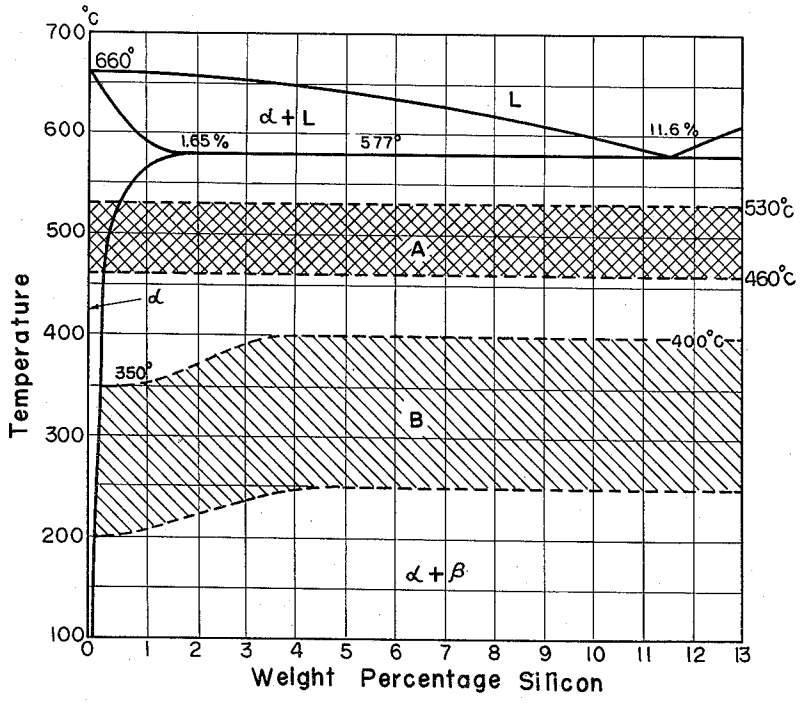
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METHOD OF FORMING A COLORED FILM ON AN ALUMINIUM ALLOY

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METHOD OF FORMING A COLORED FILM ON AN ALUMINUM ALLOY

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This invention relates to a method of forming a colored anodic film on an aluminum alloy, and in particular, to a method of working an aluminum alloy, containing a quantity of an additive alloy element in excess of its solid solubility range at the working temperature of the alloy, and then anodizing the same.

For producing a colored coating on an aluminum alloy surface, dyes or pigments have hitherto been generally used. However, as is generally known, the coating made by this process has defects of discoloring or scaling off soon. It is also known that a colored coating can be produced by anodic treatment. For instance, when an Al—5% Si alloy is anodized, the resultant film presents a grey color, not a fine jet-black color. Consequently, for the purpose of obtaining the jet-black color, the dye stuffs were mainly used. And, since the dyestuffs discolor easily, such film could be applied on the materials to be used solely in a dark place. A deep colored coating could have never been obtained by means of anodic treatment only.

Contrary to this grey colored anodic film made on an Al—Si alloy, the method of the present invention can produce a jet-black colored film on the surface of such Al—Si alloy. On aluminum alloys other than Al—Si alloy, the method of this invention can produce various deep-colored films depending upon each contained alloying element or compound. Thus, a bright yellow colored film is produced on alloys containing chromium, and a heavy dark yellowish brown colored film on alloys containing copper.

Therefore, an object of this invention is to provide a deep and characteristic colored film on the surface of the aluminum alloys by means of anodic treatment.

Another object of this invention is to provide, on the aluminum alloy surface, a colored anodic coating that does not discolor permanently even after exposure to sunlight and weather.

Another object of this invention is to provide colored light metal materials to be used on durable structures, decorative fixtures, instruments and the like.

According to this invention, aluminum is alloyed with a quantity surpassing the range of solid solubility of one or more of alloy constituents, and then the alloy is worked at a temperature lower than the typical hot working temperature, namely at a temperature where the matrix of the alloy is still fairly hard.

At such a temperature, the free constituents are contained in the state of brittle elements, compounds or eutectics, retaining their brittle property.

It must be noted that, in the succeeding operations, the alloy should not be heated higher than such temperature.

The anodizing process should be applied with a much larger current density than usually used.

Most aluminum alloys have each a solid solution range, as shown in their equilibrium diagram. Although it seems that metals such as iron and gold appear not to have the solid solution in the generally known equilibrium diagram, these metals have each an extremely slight range of solid solution (Fe: approximately 0.007–0.03%). The present invention shall cover even an alloy which has such a slight range of solid solution.

The film thus obtained in accordance with this invention presents a peculiar deep color depending upon the

alloy constituents, and the method can produce the anodic film of the characteristic deep color, such as pure jet-black, bright yellow and dark grey, said colors having never been obtained up to now.

The reasons why such a characteristic color is consonant with each constituent is obtained are assumed as follows: When several constituents are added in excess of their solid solubility range into aluminum, and castings are made by cooling the alloy slowly, the microscopic inspection of a polished casting of such alloy reveals that the elements or compounds or eutectics etc. in excess of their solid solubility limit exist in a free state among α phase. When the material in such a state is anodized, such free substances are only scattered roughly in anodic film of transparent α aluminum solid solution and do not tend to produce uniformly the characteristic deep color. When these alloys are heated and a certain temperature reached, the elements or compounds entrapped in the material begin to soften from their perimeter and present a semidiffusing condition, before the eutectic temperature or peritectic reaction temperature according to each kind of alloy is reached. A characteristic deep color can never be obtained by such elements or compounds in semi-diffusing condition.

Now, when an alloy containing such elements or compounds is wrought (rolled, extruded, forged, drawn or ironed) at a temperature where these exist as brittle substances, namely, at a fairly lower temperature than the typical hot working temperature, α matrix would be slightly softened. However, due to hardness fairly retained, the entrapped brittle elements or compounds would be pressed forcibly together with matrix by the working tools.

Thus, causing the friction between tools and metal as well as between the surface and the internal structure of metal, the brittle substances entrapped would be smashed to fine uniform particles, and on the alloy surface adjacent to the tools, for instance, rollers and dies, would be very finely and uniformly dispersed into α matrix. Upon applying the anodic treatment to such wrought material with a larger current density than usual, the α matrix is anodized to a transparent film, and the constituents or compounds, finely dispersed in the matrix, would become corresponding particles to the dispersoid in colloidal solution, and in the same manner as the colloidal solution presents a peculiar color due to dispersoid, the anodic film would have a proper color shade.

As described above, the working temperature is an important factor in the present invention. When the alloy is hot-wrought at the typical hot working temperature where the constituents contained easily diffuse, not only the greater part of constituents penetrate into the solid solution, but also free compounds or their eutectics, or free elements or their eutectics etc. diffuse into α matrix as if in supersaturated state, because they would appreciably approach the soluble condition. As the alloy does not become colloidal, though it is anodized, the film does not present its characteristic deep color shade, but only the intermediate or non-peculiar color appears.

On the contrary, this invention not only disperses finely the alloy constituents in matrix under a low temperature operation, but also enhances the characteristic deep color by anodizing the alloy with a large current density.

The accompanying drawing is a graphic illustration showing the alloy constituent and working temperature suitable for producing this invention in aluminum-silicon binary system.

To illustrate the invention more practically, we take an example of Al—Si alloy, having aluminum purity 99.7% and containing silicon 0.5%–10%.

The experiments were carried out on 10 different compositions which were cast to the thickness 15 mm. re-

spectively and heated to the temperatures of 200° C., 250° C., 300° C., 350° C., 400° C., 450° C., 500° C., and 550° C. respectively. Then, they were hot rolled from 15 mm. to 3 mm. After washing the surface, they were coldrolled to 0.75 mm. thickness and were electrolyzed as anode in 15% sulphuric acid electrolyte at the temperature of 23° C.–25° C., with the current density of 2.4 a./dm.^{2}.

The colors of the anodic film produced are shown in the following Table 1.

TABLE 1

Si, percent	0.57	0.85	1.27	1.77	2.44	2.75	3.34	5.43	7.46	9.82
Hot rolling temp., ° C.:										
200	NC	VLB	LB	LB	LB	LB	LB	PJB	PJB	PJB
250	LB	LB	LB	PJB	PJB	PJB	PJB	PJB	PJB	PJB
300	LB	PJB	PJB	PJB	PJB	PJB	PJB	PJB	PJB	PJB
350	LB	PJB	PJB	PJB	PJB	PJB	PJB	PJB	PJB	PJB
400	LB	LB	LB	B	B	B	B	PJB	PJB	PJB
450	NC	NC	NC	NC	SG	G	GB	GB	GB	GB
500	NC	NC	NC	NC	NC	SG	SG	GB	GB	GB
550	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC

NOTE.—The area of PJB indicates the most suitable condition for the invention.
NC=not colored.
VLB=very light black.
LB=light black.
PJB=pure jet black.
B=black.
GB=greyish black.
SG=slightly grey.
G=grey.

As will be seen from Table 1, the Al—Si alloys are usually hot-wrought at a temperature around 500° C. However, a pure jet-black film cannot be obtained at such working temperatures. At a lower temperature range which is covered by the present invention—namely 200° C.–400° C. for Al—Si alloy, a beautiful jet-black film can be formed.

Also, for Al—Cr binary alloys the anodic treatment has been applied, the result of which is shown in Table 2.

TABLE 2

Cr, percent	0.50	0.82	1.20	1.65	2.43	2.85	3.27	4.98
Hot rolling temp., ° C.:								
150	NC	LY	BY	BY	BY	BY	BY	BY
200	NC	LY	BY	BY	BY	BY	BY	BY
250	LY	BY	BY	BY	BY	BY	BY	BY
300	LY	BY	BY	BY	BY	BY	BY	BY
350	LY	BY	BY	BY	BY	BY	BY	BY
400	LY	LY	Y	BY	BY	BY	BY	BY
450	LGY	LGY	LGY	LGY	LGY	LGY	LGY	LGY
500	NC	NC	NC	LGY	LGY	LGY	LGY	LGY

NOTE 1.—The area of BY indicates the most suitable condition for the invention.
NC=not colored.
LY=light yellow.
LGY=light greyish yellow.
Y=yellow.
BY=bright yellow.
NOTE 2.—electrolysis condition:
Electrolyte—15% sulphuric acid solution.
Current density—2.5 a./dm.^{2}.
Temperature—20° C.
Time—40 minutes.

As will be seen from the above Table 2, a beautiful bright yellow film can be formed by hot rolling at a temperature between 250° C. and 400° C.

Now, the variation of anodic film color is made by the difference of current density as shown in Table 3.

TABLE 3

Current density (a./dm.^{2})	Al—2.43% Cr	Al—5.43% Si
0.5	Light yellow	Light black.
0.8	Bright yellow	Jet black.
1.0	do	Do.
1.2	do	Do.
1.5	do	Do.
2.0	do	Do.
3.0	do	Do.
5.0	do	Do.

The temperature of hot rolling of each alloy shown in Table 3 was 300° C. and the total quantity of current was 100 amperes×minutes respectively, and 15% sulphuric acid solution was used as electrolyte at a temperature of 23° C. As will be seen from this Table 3, the deeper color film can be obtained in holding the current density at 0.8 a./dm.^{2} and up. In this Table 3 the D.C. current was used. However, a similar result is obtainable by using the A.C. or the A.C. and D.C. superposed current. Although sulphuric acid solution is most suitable as electrolyte, oxalic acid, sulfamic acid, chromic acid or any commonly used acids can be used, and similar results can be obtained thereby.

The accompanying drawing is a diagram of Al—Si system. It shows the alloy constituent and working temperature suitable for this invention in Al—Si binary system. In this diagram, hatched area B is the section which can produce jet black, ranging from 0.7% silicon to the eutectic point (Si: about 11.6%) area, which deviates from the solid solubility limit and is far lower than the typical hot working temperature area A.

The above is only an example applied to the Al—Si alloy and the Al—Cr alloy. Similar results can be obtained on other aluminum alloys. For instance, bluish-grey color on Al—Ni binary system, dark yellowish brown color on Al—Cu binary system and pale pink color on Al—Mn system are obtainable, all of them showing their characteristics. Not only for binary alloy system, but also for multi-alloy system can this invention be applied.

As mentioned above, this invention can be applied to various alloys which contain the elements or compounds of eutectics formed between matrix and constituents or constituents themselves in the brittle conditions and dispersed as super fine particles. Therefore, we can apply this invention to various alloys as shown in Table 4. (In Table 4, (*) shows that, if the addition of alloying element is very small, the hot working temperature of the alloy should be below the solid solubility limit temperature.)

TABLE 4

Alloy	Addition range of alloying element, percent by weight	Hot wrought temperature, °C.	Anodic current density, a./dm.²	Color of oxidation film
Al—Ag	10–30	≦400*	0.8–8	brown.
Al—Au	0.3–5	≦400*	0.8–8	pink.
Al—B	0.8–5	≦400*	0.8–8	white.
Al—Ba	0.5–1.5	≦400*	0.8–8	Do.
Al—Be	0.5–2.5	≦400*	0.8–8	Do.
Al—Bi	0.5–4	≦270	0.8–8	purple grey.
Al—Ca	0.8–3	≦400	0.8–8	white.
Al—Cd	1–6	≦320	0.8–8	grey.
Al—Ce	0.5–10	≦400	0.8–8	yellow.
Al—Co	0.5–2	≦400	0.8–8	bluish grey.
Al—Cu	0.5–10	≦400	0.8–8	yellowish brown.
Al—Fe	0.5–3	≦400	0.8–8	yellowish grey.
Al—Ge	0.3–5	≦400	0.8–8	black.
Al—Li	2–8	≦400	0.8–8	brown.
Al—Li_2Si	0.8–5	≦400	0.8–8	grey.
Al—Mg	4–8	≦400*	0.8–8	white.
Al—MgAg	1–15	≦400	0.8–8	pale brown.
Al—Mg_2Si	0.5–8	≦400	0.8–8	white.
Al—Mg_2Sn	1–12	≦400	0.8–8	grey.
Al—$MgZn_2$	8–20	≦400	0.8–8	Do.
Al—Mn	0.5–3	≦400	0.8–8	pink.
Al—Mo	0.3–1	≦400	0.8–8	yellow.
Al—Ni	0.5–3	≦400	0.8–8	bluish grey.
Al—Sb	0.8–2	≦400	0.8–8	greyish white.
Al—Se	0.2–2	≦400	0.8–8	pink.
Al—Sn	0.5–5	≦200	0.8–8	grey.
Al—Ti	0.2–1.5	≦400	0.8–8	Do.
Al—V	0.2–1.5	≦400	0.8–8	Do.
Al—W	0.3–1.5	≦400	0.8–8	Do.
Al—Zn	10–25	≦250	0.8–8	Do.
Al—Zr	0.2–1	≦400	0.8–8	Do.

Certain examples of this invention are given hereunder. However, the invention is not to be limited to these examples.

Example I

An aluminum alloy containing 5.43% by weight of silicon was cast to 15 mm. thickness and heated for 5 hours in a heating furnace held at 400° C., and then, hot rolled to 3 mm. thickness at 400° C. After washing the surface, it was cold-rolled to 0.75 mm. thickness. By electrolysing the alloy in 3% oxalic acid solution for 40 minutes with the superposed current in the ratio of D.C. 2 (current density 3 a./dm.²): A.C. 1, a jet black color film was obtained.

Example II

An aluminum alloy containing 2% by weight of nickel was heated for 5 hours in the heating furnace kept at 350° C., hot rolled, and then, electrolysed in 15% sulphuric acid solution for 40 minutes with the current density 3 a./dm.². A light bluish grey color film was produced.

Example III

An aluminum alloy containing 2.12% by weight of copper was rolled and anodized by the same processes as in Example I. A dark yellowish brown film was obtained.

Example IV

An aluminum alloy containing 2% by weight of chromium was rolled and anodized by the same processes as in Example I. A bright yellow color film was obtained.

I claim:

1. The method of producing a colored film on the surface of an aluminum alloy, which consists in the steps of selecting an aluminum alloy containing more than 0.7% by weight of silicon, thermally treating the selected metal below the hot working temperature and within the range of 200–400° C., working the metal at a temperature below the hot working temperature and within the claimed range, and anodizing the said alloy with a current density larger than 0.8 amp. per dm.².

2. The method of producing a colored film on the surface of an aluminum alloy, which consists in the steps of selecting an aluminum alloy containing more than 0.7% by weight of chromium, thermally treating the selected metal below the hot working temperature and within the range of 150–400° C., working the metal at a temperature below the hot working temperature and within the claimed range, and anodizing the said alloy with a current density larger than 0.8 amp. per dm.².

3. The method of producing a colored film on the surface of an aluminum alloy, which consists in the steps of selecting an aluminum alloy containing more than 0.5% by weight of copper, thermally treating the selected metal below the hot working temperature and within the range of 150–400° C., working the metal at a temperature below the hot working temperature and within the claimed range, and anodizing the said alloy with a current density larger than 0.8 amp. per dm.².

4. The method of producing a colored film on the surface of an aluminum alloy, which consists in the steps of selecting an aluminum alloy containing more than 0.5% by weight of iron, thermally treating the selected metal below the hot working temperature and within the range of 150–400° C., working the metal at a temperature below the hot working temperature and within the claimed range, and anodizing the said alloy with a current density larger than 0.8 amp. per dm.².

5. The method of producing a colored film on the surface of an aluminum alloy, which consists in the steps of selecting an aluminum alloy containing more than 0.5% by weight of nickel, thermally treating the selected metal below the hot working temperature and within the range of 150–400° C., working the metal at a temperature below the hot working temperature and within the claimed range, and anodizing the said alloy with a current density larger than 0.8 amp. per dm.².

6. The method of producing a colored film on the surface of an aluminum alloy, which consists in the steps of selecting an aluminum alloy containing more than 0.3% by weight of gold, thermally treating the selected metal below the hot working temperature and within the range of 150–400° C., working the metal at a temperature below the hot working temperature and within the claimed range, and anodizing the said alloy with a current density larger than 0.8 amp. per dm.².

7. The method of producing a colored film on the surface of an aluminum alloy, which consists in the steps of selecting an aluminum alloy containing more than 0.3% by weight of germanium, thermally treating the selected metal below the hot working temperature and within the range of 150–400° C., working the metal at a temperature below the hot working temperature and within the claimed range, and anodizing the said alloy with a current density larger than 0.8 amp. per dm.².

8. The method of producing a deep colored film on the surface of an aluminum alloy, which consists of the steps of thermally treating the alloy below the hot working temperature and within the range of 150° C. to 400° C., thereupon working the alloy at a temperature below the hot working temperature and within the aforementioned range, said alloy containing an additive metal in a quantity greater than its solubility maximum in aluminum at said given temperature at which said working is made, then anodizing the alloy with a current density larger than 0.8 ampere per dm.².

9. The method of producing a deep colored film on the surface of an aluminum alloy, which consists of the steps of thermally treating the alloy below the hot working temperature and within the range of 150° C. to 400° C., thereupon working the alloy at a temperature below the hot working temperature and within the aforementioned range, said alloy containing an additive metal in a quantity greater than its solubility maximum in aluminum at said given temperature at which said working is made, then anodizing the alloy with a current density larger than 0.8 ampere per dm.².

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