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PROCESS FOR FORMING HARD ANODIC OXIDE FILM ON ALUMINUM BASE ALLOY

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ABSTRACT OF THE DISCLOSURE

A hard anodic oxide film is formed uniformly on an aluminum base alloy containing 1% by weight or more of copper by subjecting the aluminum base alloy to anodic oxidation using an electrolyte comprising an aqueous solution containing 5 to 40% by weight of an aromatic sulfonic acid such as sulfosalicylic acid, napthalenedisulfonic acid, naphthalene-trisulfonic acid, phenol sulfonic acid and sulfophthalic acid, and 15 to 40% by weight of sulfuric acid.

This invention relates to a process for forming on an aluminum base alloy an anodic oxide film which is hard and excellent in corrosion resistance and rigidity.

Heretofore, there have been proposed many processes for forming anodic oxide films on aluminum and aluminum base alloys, in general. For example, processes using an aqueous sulfuric acid solutions or oxalic acid solutions have been well known. For formation of hard anodic oxide films, there have been well known a "Kalcolor" process using a mixed aqueous electrolyte of sulfosalicylic acid and sulfuric acid (U.S. Pat. 3,031,387), a "Duranodic 300" process using a mixed aqueous electrolyte of sulfophthalic acid and sulfuric acid (British Pat. 962,048), a "Veroxal" process using a mixed aqueous electrolyte of sulfosalicylic acid, maleic acid and sulfuric acid (British Pat. 973,391), a "Sumitone" process using a mixed aqueous electrolyte of p-phenolsulfonic acid and sulfuric acid (Japanese patent publication No. 29,954/64) and a process using a mixed aqueous electrolyte of naphthalenedisulfonic acid and sulfuric acid (U.S. Pat. No. 3,486,991). These processes are characterized, as is clear from the patent specifications, in that aluminum as an anode is charged in an electrolyte comprising a mixed aqueous solution of a suitable aromatic sulfonic acid and a low concentration sulfuric acid, a cathode is also charged in the electrolyte and then an electric current is flowed to the electrolyte to form an anodic oxide film on the surface of aluminum and aluminum base alloys. However, the said processes have not been satisfactory as processes for forming anodic oxide films on copper-containing aluminum base alloys. That is, when copper-containing aluminum alloys, particularly those containing more than 1% by weight of copper, are treated according to the above-mentioned processes, elution of copper takes place during the anodic oxidation treatment to give anodic oxide films which are imperfect and soft to be put into practical use. For example, Al-Si-Cu alloys have been widely used for various aluminum alloy castings, and have been frequently used die castings or sand castings for cylinders, engine parts, bearings and the like products which are required to be high in abrasion resistance. Nevertheless, anodic oxide films formed by subjecting the said aluminum alloy products to anodic oxidation treatment are not uniform, thin in film thickness and low in hardness.

The present inventors made extensive studies or processses for forming anodic oxide films on aluminum base alloys. As the result, the inventors have found that a uniform and hard anodic oxide film is formed on a copper-

containing aluminum base alloy by subjecting the alloy to anodic oxidation treatment in an aqueous electrolyte containing an aromatic sulfonic acid and a high concentration sulfuric acid which solution has not been known hitherto. Particularly, it has been clarified that a hard anodic oxide film having an excellent quality is formed on an Al-Si-Cu alloy containing 6% by weight or more of silicon and 1% by weight or more of copper.

It is therefore the object of the present invention is to provide a process for forming a hard anodic oxide film on an aluminum base alloy, characterized by subjecting an aluminum alloy containing 1% by weight or more of copper to anodic oxidation treatment using as an electrolyte an aqueous solution containing 5 to 40% by weight of an aromatic sulfonic acid and 15 to 40% by weight of sulfuric acid.

In the present invention, the aromatic sulfonic acid is an essential component for forming an anodic oxide film on an aluminum base alloy. If the concentration of the aromatic sulfonic acid is less than 5% by weight, no effect of increasing the hardness of the resulting film can be observed. Further, the aromatic sulfonic acid is difficultly dissolved to a concentration of more than 40% by weight in an aqueous sulfuric acid solution of such a concentration as adopted in the present invention. If the concentration of sulfuric acid is less than 15% by weight, not only no uniform anodic oxide film can be formed on a copper-containing aluminum alloy or a high silicon content aluminum alloy, but also the cell voltage becomes higher with formation and growth of the film to easily cause burning. If the concentration of sulfuric acid is more than 40% by weight, the organic acid is lowered in solubility to decrease the hardness-improving effect of the aromatic sulfonic acid. A part of the sulfuric acid may be replaced by a water-soluble sulfate or bisulfate such as sulfate or bisulfate of an alkali metal. The use of an electrolyte comprising an aqueous solution containing 10 to 15% by weight of aromatic sulfonic acid and 15 to 25% by weight of sulfuric acid gives particularly excellent effects. The aromatic sulfonic acid used in the present invention is sulfosalicylic acid, naphthalene-disulfonic acid, napthalene-trisulfonic acid, phenolsulfonic acid, sulfophthalic acid or the like aromatic sulfonic acid having at least one sulfone group. The electrolyte used in the present invention may be incorporated with a small amount of a carboxylic acid such as oxalic or maleic acid.

Aluminum-copper alloys containing 1% by weight or more of copper which are to be treated according to the present process are not particularly limited in form but may be products of any forms such as castings, sheets, extrusions and the like. According to the present process, hard and uniform anodic oxide films can be formed on aluminum-silicon-copper alloys containing 6% by weight or more of silicon and 1% by weight or more of copper on which such films have been difficultly formed hitherto.

In the present process, the hardness of the resulting film tends to lower with increasing anodic oxidation temperature. Accordingly, the electrolyte temperature is desirably below 20° C., more advantageously within the range from 0° to 15° C. The current density is in the range from 1 to 4 amp./dm.^{2}, and the treatment period varies depending on the thickness of the resulting film.

Generally, anodic oxide films formed according to the present process are subjected to conventional sealing treatment. In case aluminum alloy products having anodic oxide films formed according to the present process are to be used for pistons, cylinders, bearings, etc., however, it is sometimes preferable that the anodic oxide films are not subjected to sealing treatment, since the films, which have not been subjected to sealing treatment, are high in oil retainability.

The present invention is illustrated in detail below with reference to examples, but it is needless to say that the invention is not limited to the examples.

Aluminum alloy materials used in the examples and in comparative examples are shown in Table 1.

TABLE 1.—CHEMICAL COMPOSITION AND SHAPE OF TEST ALUMINUM ALLOY

	Alloy composition (weight percent)											
Alloy	Cu	Si	Zn	Mg	Mn	Cr	Fe	Ni	Ti	B	Al	Shape
1	4.9	0.19		0.25	0.29		0.06	0.22		0.005	Balance	Casting.
2	4.1	0.70	0.20	0.65	0 95	0.08	0.90				do	Sheet.
3	1.6	0.40	5.90	2.50	0.25	0.35	0.50	0.15			do	Do.
4	5.0	14.5		0.57			0.38				do	Casting.
5	1.6	23.5		1.0				0.7	0.2		do	Do.

EXAMPLE 1

The aluminum alloy 1 in Table 1 was degreased, etched and desmutted according to ordinary procedures, and then subjected to anodic oxidation treatment at a current density of 2.5 a./dm.^{2} for 60 minutes at a temperature of 10° C. in an aqueous electrolyte containing 15% by weight of naphthalene-disulfonic acid, 20% by weight of sulfuric acid and 1% by weight of oxalic acid. In this case, the cell voltage was gradually increased from 20 v. to 25 v. The film formed by said anodic oxidation treatment was subjected to sealing by means of boiling water. The film had a thickness of about 60μ and a hardness of about Hv:370 in terms of Vickers hardness.

EXAMPLES 2–7 AND COMPARATIVE EXAMPLES 1–2

Example 1 was repeated, except that the electrolyte composition was varied. The results obtained were as set forth in Table 2.

TABLE 2

	Kind of alloy	Electrolyte composition (wt. percent)		Current density (amp/dm.^{2})	Electrolysis		Thickness of oxide film (μ)	Hardness of oxide film (Hv)
					Temp. (° C.)	Time (min.)		
Example number:								
2	1	Naphthalene-trisulfonic acid H_2SO_4	15 20	2.5	10	60	60	400
3	1	Phenolsulfonic acid H_2SO_4	15 20	2.5	10	60	60	400
4	1	Sulfosalicylic acid H_2SO_4	15 20	2.5	10	60	60	300
5	1	Naphthalene-disulfonic acid H_2SO_4	20 25	2.5	10	60	50	320
6	1	Naphthalene-disulfonic acid H_2SO_4	15 30	2.5	10	60	40	300
7	1	Naphthalene disulfonic acid H_2SO_4	15 20	2.5	10	60	40	350
Comparative Example:								
1	1	H_2SO_4	15	2.5	10	60	20	150
2	1	Naphthalene-disulfonic acid H_2SO_4	20 5	2.5	10	60	25	160

From Table 2, it is understood that the films formed according to the present process are greatly different in thickness and hardness from those formed according to the known processes, and that the present process can form hard and uniform anodic oxide films on copper-containing aluminum base alloys on which complete thick films have been difficultly formed hitherto.

EXAMPLE 8

The aluminum alloy 4 in Table 1 was degreased according to an ordinary procedure, and then subjected to anodic oxidation treatment at a current density of 2.5 A./dm.^{2} for 60 minutes in an electrolytic bath at 5° to 7° C. containing 15% by weight of sulfosalicyclic acid and 20% by weight of sulfuric acid. In this case, the cell voltage was gradually increased from 15 v. to 50 v. The film formed by said anodic oxidation treatment was subjected to sealing treatment by use of boiling water. The film had a thickness of about 60μ and a hardness of about Hv:500 in terms of Vickers hardness.

EXAMPLES 9–15 AND COMPARATIVE EXAMPLES 3–5

Example 8 was repeated, except that the electrolyte composition, the treatment temperature and the treatment time were varied. The results obtained were as set forth in Table 3.

TABLE 3

	Kind of alloy	Electrolyte composition (wt. percent)		Current density (amp./dm.^{2})	Electrolysis		Thickness of oxide film (μ)	Hardness of oxide film (Hv)
					Temp. (° C.)	Time (min.)		
Example number:								
9	4	Naphthalene-disulfonic acid H_2SO_4	15 30	2.5	5–7	40	40	510
10	4	Naphthalene-disulfonic acid H_2SO_4	10 30	2.5	5–7	40	40	460
11	4	Naphthalene-disulfonic acid H_2SO_4	15 18	2.5	5–7	40	40	470
12	4	Naphthalene-disulfonic acid H_2SO_4	15 20	2.5	10–12	60	65	420
13	4	Naphthalene-disulfonic acid H_2SO_4 $(COOH)_2$	15 20 1	2.5	5–7	60	60	510
14	4	Sulfophthalic acid H_2SO_4	15 20	2.5	5–7	60	45	480
15	4	Sulfophthalic acid H_2SO_4	15 20	2.5	10–12	60	65	440
Comparative Example:								
3	4	H_2SO_4	15	2.5	10–12	60	0–50	410
4	4	H_2SO_4	30	2.5	10–12	60	60	310
5	4	Naphthalene-disulfonic acid H_2SO_4	15 5	2.5	5–7	60	0–75	380

From Table 3, it is understood that according to the present process, uniform and hard anodic oxide films can be formed even on high silicon-containing aluminum base alloys. In case only the sulfuric acid concentration is made higher, a film is formed but the film formed is low in hardness as seen in Comparative Example 4. On the other hand, other known processes cannot give complete films.

EXAMPLES 16–18

The aluminum alloys 2, 3 and 5 shown in Table 1 were subjected to anodic oxidation treatment according to the present invention. The results obtained were as set forth in Table 4.

2. A process according to claim **1**, wherein the electrolyte contains 10 to 25% by weight of the aromatic sulfonic acid and 15 to 25% by weight of sulfuric acid.

3. A process according to claim **1**, wherein the aluminum alloy contains 6% by weight or more of silicon and 1% by weight or more of copper.

4. A process according to claim **1**, wherein the anodic oxidation treatment is effected at a temperature of from 0° to 15° C.

5. A process according to claim **1**, wherein the anodic oxidation treatment is effected at a current density in the range from 1 to 4 amp./dm.^{2}.

TABLE 4

Example number	Kind of alloy	Electrolyte composition (weight percent)	Current density (amp./dm.^{2})	Electroysis		Thickness of oxide film (μ)	Hardness of oxide film (Hv)
				Temp. (° C.)	Time (min.)		
16	2	Naphthalene-disulfonic acid 15 H_2SO_4 20	2.5	10	60	40	350
17	3	Naphthalene-disulfonic acid 15 H_2SO_4 20	2.5	10	60	40	430
18	5	Naphthalene-disulfonic acid 10 H_2SO_4 30	2.5	5–7	60	60	440

What is claimed is:

1. A process for forming a hard anodic oxide film on an aluminum alloy, characterized by subjecting an aluminum base alloy containing 1% by weight or more of copper to anodic oxidation treatment at a temperature below 20° C. using an aqueous electrolyte containing 5 to 40% by weight of an aromatic sulfonic acid selected from the group consisting of sulfosalicyclic acid, naphthalene-disulfonic acid, naphthalene-trisulfonic acid, phenol-sulfonic acid and sulfophthalic acid and 15 to 40% by weight of sulfuric acid.

6. A process according to claim **1**, wherein the electrolytic bath is further incorporated with oxalic or maleic acid.

References Cited

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