

UNITED STATES PATENT OFFICE

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CORROSION-RESISTANT ALUMINUM ALLOY ARTICLES AND METHOD OF MAKING THE SAME

No Drawing.

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Aluminum base alloys are for many purposes superior to pure aluminum but at least some of them are subject to more or less rapid deterioration by reason of corrosion or like action, which militates against their use in situations where they are exposed to agencies conductive to or producing such effects. Impure aluminum is also affected by the same agencies though generally to a less extent.

10 Among the most important and valuable alloys are those of high tensile strength, as for example alloys containing copper, magnesium, silicon, manganese, and zinc, in various combination and proportions as components

15 in addition to aluminum. Of these I may mention specifically the well known alloys containing one or more of the above-named elements in approximately the following percentages, and usually containing small

20 amounts of impurities, as for example iron: (A)—copper 3 to 5, magnesium 0.5, manganese 0.6; (B)—same as (A) but without magnesium and with copper 4-5.5; (C)—magnesium 0.7, silicon 0.9.

25 The high-strength alloys, including the three specifically mentioned above, require heat treatment to bring out their desirable physical properties to the fullest extent. The heat treatment usually consists in heating the finished article to a temperature of around

30 500° C. for a suitable period and then quenching, followed by aging. Alloy (A) described above, is aged at room temperature, but alloys (B) and (C) may be aged (after

35 quenching) at a temperature between 100° C., and 150° C., approximately. This is known as "artificial" aging. Alloys (B) and (C) have greater resistance to corrosion before aging than after, and experience in general

40 indicates that artificial or high temperature aging decreases resistance.

The deterioration of alloys by corrosion is a serious matter in various arts, especially where replacement of corroded parts would

45 mean virtual rebuilding, or where failure of even a single part may mean disaster, as for example in aircraft. Moreover, the deterioration does not always betray itself by excessive surface corrosion, but may be and not

50 infrequently is due to internal or inter-granu-

lar action, leaving the surface of the part with no more than the expected amount of oxidation or the like. The result is that metal which to all appearances is unharmed may nevertheless be seriously weakened, thus making it difficult to detect imperfect parts.

I have accordingly been led to devise my present invention, which has for its chief object to protect the impure aluminum or aluminum alloy article against corrosion by

60 a non-porous surface layer or coating of substantially pure aluminum or of corrosion-resistant aluminum alloy. This object can be attained by casting the alloy or impure metal against the protective aluminum, preferably

65 in the form of sheets or plates, and subjecting the ingot thus formed to pressure and heat. By such method the coating and the underlying metal can be bonded together with a tenacity exceeding the tensile strength

70 of the coating.

In practicing the process in the preferred manner it is convenient to arrange the aluminum plates or sheets in the form of a lining for the mold in which the ingot or other

75 article is to be cast, but it is not necessary, and indeed it is not in general desirable, to have all inner surfaces of the mold lined with the aluminum plates. On the contrary it usually is sufficient and in most cases advisable to

80 line only two opposite surfaces. I have found that if an ingot so surfaced is rolled down to a thin sheet or plate, say a sixteenth of an inch thick, the alloy exposed at the

85 edges in many cases is not appreciably subject to weakening corrosion, if at all, even under severe conditions. Apparently the pure aluminum with which the alloy is surfaced exerts a protective action on the uncovered edges. On the other hand, in casting

90 ingots or billets for drawing tubes, rods, wire, etc., the entire inner surface of the mold may have a lining in the form of a tube, which is to be considered the equivalent of

95 one or more plates or sheets.

In order that the ingot may be rolled down or otherwise shaped by rolling, drawing, or like operations, the casting of the alloy against the aluminum mold-lining must produce an initial bond which will withstand

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shearing or similar stresses produced in such operation tending to cause the surface plates to slip on the underlying alloy. To insure this initial bond without harmfully affecting the surfacing sheets against which the alloy is cast it is advisable to observe certain precautions.

In the first place the tendency of the molten alloy to fuse or dissolve the aluminum sheets should be restricted so that the fusion or solution produced is only superficial. A certain amount of diffusion of one metal into the other is often desirable and in some cases essential, but this diffusion can be produced by subsequent heating and working of the ingot, and if the initial diffusion or penetration of alloy-components extends too close to the outer surface of the aluminum sheets or plates the subsequent diffusion, combined with the thinning of the protective aluminum layer by working, may in effect result in converting such layer into a corrodible alloy. While care in rolling or other working, and avoidance of too high temperatures in heating the ingot for working, will aid in preventing the result alluded to, care in such operations is not always sufficient and hence the casting operation should be properly carried out. It is therefore desirable to use a mold which will conduct, absorb, or dissipate heat rapidly, and the lining sheets should be in close contact therewith, so that the heat imparted to the sheets or plates by the larger body of molten alloy, preferably at a temperature as low as possible consistent with proper casting and initial bonding, will flow to the mold walls too rapidly to permit more than surface fusion of the aluminum. Iron molds having smooth inner surfaces have been found satisfactory for the purpose, and these are preferably water-cooled.

Even with molds of the kind just described it is advisable to use lining plates of substantial thickness not only because too thin a plate is more easily melted or raised to a dissolving or diffusing temperature but also if the plate is not of sufficient thickness originally the subsequent reduction in thickness by working may make it too thin to afford the desired degree of protection.

It is also advantageous, in casting the ingot, to avoid pouring the molten alloy against any part of the mold lining, as it has been found that a stream of molten alloy flowing on the aluminum plate is apt to make a hole or a cavity therein. Such effect may be due in part, at least, to erosion or some analogous action. Avoidance of splashing of the molten alloy is also desirable. In general I try to have the alloy fold itself, so to speak, into contact with the plates, as a liquid poured gently into a vessel rolls or folds into contact with the walls. Then if there is any substantial fusion of the aluminum plate the

fused portion is not moved out of place, and deeper or more extensive fusion is therefore less likely to occur. A good method of casting is to pour the molten alloy in a gentle stream down an unlined surface of the mold, tilting the mold at first so as to incline the unlined surface and gradually straightening it up as the pouring proceeds. In this way, with the temperature of the alloy, the mass of the alloy and the mass of the lining sheets, and the rate of pouring so related that the alloy freezes against the lining surface at about the same rate as its contact therewith, the disadvantageous conditions mentioned can be avoided. What I aim at is to produce a union which is predominantly one of cohesion as distinguished from adhesion.

Contrary to expectation, my observation is that the surface oxidation ordinarily found on aluminum does not prevent the necessary initial bonding, and hence, although dirt and grease should, obviously, be removed, it has not been necessary to clean the aluminum by etching with acid or alkali, or by sand-blasting or wire-brushing, or the like abrasion. It is probable that this oxide film is one cause of the failure of attempts to bond plates of aluminum and aluminum alloy together by hot-rolling of the two in contact. I believe that in my process the molten alloy penetrates the oxide film at many points and thereby comes into cohesive or molecular contact with the metallic aluminum, and may, conceivably, dislodge or penetrate under some of the oxide particles. In strengthening this initial bond or union by rolling or other working, the numerous points or minute areas of cohesion are extended or spread out, but intervening oxide particles are not. Hence in the aggregate the area of molecular cohesion so greatly exceeds the aggregate area of the island-like non-cohering points that the latter are in effect non-existent. Whether the theory just outlined be true or not, a union comparable to such a bond in completeness and tenacity is obtainable when my process is carried out with care and intelligence.

The coating plates may be held against the inner surfaces of the mold by means of clamps, or they may have their edges seated in grooves. Making the lining in two or more parts is advantageous in that it permits expansion with less or no tendency to buckling or warping during heating by the hot alloy. In many cases annealing the coating material minimizes such tendency.

The initial bond of the surfacing plates to the alloy or impure aluminum core is made complete by heat and pressure, preferably rolling pressure, repeated as may be necessary to bring about complete union and, if desired, reduce the ingot or billet to a plate or sheet of the desired thickness. In such treatment there is more or less diffusion of alloy-components into the aluminum plates, and

care should be taken not to cause or permit this alloying action to extend too close to the outer surface. It is therefore desirable in most cases to keep the working temperature below that at which too rapid solution of copper or other non-aluminous metal or metals present takes place. For this reason, especially in the case of alloys whose physical properties are to be improved by heat-treatment, it is desirable that the temperature to which it is heated for rolling or other working should be well below the melting point of the eutectic or eutectics. For example, with an alloy of type A above referred to for which a heat-treating temperature of 520° C. is satisfactory, a working temperature between 480° and 500° C. gave perfect results, the surface sheets or layers being so completely united to the alloy that they could not be stripped off nor could separation be even started. In this example an iron mold was used, 8 inches deep, 7 inches wide, and 1.5 inches from front to back, inside measurements. The side walls were $\frac{3}{4}$ inch thick, edge walls $1\frac{1}{2}$, and bottom 3 inches thick. The lining sheets, smooth on both sides and 0.1 inch thick, were of annealed electrolytically refined aluminum 99.95 per cent pure, and were cut to allow for the expansion incident to the heat to which they were subjected in casting the alloy. The alloy contained copper 3.33 per cent, silicon 0.33 per cent, magnesium 0.49 per cent, manganese 0.40 per cent, iron 0.34 per cent, and the rest aluminum. The alloy, at a temperature of about 730° C., was poured into the open top of the mold in the ordinary manner. After removal from the mold the ingot was heated to 480° to 500° C. and while at this temperature was rolled to 0.5 inch thickness. It was then reheated to 460° C. and rolled to 0.1875 inch. The sheet was then annealed at 250° C. and cold-rolled to 0.064 inch, and finally heat-treated by holding it for twenty minutes in a fused bath of sodium and potassium nitrate at 520° C., followed by quenching in cold water and aging at room temperature.

The surface appearance of the sheet was better than that of a sheet produced according to the usual method and there was no evidence of blistering or like defects. Microscopic examination showed there were no discontinuities between the alloy and the pure aluminum coating, and indicated perfect union. Diffusion of copper from the alloy into the aluminum coating, 0.0045 inch thick, was slight but easily seen.

After aging for one week, five specimens of the sheet were tested for corrosion, along with similar pieces of the same alloy uncoated, by continuous subsection for eight weeks to a mist produced by spraying a 20 per cent solution of common salt. At the end of this time the tensile strength and elongation of the coated articles had suffered no im-

pairment. On the other hand the average of the five uncoated specimens showed a loss of 13.6 per cent in tensile strength, or more than 4 tons per square inch, and the elongation had decreased from 20.4 per cent to 7.0 per cent in 2 inches, or a loss of 65.7 per cent. Larger ingots of type A alloy, approximately 4 by 12 by 24 inches in size, with surfacing sheets $\frac{1}{4}$ inch thick, have also been cast and worked with completely satisfactory results. I have also found that fabrication of coated ingots into other articles is notably easier and can be effected at less cost than with uncoated ingots of the same alloy, as the coating eliminates or greatly decreases many of the difficulties hitherto encountered in rolling.

In speaking of heating and working the ingot after casting I do not mean to imply that the ingot must be allowed to cool below the working temperature and then reheated. On the contrary it is only when the casting has cooled too far that reheating need be resorted to, and in some cases it is advantageous to begin the working without allowing the casting to cool far enough to necessitate reheating. This is especially true with alloys of high magnesium content, or, in general, with alloys which oxidize readily. With such alloys, it appears that if the core and the coating sheets do not stick at all points air finds its way in between, with the result that in the reheating the oxide or nitride film, or whatever it may be, is materially increased and becomes too great to permit eventual attainment of a bond complete enough to prevent separation. I have found, however, that if the ingot be subjected to pressure, say a light pass between rolls, before it has cooled too far, preferably as soon as it can be taken from the mold and before it has cooled appreciably, the union can be improved to such an extent that adequate initial bond can be obtained.

I have found that alloys containing copper, say from 2 to 6 per cent, are most suitable for my process. On the other hand magnesium tends to be disadvantageous and apparently should be less than about 1 per cent to give in the casting step alone the bond needed to prevent excessive oxidation or the like between the alloy and the aluminum surfacing plates, but by pressing the plates firmly on the alloy core before the ingot has cooled down too much, preferably applying the pressure by rolling as soon as the ingot can be taken from the mold, as described just above, the desired bond can be obtained with alloys containing much higher amounts of magnesium. For the surfacing plates I prefer the high purity electrolytically refined aluminum now available on the market but ordinary commercial aluminum may be used, as may also aluminum alloys having adequate resistance to corrosion, and in the claims

the term "aluminous metal" is intended to include commercial aluminum and corrosion-resistant aluminum alloys as well as aluminum of high purity. The alloys are generally harder than aluminum and are therefore advantageous where a harder surface is desired. Alloys of aluminum and manganese, and aluminum and beryllium, are suitable for such purpose.

I am aware that it has been proposed, in British Patent No. 25,380 of 1898, and in Swiss Patent No. 18,292 of 1899, to provide an article of aluminum alloy with a coating of pure aluminum by rolling the aluminum and the alloy together, hot or cold; but such method has been found to be unsuccessful, it being impossible to produce thereby the cohesive bond which characterizes the product of my process and makes the two metals, the alloy and the aluminum, an integral unit. The lack of cohesion between the two bodies in the product of the method referred to is evidenced by the fact that if the article so made is heated the aluminum layer puffs up in the form of blisters, indicating that although the two layers may have been close together they were in fact not in actual molecular metal-to-metal contact.

It is to be understood that the invention is not limited to the specific procedure herein described but can be carried out in other ways without departure from its spirit. Nor it is confined to alloy, strictly so called, as the coated metal or metal to be coated, since it may, in general, be employed with impure aluminum as the equivalent of an alloy and the subjoined claims are intended to be so interpreted.

I claim—

1. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting a body of the alloy in contact with a plate of the aluminous metal while dissipating the heat of the alloy at a rate adapted to cause freezing of the alloy on the plate with not more than superficial fusion of the plate, whereby an initial surface-bond between the two is produced, and completing the bond by heat and pressure with the article at a temperature sufficiently below the eutectic melting point to prevent excessive inter-diffusion.

2. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting a body of the alloy in contact with a plate of the aluminous metal while dissipating the heat of the alloy at a rate adapted to cause freezing of the alloy on the plate and produce an initial bond with not more than superficial fusion of the contiguous plate surface, hot-working the article to complete the bond without causing sufficient inter-diffusion to bring non-aluminous alloy components to the surface of the alumi-

nous metal coating, and heat-treating the worked article.

3. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising lining with the aluminous metal a mold having thermally conductive walls, casting therein a body of the alloy and by regulation of the alloy temperature and pouring rate causing the alloy to freeze on the mold lining with cohesion-contact without more than superficial fusion of the lining, hot-working the article at a temperature sufficiently lower than the eutectic melting point to prevent such diffusion of non-aluminous alloy-components into the coating metal as to destroy the corrosion-resistant properties thereof, and heat-treating the worked article.

4. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting a body of the alloy against a plate of the aluminous metal without erosive movement of the alloy thereon and by regulation of the temperature and pouring rate according to the rate of heat dissipation from the contiguous surface of the plate causing the alloy to freeze on said surface and produce an initial bond with not more than superficial fusion, completing the bond by hot-working, and heat-treating the worked article.

5. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising lining a metal mold with the aluminous metal, casting in the lined mold a body of the aluminum alloy and by regulation of the temperature and pouring rate of the alloy according to the rate of heat transfer through the mold lining and the mold walls causing the alloy to freeze in cohesive contact with the lining with not more than superficial fusion thereof whereby an initial bond is produced, hot-working the article to complete the bond, and heat-treating the worked article.

6. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting against a plate of the aluminous metal a body of aluminum alloy containing copper and by regulation of factors determinative of the solidification of the alloy causing the same to freeze on the plate and produce an initial bond with not more than superficial fusion thereof, completing the bond by hot-working at a temperature too low for excessive diffusion of copper into the coating metal, and heat-treating the worked article.

7. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting a body of aluminum alloy containing copper against a lining of the aluminous metal in a mold having heat-conducting walls and by regulation of other casting conditions causing the alloy to freeze

on the lining and produce an initial bond with not more than superficial fusion of the lining or penetration of copper into the same, and hot-working the article to complete the bond, at a temperature sufficiently below the melting point of the aluminum-copper eutectic to prevent excessive penetration of copper into the aluminous coating metal.

8. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal comprising casting a body of the alloy against a plate of the aluminous metal and by regulation of the casting conditions causing the alloy to freeze on the plate and produce an initial bond with not more than superficial fusion of the plate, and hot-working the article under conditions preventing destruction of the corrosion-resistant properties of the aluminous metal by diffusion of non-aluminous alloy components into the same.

9. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting a body of the alloy against a plate of pure aluminum and by regulation of the casting conditions causing the alloy to freeze on the aluminum and produce an initial bond with not more than superficial fusion of the aluminum, completing the bond by hot-working under conditions preventing destruction of the corrosion-resistance of the aluminum by diffusion of non-aluminous alloy components into the aluminum, and heat-treating the worked article.

10. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting a body of aluminum alloy containing copper against a plate of pure aluminum and by regulation of the casting conditions producing an initial bond between the alloy and the aluminum with not more than superficial fusion of the latter or penetration of copper into the same, hot-working the article at a temperature too low for penetration of copper far enough to destroy the corrosion-resistant properties of the coating, and heat-treating the worked article.

11. Process of coating corrodible aluminum alloy with corrosion-resistant aluminous metal, comprising casting against a plate of pure aluminum a body of aluminum alloy containing copper and magnesium and by regulation of temperature and pouring conditions according to the rate of conduction of heat from the surface of the aluminum causing freezing of the alloy on the aluminum and producing thereby an initial bond with not more than superficial fusion of the aluminum plate or penetration of copper into the same, completing the bond by hot-working the article under conditions preventing destruction of the corrosion-resistant properties of the aluminum by penetration of copper

into the latter, and heat-treating the worked article.

12. A corrosion-resistant aluminous metallic article comprising a relatively thick main body of corrodible aluminum alloy and a relatively thin wrought non-porous protective coating of corrosion-resistant aluminum directly cohesively united with the main body, the article being capable of being heat-treated without blistering.

13. A corrosion-resistant aluminous metallic article comprising a relatively thick main body of heat-treated aluminum alloy and a relatively thin wrought non-porous protective coating of annealed corrosion-resistant aluminum directly cohesively united with the main body, the article being capable of being heat-treated without blistering.

14. A corrosion-resistant aluminous metallic article comprising a relatively thin main body of heat-treated aluminum alloy containing between 2 and 6 per cent of copper, and a relatively thick wrought non-porous protective coating of annealed corrosion-resistant aluminum, directly cohesively united with the main body and free from blisters.

15. A corrosion-resistant aluminous metallic article comprising a relatively thick main body of heat-treated aluminum alloy containing between 2 and 6 per cent of copper, and a relatively thick wrought non-porous protective coating of annealed corrosion-resistant aluminum, directly cohesively united with the main body and free from blisters, said article being capable of withstanding continuous contact with mist from a 20 per cent salt solution for a period of at least eight weeks without appreciable loss of tensile strength and ductility.

16. An article composed of a relatively thick body of corrodible aluminum alloy having a relatively thin wrought non-porous coating of corrosion-resistant aluminous metal directly cohering with a tenacity exceeding the tensile strength of the coating.

17. An article composed of a relatively thick body of corrodible aluminum alloy having a relatively thin wrought non-porous coating of corrosion-resistant aluminous metal directly cohering with a tenacity exceeding the tensile strength of the coating, said article being capable of withstanding continuous contact with mist from a 20 per cent salt solution for a period of at least eight weeks without appreciable loss of strength and ductility.

18. A corrosion-resistant aluminous metallic article comprising a relatively thick main body of heat-treated aluminum alloy and a relatively thin wrought-non-porous protective coating of annealed corrosion-resistant aluminum, directly cohesively united with the main body and free from

blisters, said article being capable of withstanding continuous contact with mist from a 20 per cent salt solution for a period of at least eight weeks without appreciable loss of strength and ductility.

In testimony whereof I hereto affix my signature.

EDGAR H. DIX, JR.

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CERTIFICATE OF CORRECTION.

PatentNo. 1,865,089.

June 28, 1932.

EDGAR H. DIX, JR.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, line 79, for the misspelled word "contray" read contrary; page 2, line 93, for "allow" read alloy; page 4, line 32, for "it is" read is it; page 5, line 85, claim 14, for "thin" read thick, and lines 88 and 97, claims 14 and 15 respectively for "thick" read thin; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 25th day of October, A. D. 1932.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.

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