A resin-bonding aluminum member (1) that is bonded to a resin material includes an aluminum member (2) and an anodic oxide film (3) formed on a surface of the aluminum member (2). The anodic oxide film (3) is mainly composed of alumina and contains tizaine thiol derivative. A method of producing the resin-bonding aluminum member (1) includes: forming the anodic oxide film (3) on the surface of the aluminum member (2) by applying a voltage between the aluminum member (2) used as an anode and a platinum plate, a titanium plate, or a carbon plate used as a cathode in an electrolytic aqueous solution that contains predetermined tizaine thiol derivative; and, after the anodic oxide film (3) is formed on the surface of the aluminum member (2), washing the aluminum member (2) with water at a temperature of 40°C to 60°C for 5 seconds to 120 seconds.
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RESIN-BONDING ALUMINUM MEMBER AND
METHOD OF PRODUCING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The invention relates to a resin-bonding aluminum member that is bonded to a resin material and a method of producing the resin-bonding aluminum member.

2. Description of the Related Art

[0002] In recent years, weight reduction is required in various products, such as automobiles or home electric appliances. In such products, resin components have been replacing metal components. However, for components that require high electrical conductivity or high thermal conductivity, it is difficult to completely replace metal components with resin components. For this reason, a metal member is bonded to a resin member, and then the resultant bonded component is employed.

[0003] A sufficient bonding property should be exhibited when a metal member and a resin member are bonded together. Therefore, Japanese Patent No. 1840482 describes a technique for modifying the surface of a metal member with triazine thiol derivative, or the like. Specifically, for example, electrodeposition is performed by using a metal member, such as an aluminum member, as an anode, a platinum plate, or the like, as a cathode, and an electrolytic aqueous solution that contains triazine thiol derivative as an electrodeposition solution. In this manner, the surface of the metal member used as the anode is treated. After the electrodeposition, in order to wash unreacted triazine thiol derivative, and the like, hot water washing is usually performed. Thus, an anodic oxide film that is modified by triazine thiol derivative may be formed on the surface of the aluminum member.

[0004] The anodic oxide film is formed on the surface of the aluminum member by means of the above described related art; however, when the thus formed aluminum...
member is directly bonded to a resin member, or the like, the bonding strength may be still insufficient and, therefore, a breakage may occur at the bonded portion. In addition, there is a problem that variations tend to occur in the bonding property that is exhibited when the resin-bonding aluminum member, obtained through the modification, is bonded to the resin member.

SUMMARY OF THE INVENTION

[0005] The invention provides a resin-bonding aluminum member, which exhibits a desirable bonding property when bonded to a resin material, and a method of producing the resin-bonding aluminum member.

[0006] A first aspect of the invention relates to a method of producing a resin-bonding aluminum member that is bonded to a resin material, wherein the resin-bonding aluminum member includes an aluminum member and an anodic oxide film that is formed on a surface of the aluminum member and that is mainly composed of alumina and contains triazine thiol derivative. The method includes: forming the anodic oxide film on the surface of the aluminum member by applying a voltage between the aluminum member that is used as an anode and a platinum plate, a titanium plate, or a carbon plate that is used as a cathode in an electrolytic aqueous solution that contains triazine thiol derivative expressed by the following general formula 1 (electrodeposition process); and washing the aluminum member, on which the anodic oxide film is formed, with water at a temperature of 40°C to 60°C for 5 seconds to 120 seconds (washing process).

[general formula 1]
A second aspect of the invention relates to a resin-bonding aluminum member produced by the method according to the first aspect of the invention.

In the producing method according to the first aspect of the invention, the anodic oxide film that is mainly composed of alumina and contains triazine thiol derivative is formed on the surface of the aluminum member in the electrodeposition process. Then, the aluminum member that has been undergone the electrodeposition process is washed with water at a temperature of 40°C to 60°C for 5 seconds to 120 seconds in the washing process. The resin-bonding aluminum member according to the second aspect of the invention, which is obtained through the producing method, has the anodic oxide film having an uneven surface. Thus, the resin-bonding aluminum member may be bonded to the resin material with a desirable bonding strength owing to the anchor effect that is produced when the resin material is embedded into the uneven surface of the anodic oxide film. Furthermore, it is considered that the triazine thiol derivative contained in the anodic oxide film may combine with resin molecules that constitute the resin material. As a result, it is possible to further improve the bonding strength with which the resin-bonding aluminum member is bonded to the resin material.

In the first aspect of the invention, after the electrodeposition process is
completed, the aluminum member is washed with water at a relatively low-temperature of 40°C to 60°C for a predetermined period of time, that is, 5 seconds to 120 seconds as in the above described manner. If the aluminum member that has undergone the electrodeposition is washed with water (hot water) at, for example, a temperature of 80°C, there is a possibility that hydration of the anodic oxide film may be promoted. As a result, the hydrated portion becomes fragile and, therefore, when the aluminum member is bonded to the resin material, the resultant bonded component is more likely to break at the bonded portion. Thus, the bonding strength may decrease. In contrast, in the first aspect of the invention, the aluminum member is washed with water at a temperature of 40°C to 60°C for the predetermined period of time. Thus, in the washing process, it is possible to suppress hydration of the anodic oxide film, which causes a breakage in the bonded component that is formed by bonding the aluminum member to the resin material. Hence, the resin-bonding aluminum member may be bonded to the resin material with a desirable bonding strength. In addition, in the producing method according to the first aspect of the invention, hydration of the anodic oxide film may be suppressed. Thus, variations in the bonding strength of the resin-bonding aluminum member are reduced and, as a result, it is possible to further reliably produce the resin-bonding aluminum member having a desirable bonding strength. In addition, the resin-bonding aluminum member exhibits high corrosion-resistance against acid, and the like.

Thus, according to the aspects of the invention described above, it is possible to provide a resin-bonding aluminum member that exhibits a desirable bonding property when bonded to a resin material, and a method of producing the resin-bonding aluminum member.

The resin-bonding aluminum member is bonded to the resin material. The resin material bonded to the resin-bonding aluminum member may be, for example, chlorinated polyethylene, polyethylene, polypropylene, polyvinyl chloride, polyvinyl acetate, polyacrylic ester, polymethacrylic ester, unsaturated polyester, polyester, polyamides, epoxy resin, polybutylene terephthalate, polyphenylene sulfide, or the like.

The resin material is desirably a polyphenylene sulfide resin. In this case,
triazine thiol derivative contained in the anodic oxide film of the resin-bonding aluminum member forms a covalent bond with a terminal functional group of the polyphenylene sulfide resin (PPS resin). Thus, it is possible to bond the resin-bonding aluminum member to the resin material with a further high bonding strength.

[0013] The resin-bonding aluminum member includes the aluminum member and the anodic oxide film formed on the surface of the aluminum member. The anodic oxide film is mainly composed of alumina and contains triazine thiol derivative. The content of alumina (aluminum oxide) in the anodic oxide film is desirably within a range from 98wt% to 99.5wt%. When the content of alumina is less than 98wt%, the anchor effect that is produced between the anodic oxide film and the resin material may be insufficient, resulting in a possible decrease in bonding strength between the resin-bonding aluminum member and the resin material. On the other hand, when the content of alumina exceeds 99.5wt%, the content of triazine thiol derivative in the anodic oxide film may be insufficient, resulting in an insufficient combination of the triazine thiol derivative and a polymer that constitutes the resin material. This may decrease the bonding strength between the resin-bonding aluminum member and the resin material.

[0014] The resin-bonding aluminum member may be produced through the electrodeposition process and the washing process. In the electrodeposition process, the anodic oxide film, which is mainly composed of alumina and contains triazine thiol derivative, is formed on the surface of the aluminum member by applying a voltage between the aluminum member that is used as the anode and a platinum plate, a titanium plate, or a carbon plate that is used as the cathode in the electrolytic aqueous solution that contains triazine thiol derivative expressed by the following general formula 1. Specifically, the electrodeposition process may be performed in the manner described, for example, in Japanese Patent Publication No. 5-51671.

[general formula 1]
where in the general formula 1, R denotes -OR₁, -SR₁, -NHR₁, or -N(R²)₂. R¹ denotes alkyl group, alkenyl group, phenyl group, phenylalkyl group, alkylphenyl group, or cycloalkyl group. M denotes H, Na, Li, K, 1/2Ba, or 1/2Ca, aliphatic primary amines, aliphatic secondary amines, aliphatic tertiary amines, or quaternary ammonium salt. Note that two separate letters "M" in the general formula 1 may be the same or may be different.

[0015] Specifically, the triazine thiol derivative expressed by the general formula 1 may be the triazine thiol salt of 1,3,5-triazine-2,4,6-trithiol (F), 1,3,5-triazine-2,4,6-trithiol-monosodium (FN), 1,3,5-triazine-2,4,6-trithiol triethanol amine (FTEA), 6-amino-1,3,5-triazine-2,4-dithiol (AF), 6-amino-1,3,5-triazine-2,4-dithiol monosodium (AN), 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB), 6-dibutylamino-1,3,5-triazine-2,4-dithiol monosodium (DBN), 6-diallylamino-1,3,5-triazine-2,4-dithiol (DA), 6-diallylamino-1,3,5-triazine-2,4-dithiol monosodium (DAN), 1,3,5-triazine-2,4,6-trithiol di(tetrabutyl ammonium salt) (F2A), 6-dibutylamino-1,3,5-triazine-2,4-dithiol tetrabutyl ammonium salt (DBA), 6-dithioctylamino-1,3,5-triazine-2,4-dithiol (DO), 6-dithioctylamino-1,3,5-triazine-2,4-dithiol monosodium (DON), 6-dilaurylamino-1,3,5-triazine-2,4-dithiol (DL), 6-dilaurylamino-1,3,5-triazine-2,4-dithiol monosodium (DLN), 6-stearylamino-1,3,5-triazine-2,4-dithiol (ST), 6-stearylamino-1,3,5-triazine-2,4-dithiol monopotassium (STK), 6-oleylamino-1,3,5-triazine-2,4-dithiol (DL), 6-oleylamino-1,3,5-triazine-2,4-dithiol monopotassium (OLK), or the like.
[0016] In addition, the electrolytic aqueous solution is prepared by dissolving at least
the triazine thiol derivative in water. The electrolytic aqueous solution desirably
contains 0.0001wt% to 0.1wt% of triazine thiol derivative. When the content of triazine
thiol derivative is less than 0.0001wt%, it may be difficult to sufficiently form the anodic
oxide film that is mainly composed of alumina and contains the triazine thiol derivative.
On the other hand, when the content of triazine thiol derivative exceeds 0.1wt%,
unreacted triazine accumulates on the surface of the aluminum member. This may
adversely affect bonding. More desirably, the content of triazine thiol derivative in the
electrolytic aqueous solution is within a range from 0.001wt% to 0.01wt%.

[0017] In addition, acid, or the like, may be added into the electrolytic aqueous
solution in addition to the triazine thiol derivative in order to improve conductivity of the
electrolytic aqueous solution.

[0018] The aluminum member that will undergo the electrodeposition process is
desirably subjected to alkaline etching and add treatment beforehand. In this case, the
surface of the aluminum member may be cleaned by removing oils and impure metal,
metal oxide, and the like, from the surface of the aluminum member. The alkaline
etching may be performed by immersing the aluminum member into an alkaline aqueous
solution, such as sodium hydroxide. The acid treatment may be performed by
immersing the aluminum member into an acid aqueous solution, such as sulfuric acid.

[0019] In addition, in the washing process, the aluminum member that has
undergone the electrodeposition process is washed with water at a temperature of 40°C to
60°C for 5 seconds to 120 seconds. When the temperature of water used in the washing
process is lower than 40°C, it may be difficult to sufficiently perform washing. On the
other hand, when the temperature of water exceeds 60°C, the anodic oxide film tends to
be hydrated more easily. Thus, the bonding strength of the resin-bonding aluminum
member to the resin material may decrease. More desirably, in the washing process,
water at a temperature of 45°C to 60°C is used. In addition, when the duration of
washing is less than 5 seconds, it may be difficult to sufficiently perform washing. On
the other hand, when the duration of washing exceeds 120 seconds, the production
efficiency decreases and, therefore, the producing cost of the resin-bonding aluminum member may increase. More desirably, the duration of washing is within a range from 20 seconds to 120 seconds.

[0020] The resin-bonding aluminum member is desirably used in an on-vehicle lithium battery. In this case, it is possible to sufficiently take advantage of the desirable bonding property and corrosion resistance of the resin-bonding aluminum member.

[0021] In other words, generally, the on-vehicle lithium battery is highly likely to be exposed to high humidity environment for a long period of time. Such high humidity environment promotes hydration of the anodic oxide film. As a result, the anodic oxide film tends to become fragile and, therefore, there is a possibility that the bonding between the aluminum member and the resin material may easily break. However, in the resin-bonding aluminum member according to the aspect of the invention described above, hydration of the anodic oxide film is suppressed as in the above described manner. Thus, even when the resin-bonding aluminum member is applied to the on-vehicle lithium battery that is used in a high-humidity environment, it is possible to suppress the promotion of hydration of the anodic oxide film. Hence, it is possible to maintain the bonding between the resin-bonding aluminum member and the resin material for a long period of time. In this way, when the resin-bonding aluminum member is applied to the on-vehicle lithium battery, it is possible to further remarkably exhibit the desirable bonding property of the resin-bonding aluminum member to the resin material.

[0022] More specifically, the resin-bonding aluminum member may be used as an electrode terminal, a battery case, or the like, in a lithium secondary battery.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] The features, advantages, and technical and industrial significance of this invention will be described in the following detailed description of example embodiments of the invention with reference to the accompanying drawings, in which like numerals denote like elements, and wherein:

FIG. 1 is a view that illustrates the cross-sectional structure of a resin-bonding
aluminum member according to a first example of the invention;

FIG 2 is a view that illustrates the cross-sectional structure of an anodic oxide film formed on the aluminum member according to the first example of the invention; and

FIG. 3 is a view that illustrates the cross-sectional structure of a bonded component which is formed by bonding the resin-bonding aluminum member to a resin material, according to the first example of the invention.

EXAMPLE OF THE INVENTION

First Example

[0024] An example of the invention will be described with reference to FIG. 1 to FIG. 3. In this example, as shown in FIG. 1 and FIG. 2, a resin-bonding aluminum member 1 that includes an aluminum member 2 and an anodic oxide film 3 formed on the surface of the aluminum member 2 is formed. The anodic oxide film 3 is mainly composed of alumina and contains triazine thiol derivative. As shown in FIG 2, the anodic oxide film 3 has an uneven surface. In addition, as shown in FIG 3, the resin-bonding aluminum member 1 is bonded to a resin material 4 and then used.

[0025] The resin-bonding aluminum member of the present example is formed through an electrodeposition process and a washing process. In the electrodeposition process, an anodic oxide film is formed on the surface of the aluminum member by immersing the aluminum member and a platinum plate into an electrolytic aqueous solution that contains 1,3,5-triazine-2,4,6-trithiol monosodium, and applying a voltage between the aluminum member used as an anode and the platinum plate used as a cathode. In addition, in the washing process, the aluminum member that has been undergone the electrodeposition process is washed with water at a predetermined temperature for a predetermined period of time.

[0026] In the present example, three types of resin-bonding aluminum members (sample E1, sample E2, and sample C1) were prepared by changing the washing condition in the washing process, and then the characteristics of these resin-bonding aluminum members were evaluated.
[0027] In order to prepare the resin-bonding aluminum member (sample El) of the present example, first, a plate-like aluminum member was immersed in 50 g/l aluminum hydroxide aqueous solution at a temperature of 42°C for one minute (alkaline etching). Subsequently, 98wt% sulfuric acid was dissolved into water to prepare 10 ml/l sulfuric acid aqueous solution, and then the aluminum member was immersed in the above acid aqueous solution at a temperature of 40°C for two minutes (acid treatment).

[0028] After that, 1,3,5-triazine-2,4,6-trithiol monosodium, which serves as the triazine thiol derivative, was dissolved into water to obtain the aqueous solution having a concentration of 0.003wt%, and 98wt% strong sulfuric acid was further dissolved into the above aqueous solution to obtain the resultant aqueous solution having a concentration of 2.3wt%. Thus, the electrolytic aqueous solution was prepared.

[0029] Then, the electrolytic aqueous solution was poured into an electrodeposition bath, and the temperature of the electrolytic aqueous solution was adjusted to 60°C. The aluminum member, which has undergone the alkaline etching and acid treatment, and the plate-like member (platinum plate) were immersed into the electrolytic aqueous solution. Subsequently, the anodic oxide film, which is mainly composed of alumina and contains the triazine thiol derivative, was formed on the surface of the aluminum member by applying a voltage between the aluminum member used as an anode and the platinum member used as a cathode for 75 minutes (electrodeposition process).

[0030] After that, in order to remove the residual electrolytic aqueous solution remaining on the aluminum member, the aluminum member was washed with hot water (washing process). Specifically, the aluminum member that has undergone the electrodeposition process was immersed in water at a temperature of 60°C for 20 seconds. Then, the aluminum member was dried by air blowing (temperature 80°C, 4 minutes). Thus, the resin-bonding aluminum member (sample El) was obtained.

[0031] In addition, in the present example, the other two resin-bonding aluminum members (sample E2 and sample Cl) were prepared under the different washing conditions in the washing process from that for the sample El. The sample E2 was the resin-bonding aluminum member for which the duration of washing in the washing
process was different from that for the sample El. Specifically, the sample E2 was prepared in the same manner as that for the sample El except that the washing process was performed with water at a temperature of 60°C for 120 seconds. The sample Cl was the resin-bonding aluminum member for which the temperature of water and the duration of washing in the washing process were different from those for the sample El. Specifically, the sample Cl was prepared in the same manner as that for the sample El except that the washing process was performed with water at a temperature of 80°C for 120 seconds.

[0032] Next, as shown in FIG 3, the resin-bonding aluminum member 1 of each of the sample El, sample E2 and sample Cl was bonded to the resin material 4 to form a bonded component 5. Specifically, first, the polyphenylene sulfide resin (BGX100 produced by Tosoh Corp.) was prepared and heated to a temperature of 310°C, and then bonded to the resin-bonding aluminum member of each sample inside a die that has been heated to a temperature of 140°C. In this way, the resin-bonding aluminum member 1 and the resin material 4 were bonded together, and the bonded component 5 was obtained (see FIG. 3). Note that during bonding, the ends of the resin-bonding aluminum member 1 were protruded from the resin material 4.

[0033] Next, the pulling strength of each bonded component was measured. That is, while the resin material 4 of each bonded component 5 was fixed, the end of the resin-bonding aluminum member 1, protruding from the resin material 4, was chucked and then pulled at a predetermined stress. Then, the stress, at which the bonding between the resin-bonding aluminum member 1 and the resin material 4 broke and the resin-bonding aluminum member 1 was pulled out of the resin material 4, was measured and determined as the pulling strength. Measurement of the pulling strength was performed with the tension/compression tester Autograph AG-50KNIS (MO) produced by Shimadzu Corp. at room temperature and at a tension speed of 50 mm/minute. The results were shown in Table 1.

Table 1
As is apparent from Table 1, the sample E1 and the sample E2 respectively exhibited significantly high pulling strengths as compared with the sample C1. Thus, it may be understood that the sample E1 and the sample E2 can be bonded to a resin material with a desirable bonding strength.

The reason why the bonding property to the resin material differed between the samples E1 and E2 and the sample C1 as described above will be considered. The sample E1 and the sample E2 are the resin-bonding aluminum members that were prepared through washing with water at a temperature of 60°C for 20 seconds or 120 seconds. On the other hand, the sample C1 is the resin-bonding aluminum member that was prepared through washing with water at a temperature (80°C), higher than those for the sample E1 and sample E2, for 120 seconds. Thus, because the sample C1 was washed with water at a high temperature, that is, 80°C, the anodic oxide film was presumably hydrated. As a result, the anodic oxide film became fragile and, as shown in Table 1, exhibited the low bonding property to the resin material. In contrast, because the sample E1 and the sample E2 were washed with water at a relatively low temperature for a predetermined period of time, hydration of the anodic oxide film may be presumably suppressed or prevented. As a result, the sample E1 and the sample E2 each exhibited the desirable bonding property to the resin material, as shown in Table 1.

As described above, according to the present example, it is possible to prepare the resin-bonding aluminum member (sample E1 and sample E2) having a desirable bonding property to the resin material.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Washing Temperature (°C)</th>
<th>Washing Duration (s)</th>
<th>Pulling Strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample E1</td>
<td>60</td>
<td>20</td>
<td>975</td>
</tr>
<tr>
<td>Sample E2</td>
<td>60</td>
<td>120</td>
<td>975</td>
</tr>
<tr>
<td>Sample C1</td>
<td>80</td>
<td>120</td>
<td>175</td>
</tr>
</tbody>
</table>
CLAIMS:

1. A method of producing a resin-bonding aluminum member that is bonded to a resin material, wherein the resin-bonding aluminum member includes an aluminum member and an anodic oxide film that is formed on a surface of the aluminum member and that is mainly composed of alumina and contains triazine thiol derivative, the method comprising:
   forming the anodic oxide film on the surface of the aluminum member by applying a voltage between the aluminum member used as an anode and a platinum plate, a titanium plate, or a carbon plate used as a cathode in an electrolytic aqueous solution that contains triazine thiol derivative expressed by a following general formula 1; and
   after the anodic oxide film is formed on the surface of the aluminum member, washing the aluminum member with water at a temperature of 40°C to 60°C for 5 seconds to 120 seconds,

   [general formula 1]

   ![General Formula 1](image)

   where in the general formula 1, R denotes -OR, -SR, -NHR, or -N(R^2)^2, R^1 denotes hydrogen, alkyl group, alkenyl group, phenyl group, phenylalkyl group, alkylphenyl group, or cycloalkyl group, M denotes H, Na, Li, K, 1/2Ba, or 1/2Ca, aliphatic primary amines, aliphatic secondary amines, aliphatic tertiary amines, or quaternary ammonium salt.

2. The method of producing the resin-bonding aluminum member according to claim
1. wherein the resin material is a polyphenylene sulfide resin.

3. The method of producing the resin-bonding aluminum member according to claim 1 or 2, wherein the resin-bonding aluminum member is used in an on-vehicle lithium battery.

4. A resin-bonding aluminum member produced by the method according to any one of claims 1 to 3.