

UNITED STATES PATENT OFFICE

FRANCIS C. FRARY, OF OAKMONT, PENNSYLVANIA, ASSIGNOR TO ALUMINUM COMPANY OF AMERICA, OF PITTSBURGH, PENNSYLVANIA, A CORPORATION OF PENNSYLVANIA

CORROSION-RESISTANT ALUMINUM ALLOY ARTICLE

No Drawing.

Application filed November 30, 1929. Serial No. 410,877.

Aluminum base alloys are for many purposes superior to pure aluminum, especially the so-called strong alloys, but these alloys are in general subject to attack by corrosive agencies, and the corrosion thus caused results in a loss of tensile strength and elongation. This corrodibility militates seriously against the use of the alloy in certain fields, as for example in aircraft, where failure of even a single part may mean disaster. For the purpose of overcoming the defect it has been proposed to provide articles of strong alloy with a coating of pure or substantially pure aluminum which has high resistance to corrosion, and alloy thus protected, sold under the name "Alclad", has gone into extensive use.

Aluminum has, however, low tensile strength in comparison with the alloys referred to, and hence an alloy article protected by an aluminum coating or layer has less strength, weight for weight, than an unprotected article of the same alloy. Where for an adequate margin of safety the protective coating is a substantial proportion of the total weight the difference in strength may be an important item, amounting in some cases to as much as 10 per cent. Moreover, aluminum is a soft metal, far softer than the alloys referred to, and hence a coating of aluminum gives the article a surface which is not adapted to stand abrasive or erosive agencies.

Need has therefore been felt for protected articles of greater strength and surface hardness, at the same time possessing the desired resistance to corrosion, and I have accordingly been led to devise my present invention, which has for its chief object the provision of an article of strong alloy, with a protective coating of another strong alloy which may be hardened by suitable thermal processing and possesses the necessary corrosion-resistance.

The strong aluminum alloys require heat-treatment to develop their desirable properties to the fullest extent. This treatment usually consists in heating the finished article to an elevated temperature, say around 500° C., quenching to a low temperature by means of a cooling medium, and then "aging" the

alloy. Aging of the quenched alloy may be effected in different ways, depending upon the nature of the alloy. Some aluminum alloys "age" spontaneously, at room temperature, and develop full strength without further treatment, while others do not age in that way or do so only in small degree. In the case of these latter alloys, if it is desired to fully develop their advantageous physical properties they must, after they have been heated and quenched, be subjected to "artificial aging", which consists in heating the alloy to a temperature between approximately 100° and 150° C. Alloys which age at room temperature and alloys which require artificial aging can be conveniently described as "spontaneously ageable" and "artificially ageable", respectively.

In general, alloys which age spontaneously at room temperature are not as susceptible to corrosion attack as are those which have been artificially aged. On the other hand, alloys which have undergone aging as part of their heat-treatment generally have better physical properties than when aging is omitted. I have found, however, that an aluminum alloy containing about 0.7 per cent of magnesium and about 0.9 per cent of silicon, which is one of the alloys capable of artificial aging, possesses, in the quenched condition without aging, its maximum resistance to corrosion and at the same time has the hardness and tensile strength required for my purpose. On the other hand, an aluminum alloy containing approximately 3 to 5.5 per cent copper, 0.5 per cent magnesium, and 0.6 per cent manganese, ages spontaneously. I therefore use the latter alloy (aluminum-copper-magnesium-manganese) as the base or core of my article and provide it with a protective coating of the first-mentioned aluminum alloy, containing magnesium and silicon. Then when the article is heated and quenched I have an article consisting of a base or core composed of an alloy which ages spontaneously, at room temperature, and a coating alloy which does not age spontaneously but nevertheless possesses a high degree of hardness and tensile strength, so that the article as a whole has not only the important

characteristic of resistance to corrosion but also a degree of hardness and tensile strength only slightly less than that which would be possessed by the same article if made wholly of the base alloy. On the other hand, if my article is artificially aged the strength of the base or core would be decreased, and while the strength of the coating would be slightly increased its corrosion resistance would be materially lessened.

Corrosion tests of the coated article described above show that the coating is in respect to corrosion-resistance comparable to aluminum itself. For example, a test bar of the alloy-coated metal, after being subjected to mist from a spray of 20 per cent salt solution for two years, showed a tensile strength of 58,180 pounds per square inch, as against 59,260 pounds before the test, the loss of strength being roughly 1.8 per cent. This was the greatest loss sustained, the lowest being less than 0.2 per cent. The metal used for the coating also exhibits a Brinell hardness of 64, and is thus well suited to uses where abrasion- and scratch-resistance is important. In the test referred to, the elongation decreased less than 7.5 per cent and the yield point 6.6 per cent.

In making the article in the preferred way an ingot is made by casting the base alloy against the protective alloy, which latter may be in the form of plates or sheets. The ingot is then subjected to heat and pressure, as by rolling and intermediate heating, to complete the initial bond produced by the casting, the working being continued to produce a sheet or plate of the desired thickness for fabrication.

It is convenient to arrange the protective alloy plates or sheets in the form of a lining for the mold in which the ingot or other 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 plates. On the contrary it usually is sufficient and in most cases advisable to line only two opposite surfaces, though in casting 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 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 base alloy against the alloy mold-lining must produce an initial bond which will withstand shearing or similar stresses produced in such operations 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 surfacing 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 components of the base alloy extends too close to the outer surface of the sheets or plates of the protective alloy the subsequent diffusion, combined with the thinning of the protective 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. In some cases it may be desirable or even necessary to heat-treat the protective alloy plates, or make them of heat-treated alloy, without, however, artificial aging. This preliminary heat treatment puts in solid solution those alloy constituents which form with the aluminum a low-melting eutectic, thus eliminating (by such solution) as much as possible of the low-melting eutectic.

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 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 alloy plate the fused portion is not moved out of place, and deeper and 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.

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. In rolling I have observed that there is greater tendency for the coating alloy to rise or "lift" with the rolls than is the case where pure aluminum is used as the protective metal, but this tendency can be overcome by using lighter passes or less reduction per pass.

Contrary to expectation, my observation is that the surface oxidation ordinarily found on the protective alloy 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 alloy by etching with acid or alkali, or by sand-blasting or wire-brushing, or the like abrasion. It is believed that in the process described 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 the operation is carried out with care and intelligence.

As stated above, the preferred protective alloy contains approximately 0.7 per cent magnesium and 0.9 per cent silicon, but these proportions can be varied, remembering, however, that in general the larger the amounts of the ingredients named the harder the alloy is to work. The alloys should not contain copper beyond what may be present as an inconsequential impurity, but should contain enough magnesium and silicon to give an effective amount of the compound Mg_2Si . It may contain one or more other metals in small amount, such as nickel, manganese, chromium and titanium, which tend to increase the hardness of the alloy without seriously impairing its resistance to corrosion. The base or core alloy is preferably one containing 3 to 5.5 per cent of copper, 0.5 per cent magnesium, and 0.6 per cent manganese, with or without other ingredients sometimes used in aluminum-copper alloys. The proportions named can be varied, and the manganese can be omitted entirely, with some decrease of tensile strength in the heat-treated article. So also the magnesium, but the omission of this element destroys or at least impairs the capability of spontaneous aging and is not recommended.

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 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 components of the cast alloy into the coating plates, and care should be taken not to cause or permit this alloying action to extend too close to the

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 core 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 on the casting, is materially increased and may become too great to permit eventual attainment of a bond complete enough to prevent separation.

However, 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 an adequate initial bond can be obtained.

I do not claim the process herein described, but what I claim as my invention is:

1. A corrosion-resistant article of aluminous metal comprising a main body or core of aluminum-copper alloy and a hard, wrought, protective coating of copper-free aluminum alloy cohesively united with the core, the coating alloy being resistant to corrosion after heat-treatment without artificial aging, and both alloys being susceptible of substantial improvement in physical properties by heat-treatment without artificial aging.

2. An article composed of corrodible spontaneously ageable aluminum alloy of high tensile strength and a hard protective coating of corrosion-resistant artificially ageable aluminum alloy of high tensile strength cohesively united with the core and containing the compound Mg_2Si , both alloys having the physical properties characteristic thereof when heat-treated without artificial aging.

3. A corrosion-resistant aluminous metallic article comprising a main body or core of spontaneously ageable aluminum-copper alloy cohesively united with the core and containing magnesium, and a hard corrosion-resistant coating of artificially ageable copper-free aluminum alloy containing magnesium and silicon, the article having been heat-treated without artificial aging as evidenced by a tensile strength exceeding about 55000 pounds per square inch and a Brinell hardness not less than about 60, the article also being capable of withstanding prolonged exposure to mist from a 20 per cent salt solution without material loss of tensile strength.

4. A heat-treated corrosion-resistant aluminous metallic article comprising a main body or core of readily corrodible spontaneously ageable aluminum-copper alloy containing magnesium and manganese and a cohesively joined coating of copper-free corrosion-resistant aluminum alloy containing magnesium and silicon and at least one other constituent adapted to have a hardening effect upon the alloy.

5. A corrosion-resistant article of aluminous metal, comprising a main body or core of spontaneously ageable aluminum alloy containing, approximately, 3 to 5.5 per cent copper, 0.5 per cent magnesium, and 0.6 per cent manganese, and a hard cohesively joined coating of copper-free corrosion-resistant artificially ageable aluminum alloy containing, approximately, 0.7 per cent magnesium and 0.9 per cent silicon.

6. A corrosion-resistant article of alumi-

nous metal, comprising a main body or core of aluminum alloy containing, approximately, 3 to 5.5 per cent copper, 0.5 per cent magnesium, and 0.6 per cent manganese, and a hard, cohesively joined coating of copper-free aluminum alloy containing, approximately, 0.7 per cent magnesium and 0.9 per cent silicon, the article being heat-treated without artificial aging, as evidenced by the physical properties due to such treatment and by the corrosion-resistance of the coating alloy.

7. A heat-treated corrosion-resistant article of aluminous metal, comprising a main body or core of spontaneously ageable aluminum-copper alloy containing magnesium; and a hard, corrosion-resistant protective coating of artificially ageable aluminum alloy containing magnesium and silicon, cohesively united to the main body and possessing greater resistance to corrosion before artificial aging than after; both the main body or core and the coating of the article having the physical properties produced in the respective alloys after heat-treatment without artificial aging.

In testimony whereof I hereto affix my signature.

FRANCIS C. FRARY.