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## METHOD OF PRODUCING DUPLEX METAL ARTICLES

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This application is a continuation-in-part of our copending application Serial No. 54,946, filed December 17, 1935.

This invention relates to the surface hardening of corrosion-resistant aluminous duplex metal articles while retaining the protective character of the coating.

Although the resistance to corrosion of many aluminum base alloys is satisfactory under ordinary service conditions, yet there are some applications where these alloys are exposed to severe corrosive conditions. A very effective method of protecting articles made from these alloys is to provide them with a coating of aluminum or an aluminum base alloy having adequate resistance to corrosion, as described in U. S. Patent 1,865,089 to Dix. While an aluminum coating provides a satisfactory electrolytic protection in many cases, yet the metal is inherently soft, especially the high purity metal, and can therefore be easily scratched. Where a harder surface is desired, an aluminum base alloy may be used in place of the aluminum, as mentioned in the Dix patent. A particular application of the use of an alloy coating is disclosed in U. S. Patent 1,805,448 to Frary. The improvement consists in providing a coating for a heat treated and spontaneously aging aluminum base alloy containing copper, said coating consisting of a copper-free aluminum base alloy, preferably one which contains magnesium and silicon, and which is also capable of improvement in physical properties by heat treatment without artificial aging.

Although duplex metal articles of the foregoing kind having an aluminum-magnesium-silicon alloy coating are satisfactory from the standpoint of service, yet some difficulties are encountered in fabricating these articles because of the danger of oxidation from heating such alloy coatings prior to uniting them to the core, and because of the greater resistance to deformation possessed by such articles as compared to similar articles having an aluminum coating. The precautions and additional work incident to making such articles increase the cost of manufacture, and hence it is preferred, whenever possible, to make duplex metal articles having an aluminum coating. Our invention is directed to a new and simpler method of making such duplex metal articles having alloy coatings. While the product of our invention is not in some ways as satisfactory as the more highly alloyed coatings described by Frary and Dix, it is nevertheless useful for many purposes, and it is a distinct improvement over articles having an aluminum coating in respect to the hardness of the coating. Furthermore, it is possible to make duplex articles having a core alloy that is artificially aged after solution heat treatment.

Our invention has as its principal object the provision of a method of hardening an initially soft magnesium-free aluminous protective coating on a strong alloy core. Another object is to provide a method of hardening the coating of a previously formed aluminous duplex metal article. Still another object is to provide a method of reducing the cost of making abrasion resistant duplex metal articles of aluminum base alloys.

Our invention is based on the discovery that previously bonded and worked aluminous duplex metal articles having properties of the kind described by Frary in U. S. Patent 1,805,448 in sufficient degree to be useful for some purposes, can be made more advantageously by hardening the coating after it has been joined to the alloy core than by uniting an alloy coating with the core. The duplex article treated in this manner retains its corrosion resistant property. To effect the hardening of the coating, the core alloy should contain at least a few tenths of a per cent of magnesium, preferably at least 0.4 per cent, in addition to any other elements that may be present such as copper, and the aluminous coating should be initially free from magnesium and relatively soft. In referring to the coating material as being initially free from magnesium, we mean that the coating should not initially contain more than 0.10 per cent of this element as an impurity, although, as a matter of general practice, we prefer to use coatings containing less than 0.05 per cent of this element. The method we use to improve the hardness and abrasion resistance of the coating consists in heating the duplex article within the range of temperature normally employed for the solution heat treatment of the core, but for a longer time than is required for that treatment alone, in order to obtain a sufficient diffusion of magnesium throughout the coating until at least some of it reaches the external surface of said coating. We have found that heating the article between 800 and 970° F. for a period of ½ to 12 hours, depending upon the composition of the core alloy and the thickness of the coating, is sufficient to introduce the desired amount of magnesium into the coating.

The hardening effect of magnesium in the coating is enhanced by providing a substance in

the coating material which is capable of combining with this element to form an intermetallic compound. Silicon, for example, combines with magnesium to form the intermetallic compound $Mg_2Si$, which, in turn, is soluble in aluminum and can be precipitated from a supersaturated solution by suitable treatment to produce a harder alloy. In making duplex aluminous metal articles of the kind here described, we prefer to provide from 0.2 to 0.5 per cent silicon in the coating, depending on the hardness desired. In general, it is preferred that no more silicon be present than will completely combine with the magnesium to form $Mg_2Si$. Also, as a practical matter, the amount of magnesium and silicon that may be used in the coating is limited by the solubility of $Mg_2Si$ in aluminum at the temperature of the solution heat treatment being employed. Since this temperature does not exceed 970° F. for the magnesium-containing alloys, the maximum amount of $Mg_2Si$ that can be dissolved in the coating is about 1.2 per cent. This amount of $Mg_2Si$ contains about 0.75 per cent magnesium and 0.45 per cent silicon.

The duplex articles which have been subjected to our thermal treatment still retain their duplex character; that is, the coating remains resistant to corrosion and protects the underlying metal. The thermal treatment does not cause any substantial absorption and disappearance of the coating as such, since within the time required to obtain a diffusion of magnesium to the external surface of the coating, only the magnesium, and copper, to a lesser extent, can migrate from the core into the coating in substantial amount. The relatively insoluble constituents in the core alloy remain in the core during the treatment, and, hence, at the end of the treatment the coating is substantially devoid of insoluble constituents coming from the core alloy.

Where the core alloy contains copper, from 0.1 to 1 per cent chromium may be included in the coating material to minimize any undesired effect of diffused copper, as is described in our U. S. Patent 1,975,105. The presence of the chromium, however, does not affect the hardening effect of the magnesium to any substantial extent, and it may therefore be disregarded as far as attaining the object of our invention is concerned. Still other elements may also be present in the coating which do not affect the behavior of magnesium in improving the surface hardness and abrasion resistance of the coating, but which may improve certain other properties thereof. For example, it may be desirable to add one or more of the following elements: 0.1 to 2 per cent zinc, 0.1 to 1 per cent cadmium, 0.01 to 0.1 per cent tin, and 0.05 to 1.5 per cent manganese.

As stated hereinabove, the diffusion thermal treatment should be conducted within the temperature range normally employed for the solution heat treatment of the core alloy, or the range within which substantially all of the magnesium present can be dissolved. In order to obtain an increased hardness in the coating, however, it is necessary to continue the thermal treatment for a longer time than would otherwise be required to dissolve the soluble constituents in the core. The thermal treatment should be continued until at least some of the magnesium has diffused to the external surface of the coating and preferably until the magnesium has reached the surface over the entire area of the coating. Since the process of introducing the magnesium into the coating is one of diffusion, it is possible to have a gradation in concentration between the inner or bonded face of the coating and its external surface. For this reason, the magnesium may reach the surface sooner in some regions than in others, and in those regions the surface becomes hardened. The permeation of the coating with magnesium in this manner does not materially change the corrosion resistance of the coating, even though the magnesium is associated with other elements such as silicon. As a matter of fact, alloys having magnesium or $Mg_2Si$ as the principal added alloying constituent are known to have a high degree of resistance to corrosion independently of any association with another alloy.

In order to obtain the desired diffusion of magnesium into the coating, it is preferred to have at least 0.4 per cent of this element in the core alloy. The magnesium may either be the principal added element in the alloy, as in the case of alloys containing from 2 to 6.5 per cent of the element and less than 1 per cent of other elements, or it may be a supplementary constituent, as in the case of many of the heat treated aluminum base alloys which contain copper as the chief added element. Alloys containing from 3 to 6 per cent copper, 0.4 to 2 per cent magnesium, with or without the addition of 0.1 to 1.5 per cent manganese, and 0.5 to 2 per cent silicon are representative of the latter type of alloy which is heat treated and aged to develop the maximum strength and hardness. It is essential, in any event, that there should be some magnesium in the alloy that is free to migrate from the core into the coating under the influence of heat.

Aluminous duplex metal articles of the kind adapted to receive the diffusion thermal treatment usually have a protective coating equivalent to about 5 per cent or more of the total thickness of the article, but thinner coatings may be advantageously used under some conditions, as in the case of certain classes of sheet employed in the construction of aircraft. It has been found that, as a matter of practical experience with duplex sheet articles, the use of coatings having a thickness equal to 5 per cent of the total thickness of the sheet insures satisfactory performance both from the standpoint of manufacture and subsequent service.

As an example of the manner in which our invention may be carried out, the production of an aluminous duplex metal article will be described. The core alloy is first melted in the usual manner, such as one having the following composition: 4.2 to 5 per cent copper, 0.6 per cent manganese, 1.5 to 1.75 per cent magnesium, and balance aluminum, with total impurities of iron and silicon less than 1 per cent. The molten alloy is cast in a mold between plates of an aluminum base alloy containing 0.2 to 0.5 per cent silicon and 0.25 per cent chromium, in addition to the usual impurities. The foregoing method and details of operation are more fully described in U. S. Patent 1,865,089 to Dix. The duplex ingot produced in this manner is then given an initial working to insure a firm bond between the core and the coating. Following this preliminary working, the ingot may then be hot and cold rolled according to the customary practice that is followed in fabricating this type of strong alloy. A sheet of 20 gauge thickness produced in the foregoing manner may be heat treated at 920 to 930° F. for 1 hour to insure a

thorough diffusion of the magnesium into the coating, whereas a 15-minute treatment would suffice for the usual solution heat treatment of the core alloy.

In an actual test on a 26 gauge duplex sheet consisting of an initial coating alloy composed of aluminum, 0.32 per cent silicon, 0.13 per cent iron, and 0.26 per cent chromium, and a core alloy consisting of commercially pure aluminum, 4.2 per cent copper, 0.6 per cent manganese, and 1.5 per cent magnesium, it was found that the corrosion resistance of the sheet, as determined by a 72-hour exposure to an alternate immersion test in the usual $NaCl-H_2O_2$ solution, was virtually the same or slightly better where the sheet had been heated at 930° F. for 1 hour than where it had been heated at that temperature for only 15 minutes, the normal period of heat treatment. The test thus indicates that the diffusion treatment has not destroyed the corrosion resistance of the duplex sheet.

Although the production of a duplex metal article has been described in terms of the method given in U. S. Patent 1,865,089, it is nevertheless possible to produce aluminous duplex articles by other methods. Regardless of the manner in which the article may have been produced, our method may be employed to harden an initially soft coating intimately united to the core, if the core alloy contains about 0.4 per cent or more of magnesium and the coating is initially free from this element.

The term "aluminum" as herein employed refers to the commercially available metal which contains the usual iron and silicon impurities, while the term "aluminum base alloys" refers to those alloys containing more than 50 per cent aluminum. The term "aluminous metal" includes both aluminum and aluminum base alloys.

We claim:

1. The method of increasing the abrasion resistance and surface hardness of a previously worked corrosion-resistant aluminous duplex metal article composed of a relatively corrodible aluminum base alloy core containing at least 0.4 per cent magnesium and copper in excess of magnesium, and insoluble constituents and an initially, relatively soft copper and magnesium-free aluminous coating bonded to said core while substantially maintaining the respective identities of the core and coating, said method comprising heating said duplex metal article at 800 to 970° F. for a time sufficient to cause a diffusion of magnesium to the external surface of the coating but causing no diffusion of copper and insoluble constituents from the core alloy to the said external surface of the coating or no substantial decrease in the corrosion resistance of the coating.

2. The method of increasing the abrasion resistance and surface hardness of a previously worked corrosion-resistant aluminous duplex metal article composed of an aluminum base alloy core containing about 3 to 6 per cent copper, 0.4 to 2 per cent magnesium and insoluble constituents, and a relatively soft, initially copper and magnesium-free aluminous coating bonded to said core while substantially maintaining the respective identities of the core and coating, said method comprising heating said duplex metal article at 800 to 970° F. for ½ to 12 hours until at least some magnesium has diffused to the external surface of the coating but none of the copper and insoluble constituents have diffused from the core alloy to the said external surface of the coating and with no substantial decrease in the corrosion resistance of the coating.

3. The method of increasing the abrasion resistance and surface hardness of a previously worked corrosion-resistant aluminous duplex metal article composed of an aluminum base alloy core containing 3 to 6 per cent copper, 0.4 to 2 per cent magnesium, 0.1 to 1.5 per cent manganese, 0.5 to 2 per cent silicon and insoluble constituents, and a relatively soft, initially copper and magnesium-free aluminous coating bonded to said core while substantially maintaining the respective identities of the core and coating, said method comprising heating said duplex metal article at 800 to 970° F. for ½ to 12 hours until at least some magnesium has diffused to the external surface of the coating but none of the copper and insoluble constituents have diffused from the core alloy to the said external surface of the coating and with no substantial decrease in the corrosion resistance of the coating.

4. The method of increasing the abrasion resistance and surface hardness of a previously worked corrosion-resistant aluminous duplex metal article composed of a relatively corrodible aluminum base alloy core containing at least 0.4 per cent magnesium and copper in excess of magnesium and insoluble constituents and a relatively soft, initially copper and magnesium-free coating of an aluminium base alloy containing from 0.2 to 0.5 per cent silicon while substantially maintaining the respective identities of the core and coating, said method comprising heating said duplex metal article at 800 to 970° F. for ½ to 12 hours until at least some magnesium has diffused to the external surface of the coating but none of the copper and insoluble constituents have diffused from the core alloy to the said external surface of the coaitng and with no substantial decrease in the corrosion resistance of the coating.

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