
2. Stripping the damaged anodic coat
3. Sanding to reproduce the original texture
4. Re-anodizing to rebuild oxide thickness to be even with the undamaged area
5. Re-coloring the damaged portion of the part to match with the undamaged area
6. Sealing
7. Removing mask

Color Measurement

The quality of color produced on the aluminum alloy was determined by measuring color values using a Minolta CM 3700d Spectrophotometer [5]. The color was evaluated in terms of L*, a* and b* values of a colorimetric system, where,

- L* (lightness) value - 0 is black, 100 is white
- a* (red-green) value – positive values are red, negative values are green and 0 is neutral
- b* (yellow-blue) value – positive values are yellow, negative values are blue and 0 is neutral
- Gloss at 85° - gloss units returned when measured at 85° from perpendicular to surface

SEM Analyses

Specimen for SEM examination was prepared by cryo-fracture technique. An approximately 3.2 mm by 25.4 mm size sample was cryogenically frozen and fractured by dipping in a bottle of liquid nitrogen. The edge of the fractured specimen was then scanned and recorded by SEM. All specimens for SEM analysis were gold-palladium coated to highlight the surface profiles.

RESULTS AND DISCUSSION

Batch Color Anodized Repair

Several experiments have been conducted and we are able to repair the damaged electrolytic colored anodized panel and reproduce the original appearance. A typical example of batch repaired AA5657 colored anodized panel is shown in Figure 2. The coating thickness comparison is shown in Table I. For all practical purposes, both optical properties and coating thickness of these two panels are matched very well.

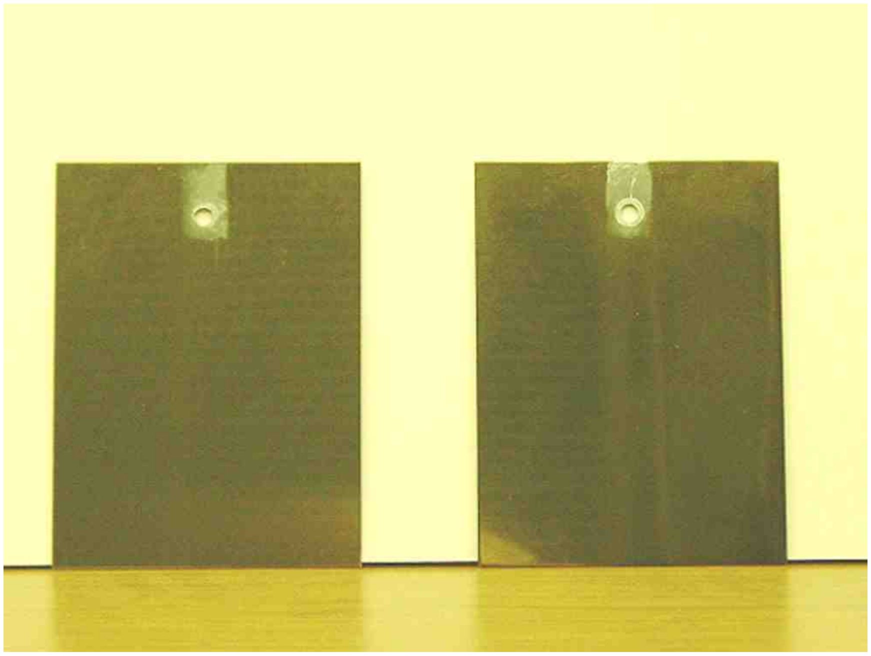

Figure 2. Photos of original (left) and batch repaired (right) panels.

Table I. Optical properties and coating thickness for the original and repaired panels.

AA5657	L*	a*	b*	85°	Thickness (µm)
Original	69.36	1.82	22.25	109.3	10.5
Repaired	68.63	1.90	22.53	110.0	9.3

Spot Anodizing Repair

This technology is designed to repair the damaged color anodized parts without disassembling, which includes stripping the damaged anodic coat, sand the aluminum surface to the original texture, re-anodizing and re-coloring the damaged portion of the part. Naturally, the repair area has to match the rest of the original coating in terms of thickness, texture and color.

Currently, we found that the spot re-anodizing repair has a major borderline problem, which is quite visible to human inspection. The following SEM micrographs illustrate reasons for the borderline problem. Figures 3 & 4 show the cross-sectional micrographs of the original and the repaired oxide structures respectively. The repaired pore sizes appear to be larger than the original.

Figures 5 & 6 show the surface micrographs of the original and the repaired surfaces respectively. The surface morphology looks similar.

Figures 7 shows the surface micrograph of the spot-repaired region. The borderline shown as a trench is clearly visible. Figure 8 shows the cross-sectional view of the borderline (i.e. shattered surfaces). The repaired surface appears to be a bit rougher than the original surface.

Figures 9 & 10 show the polished cross-section of the borderline at two magnifications. This picture clearly shows that during re-anodizing, the aluminum substrate surface was consumed and recessed to grow oxide. The oxide thickness versus substrate surface dissolution depth is about 2 to 1. If one of the repair objectives is to rebuild the oxide thickness to be flush with the original coating surface, the substrate surface being repaired has to recess to a depth of the original coating thickness (e.g. 10 μm recess for a 10 μm original coating thickness). For spot repair, the substrate underneath the repaired area will be lower than the original substrate, and the coating will be twice as thick as the original. These step changes between the original and repaired surfaces are clearly visible as borderline problem.

In addition, a portable electrolytic coloring method to re-color the re-anodized area has yet to be developed. However, the color anodic coat is translucent, and applying electrolytic coloring cannot solve the borderline problem.

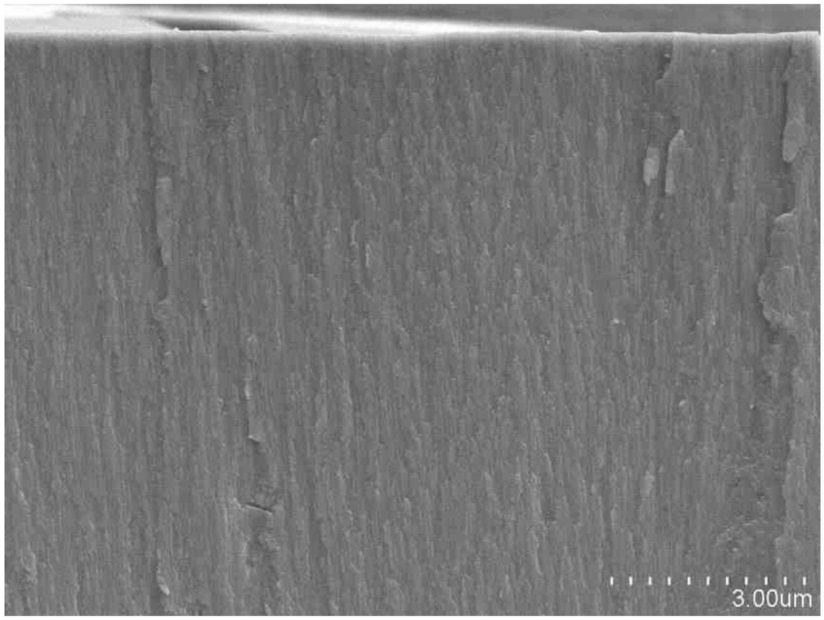

Figure 3. Cyro-fractured cross-sectional micrograph of the original anodized coating.

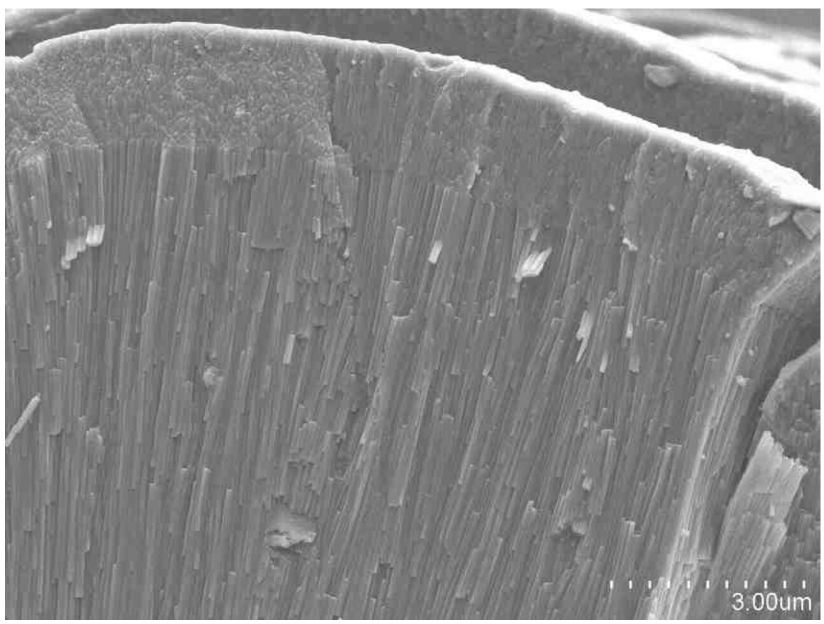

Figure 4. Cyro-fractured cross-sectional micrograph of the repaired anodized coating.

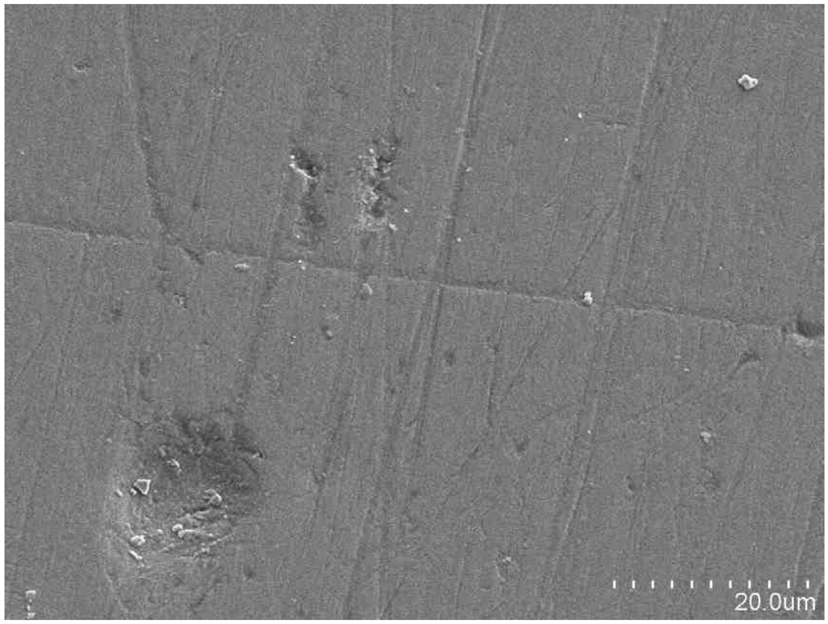

Figure 5. Surface micrograph of the original anodized coating.

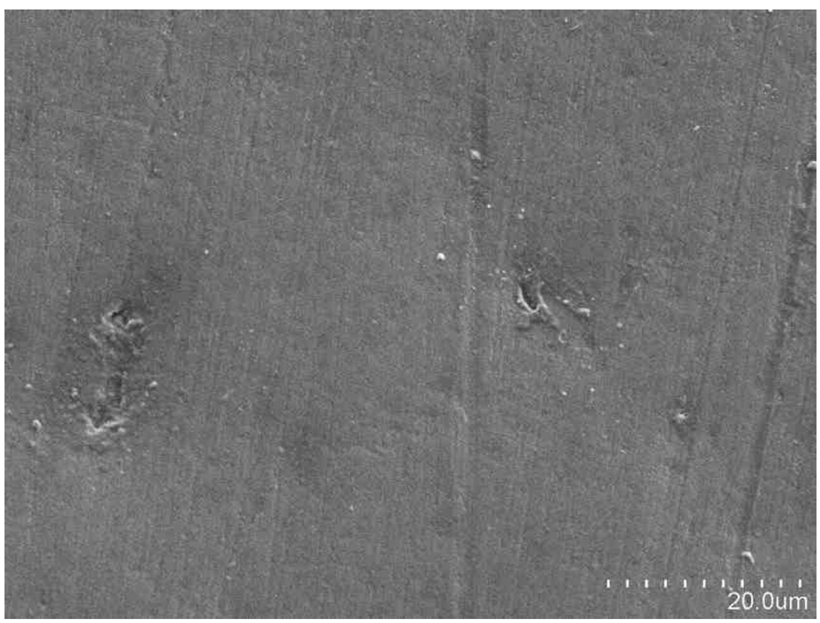

Figure 6. Surface micrograph of the repaired anodized coating.

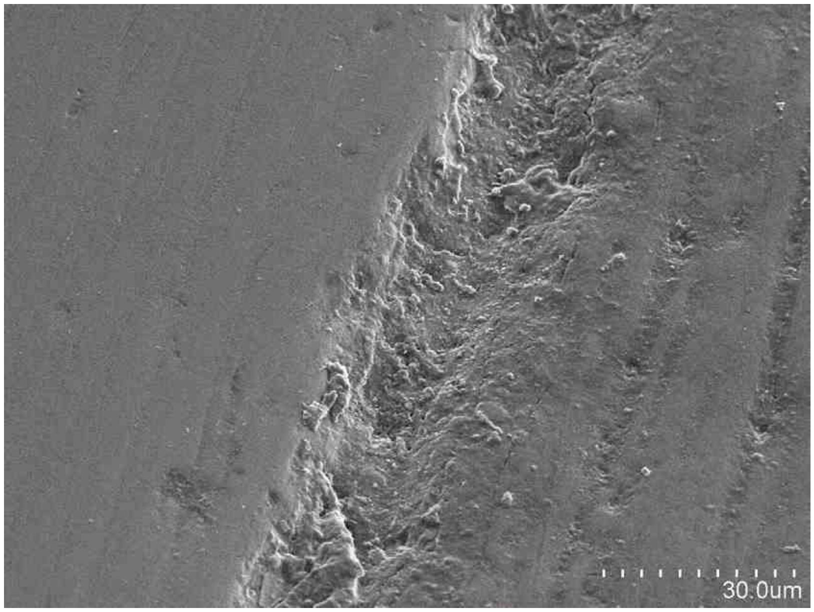

Figure 7. Micrograph of the borderline between original (left) and repaired (right) surfaces.

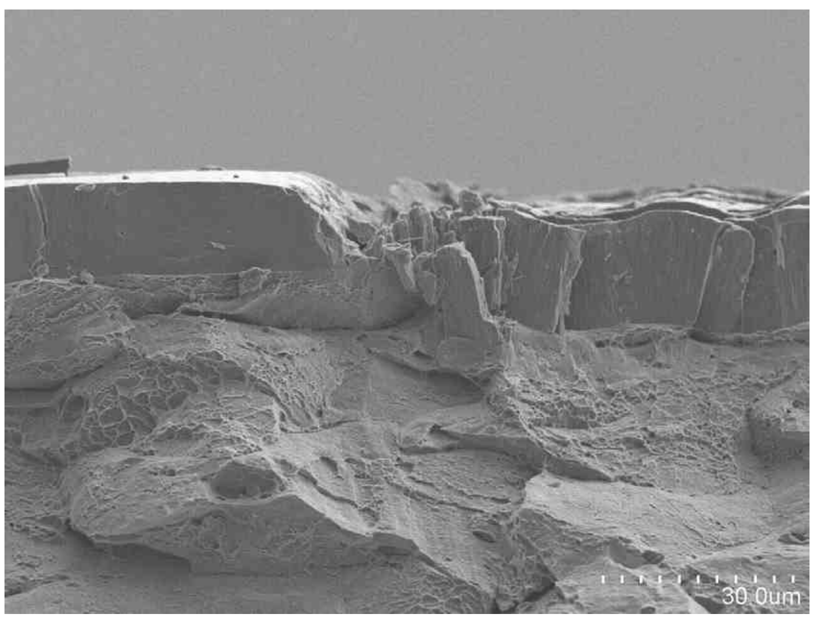

Figure 8. Micrograph of the cyro-fractured cross section of the borderline (i.e. shattered surfaces) between the original (left) and repaired anodized coating.

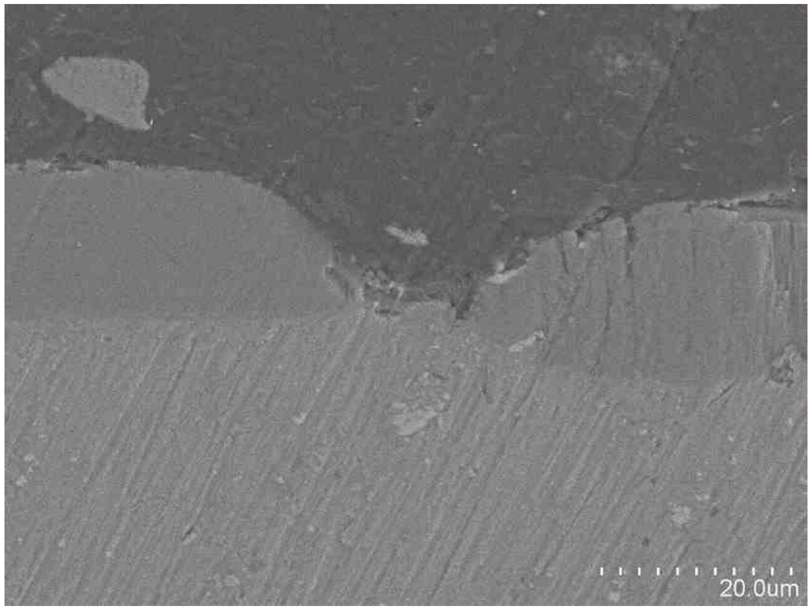

Figure 9. Micrograph of a polished cross-section of a borderline between original (left) and repaired (right) anodized coating.

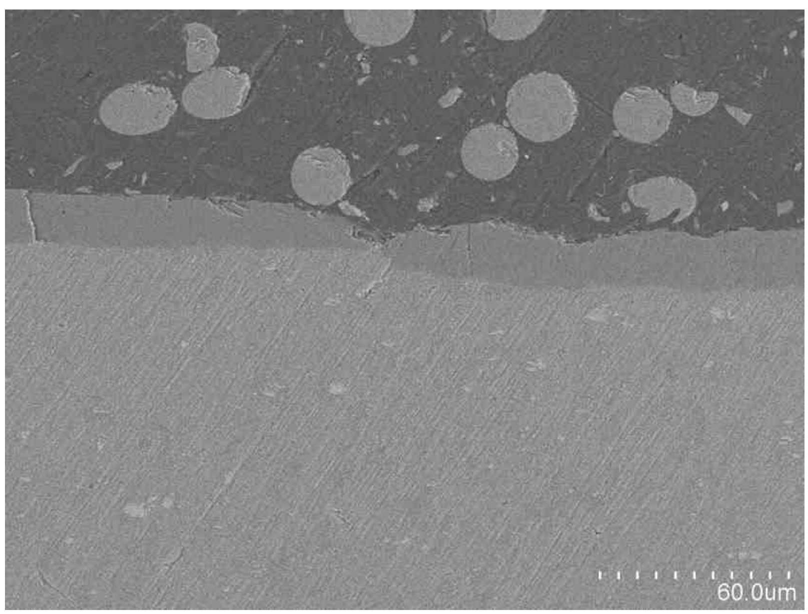

Figure 10. Micrograph of a polished cross-section of a borderline between original (left) and repaired (right) anodized coating.

For surface damages (scratches and chipped oxide) without any dents, there are two approaches to repair the surfaces; the first one is a full panel repair in some large anodizing repair facilities. This method is to repair the panel by stripping off the oxide coating first, reproducing the original surface texture and then re-growing and re-coloring the anodic oxide using the following batch color anodization process to match the original coating thickness and color. The following procedure can be used.

1. Cleaning in alkaline and/or acid cleaners to remove surface grease and dirt
2. Surface pretreatment including etching and/or bright dip
3. Anodizing to a desired coating thickness and specific characteristics
4. Coloring the aluminum oxide coating via electrolytic process
5. Sealing and closing the pores in the anodic film to provide a surface resistant to staining, abrasion, and crazing.

This method for repairing color-anodized oxide has been successfully demonstrated in our laboratory and proves to be a good method to repair the whole damaged panel.

The second approach is a spot repair method to restore the damaged panel. The advantage of this approach is that it potentially can repair the damaged panels on the spot without disassembling. After numerous attempts, some very challenging technical issues were identified: (1) noticeable borderline between the original and repaired anodized surfaces, and (2) no electrolytic method available in the market for spot coloring the repaired (i.e., re-anodized) area.

ACKNOWLEDGMENTS

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