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[54] **METHOD OF FORMING AN INTEGRAL COLORED ANODIC OXIDE ON ALUMINUM PRESSURE DIE CASTINGS**

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[52] **U.S. Cl.** **204/29,** 204/32, 204/58
[51] **Int. Cl.** **C23b 9/02**
[58] **Field of Search** 204/58, 29, 32

[56] **References Cited**

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[57] **ABSTRACT**

An integral colored anodic oxide film free from irregular patterns of metal flow, seams and cold shuts can be formed on die castings by subjecting the surface of pressure die castings of an aluminum alloy comprising 0.1 – 1.3 percent by weight of chromium, 0.2 – 3.4 percent by weight of manganese, said chromium and manganese being present in the amounts which are within the area of quadrilateral ABCD shown in the FIGURE, up to 0.3 percent by weight of impurities and the balance of aluminum, to roughening and brightening treatments, and thereafter subjecting thus treated products to anodizing treatment. Mechanical strength and castability of the alloy is further improved by addition of cobalt or zinc.

9 Claims, 1 Drawing Figure

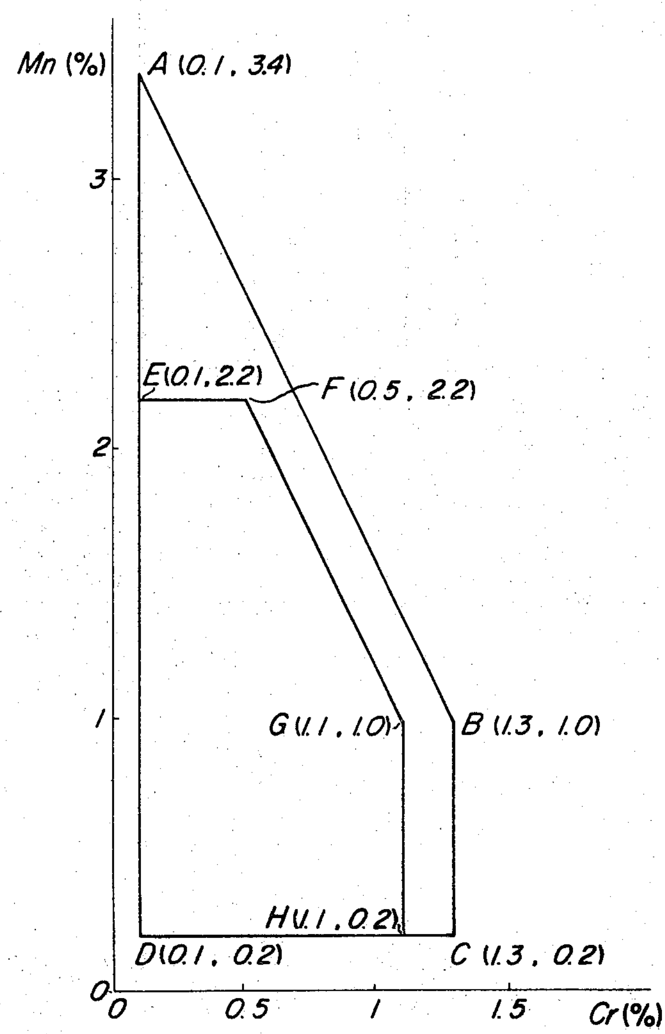

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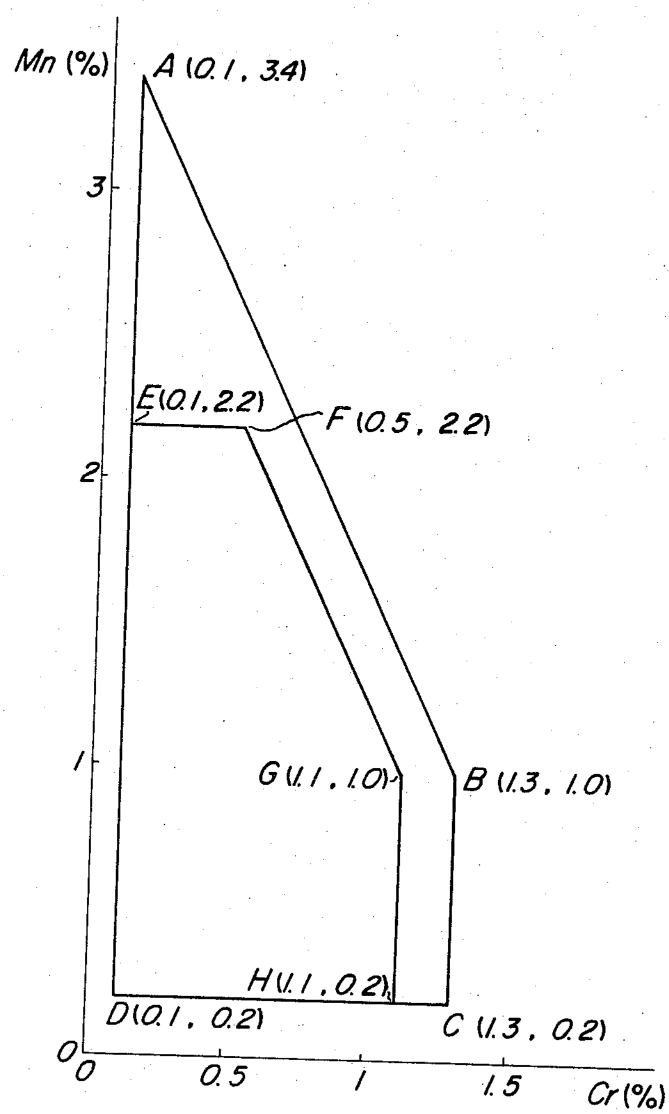
FIG. 1



METHOD OF FORMING AN INTEGRAL COLORED ANODIC OXIDE ON ALUMINUM PRESSURE DIE CASTINGS

The present invention relates to a method for forming an integral and uniform golden, yellowish brown, brown or reddish brown colored anodic oxide film on aluminum pressure die castings.

When the conventionally used pressure die casting aluminum alloy is subjected to anodizing treatment, irregular patterns of metal flow, seams and cold shuts are conspicuously formed. Therefore, such products have not been able to be utilized for decoration which aims at uniformity of surface color. Being different from sand castings or permanent mold castings, in the production of the pressure die castings, melt of aluminum alloy is pressure injected, namely, the melt is charged into dies under a high pressure in turbulent flow state. Therefore, in the pressure die casting, opportunities for contacting the melt of aluminum alloy and air much more occasionally occur than in sand casting methods and permanent mold casting methods and hence oxide of aluminum forms irregular patterns of metal flow and seams in the direction of the melt flow and cold shuts at joints where the melts collide with each other. Since these defects are contained on the surface and in the inner part of the die castings, anodizing treatment results in an unevenly colored oxide film. In case of the conventionally known pressure die casting aluminum alloys, even if these irregular patterns of metal flow, seams and cold shuts are physically or mechanically removed by buffing or blasting treatment before anodizing treatment, they are again formed when the die castings are subjected to chemical polishing and then to anodizing treatment. This phenomenon is especially clearly recognized with alloys which form relatively light colored anodic oxide film.

As the result of the inventor's research on pressure die casting aluminum alloys and a method for surface treatment of the die castings, it has been found that an integral and uniform colored anodic oxide film is formed by subjecting the products obtained by die casting the Al-Mn-Cr alloys to suitable surface treatment. Hitherto, such alloys have been known as those for forming a colored anodic oxide film on wrought products, for example, in Japanese Patent Publication No. **16218/63**. However, such alloys have not been used as colored die castings for decoration obtained by integral color anodizing (or self-color anodizing), because the irregular patterns of metal flow, seams, and cold shuts cause unevenness of color.

The FIGURE is a graph which shows the composition ranges of chromium and manganese in the alloy of the present invention.

The present invention provides a method for forming an integral and uniform colored film on aluminum pressure die castings which comprises die casting by the known method an alloy comprising 0.1 – 1.3 percent by weight of chromium, 0.2 – 3.4 percent by weight of manganese, said chromium and manganese being present in the amounts which are within the area of quadrilateral ABCD shown in FIG. **1**, up to 0.3 percent by weight of impurities and the balance of aluminum, roughening the surface of thus obtained die castings, subjecting the products to brightening treatment and thereafter subjecting the products to the anodizing treatment in the usual known methods, preferably in aqueous electrolyte containing 5 to 20 percent by weight of sulfuric acid.

When the chromium content in the alloy is less than 0.1 percent by weight, effective coloration is not attained. With increase of the content of chromium, yellowish color is increased, but the content of higher than 1.3 percent by weight is not preferred because it becomes necessary to raise the melting temperature of the alloy during the die casting procedure, whereby operation of pressure die casting becomes difficult due to increase of oxidation loss of the aluminum alloy and difficulty in parting from the pressure die casting dies.

Less than 0.2 percent by weight of manganese provides no effect on coloration. With increase of the content of manganese, the anodic oxide film is rendered reddish. However, when the content exceeds 3.4 percent by weight, irregular patterns of metal flow, seams and cold shuts begin to appear and it becomes difficult to obtain the desired integral and uniform anodic colored film. Therefore, the content of manganese should be not more than 2.2 percent by weight to obtain especially uniform anodic colored film.

Furthermore, the contents of chromium and manganese should be present in the amounts below the straight line connecting points A and B in FIG. **1** and when the contents exceed the values shown by the line AB, a film having uneven color is formed. An anodic oxide film having various color tones of from golden color to brown and reddish brown colors is obtained by suitably controlling the contents of chromium and manganese within said range. That is, when the weight ratio of manganese to chromium is lower than about 1.3, the film turns yellowish brown, when it is about 1.3 – 3, the film turns golden color or brown color and when it is higher than about **3**, the film turns reddish brown. A more uniform and decorative colored anodic oxide film on aluminum pressure die castings is obtained by controlling chromium and manganese in the amounts which are within the pentagonal area DEFGH shown in the FIGURE. Moreover, regarding iron and silicon contained in the alloy of the present invention as impurities, it is necessary that iron be up to 0.2 percent by weight and silicon be up to 0.1 percent by weight because they cause the film to have greyish black color and prevent coloration of alloying elements added.

Furthermore, mechanical strength and castability of pressure die casting aluminum alloys can be improved by adding cobalt or zinc to the alloy. That is, addition of 0.005 – 0.8 percent by weight of cobalt can improve soldering of the melt of aluminum alloy to dies for pressure die casting and prevent hot tear of the die castings. The soldering of general pressure die casting aluminum alloys is prevented by adding 0.6 – 1.0 percent by weight of iron. However, in case of the alloy of the present invention, addition of more than 0.2 percent by weight of iron causes the anodic oxide film to turn greyish black. Since removal of the die castings from dies becomes easy by addition of cobalt, it becomes possible to obtain products of more complicated shape. The addition of cobalt has the additional effect of increasing the mechanical strength of the product without giving an adverse effect on the colored film. In addition, cobalt has an effect of reducing the anodizing treatment time, thereby improving working efficiency. When the content of cobalt is lower than 0.005 percent by weight, the effects are small and when it exceeds 0.8 percent by weight, the colored film becomes greyish which is not preferred.

Zinc has an effect of increasing the mechanical strength of die castings without giving adverse effect on color tone of the oxide film. For example, Brinell hardness of Al-0.5 percent Mn-0.3 percent Cr alloy is H_B 27, but when the alloy contains 5 percent of zinc, Brinell hardness of the alloy becomes H_B 31. As mentioned above, with increase of the mechanical strength of die casting alloy, prevention of deformation of the die castings during parting from the dies and during handling can be expected. When content of zinc is less than 0.1 percent by weight, there is attained no such effect and when it exceeds 5.0 percent by weight, irregular patterns of metal flow, seams and cold shuts appear in the anodic oxide film.

Of course, respective effects of cobalt and zinc can also be expected by adding cobalt and zinc in the ranges as mentioned above.

The alloy of the present invention can be die cast by the usual pressure die casting method. Roughening of the surface of the die castings obtained may be conveniently effected by the generally known methods. Selection of abrasive materials for blasting treatment, treating time, etc. can be optionally determined depending upon the surface state of the product desired. Chemical brightening treatment is an essential treatment and its treatment may be effected by the generally known methods. The anodic oxide film of the die castings subjected to no such treatment has a greyish black color and the desired film having light uniform golden, yellowish brown, brown and reddish brown color tone cannot be obtained.

The die castings obtained in accordance with the method of the present invention are excellent in weathering resistance and corrosion resistance and can successfully be used for building materials, ornaments, etc. Even such products as of complicated three dimensional design can be mass-produced at low cost by die casting methods. Therefore, it can be expected that the products will be highly utilized for building panels, houses, furnitures, utensils, vehicles, etc.

In the FIGURE, the area of quadrilateral ABCD shows the composition ranges of chromium and manganese in the alloy of the present invention and the area

of pentagonal DEFGH shows the optimum composition ranges of chromium and manganese in the alloy of the present invention.

The Examples which follow illustrate but in no way limit the present invention.

EXAMPLE 1

A die cast product was produced by die casting an aluminum alloy comprising 0.3 percent by weight of chromium, 0.5 percent by weight of manganese, 0.12 percent by weight of iron, 0.07 percent by weight of silicon and the balance being aluminum. Said product was subjected to sand blasting treatment to render the surface completely aventurine. Thus treated, the product was dipped in a chemical polishing solution comprising 70 percent by weight of phosphoric acid, 3 percent by weight of nitric acid and the balance of water at a temperature of 95°C for 90 seconds and thereafter rinsed with water. Then, the product was subjected to anodizing treatment in a 10 percent aqueous solution of sulfuric acid at 20°C under a current density of 2 A/dm^2 for 30 minutes to obtain a uniform golden colored film free from irregular patterns of metal flow, seams and cold shuts on the surface of the die cast product. Thus obtained die cast product had a Brinell hardness of H_B 27.

EXAMPLE 2

A die cast product was produced by die casting an aluminum alloy comprising 0.2 percent by weight of chromium, 2.1 percent by weight of manganese, 0.14 percent by weight of iron, 0.06 percent by weight of silicon and the balance of aluminum. Said product was subjected to aluminum particle blasting treatment to render the surface thereof completely aventurine. Thus treated, the product was subjected to electro-polishing and then to anodizing treatment in a 15 percent aqueous solution of sulfuric acid at 20°C under a current density of 2.0 A/dm^2 for 40 minutes to form a uniform reddish brown anodic oxide film free from irregular patterns of metal flow, seams and cold shuts on the die cast product.

EXAMPLES 3 – 13

The following Table 1 shows the Examples of the similar methods with those of Examples 1 and 2.

Table 1

Example No.	Compositions of alloy (wt%)							Brinell hardness of die castings (H_B)
	Cr	Mn	Co	Zn	Fe	Si	Al	
3	0.7	0.3	—	—	0.13	0.07	balance	—
4	1.1	0.7	—	—	0.09	0.07	do.	—
5	0.3	0.5	0.5	—	0.11	0.08	do.	35
6	0.5	0.9	0.8	—	0.10	0.10	do.	—
7	0.2	1.9	0.6	—	0.10	0.05	do.	—
8	0.3	0.5	—	5.0	0.12	0.07	do.	31
9	0.9	1.1	—	3.0	0.10	0.05	do.	—
10	0.7	1.2	0.3	2.0	0.11	0.08	do.	—
11	0.2	2.0	0.3	1.0	0.09	0.07	do.	—
12	0.2	0.6	0.5	2.0	0.10	0.06	do.	38
13	0.6	0.3	0.5	—	0.10	0.08	do.	—

Pretreatment		Anodizing treatment			Color tone of anodic oxide film	Thickness of film (μ)
Roughening	Brightening	Electrolyte	Current density (A/dm^2)	Electrolysis time (min)		
Liquid honing	chemical polishing	15% H_2SO_4	2.0	30	yellowish brown	20
aluminum particle blasing	do.	do.	1.0	30	do.	10
steel shot blasting	do.	10% H_2SO_4	2.0	20	gold	13
do.	do.	do.	1.5	30	do.	15
aluminum particle blasting	do.	15% H_2SO_4	2.0	40	reddish brown	27
sand blasting	do.	do.	2.0	30	gold	20
aluminum particle blasting	electro-polishing	do.	3.0	10	yellowish brown	9
steel shot blasting	chemical polishing	do.	2.0	15	brown	10
do.	do.	do.	2.0	40	reddish brown	28
aluminum particle blasing	do.	do.	2.0	20	gold	14
"chemical" treatment for gaining aventurine surface		do.	2.0	15	yellowish brown	10

The anodic oxide films obtained in the above Examples were all colored films free from irregular patterns of metal flow, seams and cold shuts.

What is claimed is:

1. A method for forming a uniform, even, integral colored film on aluminum die castings, comprising:
   subjecting the surface of an aluminum pressure die casting to a series of steps,
   said aluminum casting comprising an aluminum alloy comprising 0.1–1.3 percent by weight chromium; 0.2–3.4 percent by weight manganese; said chromium and manganese present in amounts within the area of quadrilateral ABCD shown in FIG. 1; up to 0.3 percent by weight impurities; 0.005–0.8 percent by weight cobalt; and the balance of aluminum;
   said steps comprising:
   subjecting said aluminum pressure die casting to roughening treatment,
   then subjecting said aluminum casting to brightening treatment,
   and thereafter subjecting the aluminum casting to anodizing treatment in an aqueous electrolyte containing 5–20 percent by weight sulfuric acid, for forming an integral, uniform anodic oxide film having a color selected from the group consisting of gold, yellowish brown, brown and reddish brown.

2. The method according to claim 1, wherein the amounts of chromium and manganese contained in said aluminum alloy are within the area of pentagonal DEFGH shown in FIG. 1.

3. The method according to claim 1, wherein said aluminum alloy additionally comprises up to 0.2 percent by weight iron.

4. The method according to claim 1, wherein said aluminum alloy additionally comprises up to 0.1 percent by weight silicon.

5. A method for forming a uniform, even, integral colored film on aluminum die castings, comprising:
   subjecting the surface of an aluminum pressure die casting to a series of steps,
   said aluminum casting comprising an aluminum alloy comprising 0.1–1.3 percent by weight chromium; 0.2–3.4 percent by weight manganese; said chromium and manganese present in amounts within the area of quadrilateral ABCD shown in FIG. 1; up to 0.3 percent by weight impurities; 0.1–5.0 percent by weight zinc; and the balance of aluminum;
   said steps comprising:
   subjecting said aluminum pressure die casting to roughening treatment,
   then subjecting said aluminum casting to brightening treatment,
   and thereafter subjecting the aluminum casting to anodizing treatment in an aqueous electrolyte containing 5–20 percent by weight sulfuric acid, for forming an integral, uniform anodic oxide film having a color selected from the group consisting of gold, yellowish brown, brown and reddish brown.

6. The method according to claim 5, wherein the amounts of chromium and manganese contained in said aluminum alloy are within the area of pentagonal DEFGH shown in FIG. 1.

7. The method according to claim 5, wherein said aluminum alloy additionally comprises up to 0.2 percent by weight iron.

8. The method according to claim 5, wherein said aluminum alloy additionally comprises up to 0.1 percent by weight silicon.

9. A method according to claim 5, wherein said aluminum alloy additionally contains 0.005–0.8 percent by weight of cobalt.

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