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ALUMINUM COATED ARTICLES

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This invention relates to aluminum coated ferrous metal articles, and relates more particularly to aluminum coated articles of the character obtained by applying a flux of a fluoride salt of zirconium or titanium to the ferrous metal base and then dipping the fluxed base in molten aluminum. This application is a continuation in part of my copending application Serial No. 214,015, filed March 5, 1951, now abandoned, which is itself a division of my earlier application Serial No. 121,894, filed October 17, 1949, now abandoned.

I have discovered that steel and other ferrous metals may be readily and speedily coated with aluminum if the ferrous metal is first treated with a flux composed essentially of a fluoride salt of zirconium or titanium. An advantageous procedure based on this discovery is to dip the ferrous metal to be coated, after it has first been thoroughly cleaned, in a hot aqueous solution of the zirconium or titanium flux salt, then dry the ferrous metal (whereby a thin residue of the flux salt is deposited quite uniformly over the surface of the metal), and then immerse the ferrous metal in molten aluminum. Then, following withdrawal of the ferrous metal from the molten aluminum and cooling to room temperature, the ferrous metal is found to be coated with a continuous, tightly adherent protective layer of aluminum metal which may range in thickness from a few ten-thousandths to a few thousandths of an inch, depending upon such factors as temperature of the molten aluminum, time of immersion, and rate of withdrawal of the ferrous metal from the molten aluminum. This method of coating ferrous metal articles with aluminum is described and claimed in my copending application Serial No. 267,303, filed January 19, 1952, now Patent No. 2,686,355 and so is not further described herein.

I have further discovered that ferrous metal articles coated with aluminum by a method using a fluoride salt of zirconium or titanium as a flux are different from and distinctly superior to aluminum coated ferrous metal articles known heretofore and produced by other methods. The former, which constitute the aluminum coated ferrous metal articles according to the present invention, are characterized by the fact that the aluminum layer is bonded to the ferrous metal base by an intermediate intermetallic layer composed essentially of 0.1%, and generally at least 0.2%, up to 1%, and sometimes even up to 2.5%, by weight of one of the metals zirconium and titanium, and from 35% to 65% by weight each each of iron and aluminum. Generally, the amount by weight of iron in the intermetallic layer is greater than the amount by weight therein of aluminum—most commonly the amount of iron therein is from 50% to 60% by weight, and the amount of aluminum is from 40% to 50% by weight.

It is thus apparent that the aluminum coated articles of this invention comprise three layers bonded together. These layers are denoted respectively as the ferrous metal base, the intermetallic layer, and the aluminum layer. As is customary in the hot-dip coating art, the term

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"coating" is used to denote collectively both the intermetallic layer and the aluminum layer.

It is of course contemplated that commercial aluminum metal will ordinarily be used to form the coating. Such metal may contain a small fractional percentage of zirconium or titanium (generally less than 0.1%). In aluminum coated ferrous metal articles according to this invention, the intermetallic layer is recognizably different from one that might be formed from direct combination of iron with commercially pure zirconium-bearing or titanium-bearing aluminum, for in the aluminum coated articles of this invention, the intermetallic layer contains a proportion of zirconium or titanium to aluminum that is at least twice as great as the proportion thereof to aluminum in the aluminum layer.

Advantageously (though not necessarily) aluminum coated ferrous metal articles according to this invention are cold worked subsequent to applying the aluminum coating to the ferrous metal base. Thereby a cold-worked aluminum layer is formed, and at the same time the ferrous metal likewise becomes cold worked if the structure previously was that of hot worked or annealed metal. The intermetallic layer by which the aluminum coating is bonded to the ferrous metal base of articles according to this invention permits such cold working to be effected without crackng of the aluminum layer or separation thereof from the ferrous metal base. Rather, when the coating is formed of reasonably pure commercial aluminum, the tightness of the bond between the aluminum layer and the ferrous metal remains unaffected by cold working of the coated article, and at the same time the brightness and smoothness of the surface of the aluminum layer is substantially enhanced and otherwise its physical properties are improved.

Commercially pure aluminum generally contains silicon as an impurity. For many purposes silicon is not objectionable in aluminum, and indeed, it has heretofore been proposed to incorporate quite considerable amounts of silicon in aluminum which is to be applied as a coating on steel. In aluminum coated steel articles according to the present invention, however, and especially in such articles as are to be cold worked after coating, the amount of silicon present in the aluminum should be less than 5% by weight, and preferably should not exceed 3.5% by weight.

The manner in which the zirconium or titanium is introduced into the composition of the intermetallic layer of articles according to this invention, at least to the extent that its proportion therein to aluminum exceeds the corresponding proportion in the aluminum layer, is not well understood. That it enters the intermetallic layer by reduction from the flux salt has been quite well established. Such is shown, for example, by the fact that when a zirconium flux salt is employed, an intermetallic layer containing zirconium is formed; and correspondingly, when a titanium flux salt is used, an intermetallic layer containing titanium is formed. Evidently the zirconium or titanium which is reduced from the flux salt by reaction with the molten aluminum in the immediate vicinity of the surface of the ferrous metal article tends to accumulate in the intermetallic layer which forms at the interface of the solid iron and the molten aluminum, in preference to simply becoming dispersed in the molten aluminum. In a typical case, the amount of flux used will provide a total of about 0.10 gram of zirconium per square foot of ferrous metal, and the coating weight will be about 6 grams per square foot. Assuming the intermetallic layer to constitute about one third by weight of the coating, it would be theoretically possible in this case for the zirconium to amount to 5% by weight of the intermetallic layer, if all of the zirconium of the flux entered such layer. However, such quantitative collection of the zirconium (or titanium) from the flux in the intermetallic layer does not seem to occur. It has been observed that the longer the steel or other ferrous metal article remains in contact with the molten aluminum, the smaller is the amount of zirconium or titanium in the intermetallic layer. (Even after a considerable period of immersion, however, the proportion of zirconium or titanium to aluminum in the intermetallic layer is twice or more as great as the corresponding proportion in the aluminum layer.) Thus it appears that much of the zirconium or titanium reduced from the flux salt by the molten aluminum initially enters the intermetallic composition; but then, with continued immersion of the ferrous metal article in the molten aluminum, and especially with agitation of the molten aluminum in contact with the ferrous metal, the zirconium or titanium tends to diffuse out into the molten aluminum.

The manner in which the inclusion of zirconium or titanium in significant amounts beneficiates the intermetallic layer likewise is obscure. There is some evidence that the incorporation of the freshly reduced zirconium or titanium in the intermetallic layer at the time of its formation affects its composition by reducing somewhat its proportion of iron to aluminum. Thereby it may favor the formation of one or more iron-aluminum compounds having a crystal structure and other characteristics which contribute to an adherent bond between the ferrous metal base and the aluminum coating, but a bond which permits the coated article to undergo drastic plastic deformation. Whatever its effect may be, however, I have found that aluminum coatings on ferrous metal articles according to the present invention are remarkably adherent and afford an exceptionally high degree of corrosion protection to the underlying ferrous metal. For example, aluminum coated wire according to this invention is consistent in its ability to be bent into a multi-turn coil on a mandrel of its own diameter, without cracking or separation of the aluminum layer from the underlying base metal; and, similarly, an aluminum coated steel strip about 1/32 inch thick may be bent through 180° and flattened against itself without cracking or detachment of the aluminum layer. Also the corrosion protection afforded by this tightly adherent coating, which presumably is due to the excellence of the bond between the coating layer and the base metal, has been found to be much superior to that of a coating of zinc of equal thickness on the best grades of galvanized or "Bethanized" (zinc electroplated) steel, and is fully equivalent to the protection afforded by substantially greater thicknesses of aluminum on aluminum clad steel sheets prepared by rolling an aluminum cladding sheet and a steel base sheet together and then heating.

Commercially pure aluminum is employed as the coating metal in making aluminum coated steel articles according to this invention. While such aluminum may contain a small fractional percentage of titanium or zirconium, it has been found that the aluminum coated steel article of the invention contains at least twice as much zirconium or titanium in its intermetallic layer as could be expected to accumulate there from the aluminum itself. For example, one sample of aluminum coated steel prepared using potassium zirconium fluoride as the flux salt, on which the aluminum layer contained 0.16% zirconium, was found to have an intermetallic layer containing 0.53% by weight of zirconium and approximately 47% by weight aluminum. On the basis of the zirconium content of the aluminum layer, and taking into account the extent to which the aluminum had been diluted by iron in the intermetallic layer, not more than about 0.07% by weight of zirconium could have been expected in the intermetallic layer were it all derived from the metal of the aluminum layer. This particular sample was prepared by immersing the steel for only three seconds in the bath of molten aluminum maintained at a temperature of 1240° F. In another sample which was prepared in the same manner, save only that the time of contact between the steel and the molten aluminum was ten times as long (thirty seconds), the aluminum layer was found on analysis to contain 0.13% zirconium, the zirconium content of the intermetallic layer was found to be 0.16% and the aluminum content of the intermetallic layer was again found to be 47%; i. e., the proportion of zirconium to aluminum in the intermetallic layer was well over twice as great as could be expected on the basis of simple dilution of the aluminum by iron in the intermetallic layer.

A common impurity in commercially pure aluminum is silicon. Primary commercial aluminum of the 99% grade contains substantially less than 1% of silicon. When, however, the metal is held in the molten state for a substantial period of time in melting vessels comprising a silica-bearing refractory (and even alumina refractory generally contains a siliceous binder) its silicon content may increase very substantially on account of reduction of the silica by the molten aluminum.

It has been proposed heretofore to employ rather substantial amounts of silicon, with or without the addition of magnesium, in aluminum used for coating steel, in order to increase the ductility of the coating. There is substantial evidence that silicon inhibits the formation of the brittle iron-aluminum compound having the formula $FeAl_3$. When an intermetallic layer made up largely of this compound forms between a steel base and an aluminum coating layer, and when the thickness of such layer becomes substantial (as it does when steel is aluminum coated or aluminum clad by heretofore known procedures), the aluminum-to-iron bond is weakened by the inability of the relatively thick, brittle intermetallic layer to undergo deformation. If, however, the aluminum contains considerable silicon, and if thereby the formation of $FeAl_3$ is inhibited enough so that only a rather thin intermetallic layer is formed, the ability of the aluminum coated article to withstand deformation will be improved. It is evidently in this fashion that silicon enhances the ductility of aluminum coated steel articles made by heretofore known procedures.

I have found that it is most undesirable to employ aluminum containing more than 5% silicon in makiog aluminum coated articles according to the present invention which are to be cold worked or which normally should be expected to be subject to mechanical deformation in use (such as sheet, strip, and wire). In fact I prefer to maintain the silicon content of the aluminum coating metal at a value which does not exceed 3.5%. If the coating metal contains more than 5% silicon, the coating formed thereby on steel articles according to this invention is subject to quite severe cracking when bent sharply or otherwise mechanically deformed. Even with coating metal containing less than 5% but more than 3.5% silicon, some cracking may occur if the article undergoes severe deformation. To insure against cracking of the coating under all ordinary conditions of use, the silicon content of the aluminum should be kept below 3.5%. Of course, when the coated article is one that in all likelihood will not be subject to mechanical deformation subsequent to coating, such as heavy structural shapes, pole line hardware, etc., then it is not so important to maintain the silicon content of the aluminum at a low level.

When aluminum coated steel is prepared by the method of my aforementioned application Serial No. 267,303, the inhibiting effect of silicon to insure the formation of a desirably thin intermetallic layer is not necessary. In the first place, the method of said application does not require and does not ordinarily entail contact between the molten aluminum and the steel article for more than a few seconds. Such short time of contact does not allow for the formation of a thick intermetallic layer of any composition. In the second place, as indicated above, there is evidence that the presence of significant amounts of zirconium or titanium in the intermetallic layer of aluminum coated steel articles according to the present invention may substantially alter the composition of the intermetallic layer from one in which the compound $FeAl_3$ is the major constituent. Both of these circumstances would operate to dispense with the necessity of incorporating silicon in the aluminum for the purpose of inhibiting the formation of the intermetallic layer.

The employment of an aluminum coating metal containing an amount of silicon below the above-stated limits (below 5%, and preferably below 3.5%) is desirable not only to improve the ability of the aluminum coating to withstand severe deformation without cracking, but also to improve the appearance of the product. Ferrous metal articles coated with aluminum containing the rather high percentages of silicon heretofore considered advantageous for reasons of ductility are dull and dirty in appearance. They are characterized by a rather dark, lusterless gray color, and commonly the surface coloration is uneven. Aluminum coated steel articles made with an aluminum coating metal which is low in silicon in accordance with this invention, on the other hand, are of an attractive bright silvery appearance, which is uniform over the entire area of the article. Even when such articles have been merely coated, and not further treated, they are characterized by a bright attractive appearance. If, in addition, such articles are cold worked following the coating operation, the brightness and luster of the coating surface is markedly increased. Indeed, aluminum coated steel wires and sheets which have been cold drawn or cold rolled subsequent to coating, are indistinguishable, by appearance only, from corresponding articles of bright-finished aluminum. Moreover, the bright appearance of such articles is substantially as durable and permanent as that of aluminum itself. A further advantage of the cold worked coated articles is that the coating has the improved characteristics of cold worked metal; and also the hardness, tensile strength, and other properties of the ferrous metal base are much improved.

Various theoretical or speculative explanations to account for the improved character of aluminum coated steel articles according to this invention have been set forth above. The possibility that the zirconium or titanium present in the intermetallic layer affects the composition of such layer insofar as concerns the proportions of its major constituents (iron and aluminum) is an example thereof. While such theoretical considerations are supported by some experimental evidence, they are not to be taken as firmly established, nor is the present invention predicated on or limited to their correctness. So far as the present invention is concerned, the facts are (1) that in articles according to the invention the intermetallic layer contains a significant proportion of zirconium or titanium—more than can be accounted for on the basis of such zirconium or titanium as might be present in the aluminum coating metal, and (2) that these articles are superior to heretofore known aluminum coated steel articles in their resistance to corrosion, the adherence of the coating to the base metal, and the ability of the coated article to withstand severe deformation or mechanical working. It is on these observed facts, rather than on the theoretical or speculative reasons suggested by observations made to date to account for them, that the present invention is predicated.

I claim:

1. An aluminum coated ferrous metal article, characterized in that the aluminum layer is bonded to the ferrous metal base by an intermediate intermetallic layer composed essentially of 35% to 65% by weight each of iron and aluminum and from 0.2% to 2.5% by weight of one of the metals zirconium and titanium, the proportion of said last-mentioned metal to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum layer.

2. An aluminum coated ferrous metal article, characterized in that the aluminum layer is bonded to the ferrous metal base by an intermediate intermetallic layer composed essentially of 35% to 65% by weight each of iron and aluminum and from 0.1% to 1% of one of the metals zirconium and titanium, the proportion of said last-mentioned metal to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum layer.

3. An aluminum coated ferrous metal article, characterized in that the aluminum layer is bonded to the ferrous metal base by an intermediate intermetallic layer composed essentially of 0.2% to 2.5% by weight of zirconium, from 50% to 60% by weight of iron, and from 40% to 50% by weight of aluminum, the proportion of zirconium to aluminum being at least twice as great in the intermetallic layer as in the aluminum coating layer.

4. An aluminum coated ferrous metal article, characterized in that the aluminum layer is bonded to the ferrous metal base by an intermediate intermetallic layer composed essentially of 0.2% to 2.5% by weight of titanium, from 50% to 60% by weight of iron, and from 40% to 50% by weight of aluminum, the proportion of titanium to aluminum being at least twice as great in the intermetallic layer as in the aluminum coating layer.

5. An aluminum coated ferrous metal article, characterized in that the aluminum layer is bonded to the ferrous metal base by an intermediate intermetallic layer composed essentially of 50% to 60% by weight of iron, 40% to 50% by weight of aluminum, and 0.1% to 1% by weight of zirconium, the proportion of zirconium to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum layer.

6. An aluminum coated ferrous metal article, characterized in that the aluminum layer is bonded to the ferrous metal base by an intermediate intermetallic layer composed essentially of 50% to 60% by weight of iron, 40% to 50% by weight of aluminum, and 0.1% to 1% by weight of titanium, the proportion of titanium to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum layer.

7. An aluminum coated ferrous metal article, characterized in that the aluminum layer is aluminum of commercial purity containing a small amount of silicon but less than 5% thereof by weight, and further characterized in that such aluminum layer is bonded to the ferrous metal base by an intermetallic layer composed essentially of 35% to 65% by weight each of iron and aluminum and from 0.2% to 2.5% by weight of one of the metals zirconium and titanium, the proportion of said last-mentioned metal to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum layer.

8. An aluminum coated ferrous metal article, characterized in that the aluminum layer is aluminum of commercial purity containing a small amount of silicon but not more than 3.5% thereof by weight, and further characterized in that such aluminum layer is bonded to the ferrous metal base by an intermetallic layer composed essentially of 50% to 60% by weight of iron, 40% to 50% by weight of aluminum, and 0.1% to 1% by weight of one of the metals zirconium and titanium, the proportion of said last-mentioned metal to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum layer.

9. An aluminum coated ferrous metal article comprising a cold worked ferrous metal base, an intermetallic layer tightly adherent to said base and composed essentially of 35% to 65% by weight each of iron and aluminum and from 0.2% to 2.5% by weight of one of the metals zirconium and titanium, the proportion of said last-

mentioned metal to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum coating layer, and a cold worked bright smooth-surfaced aluminum layer tightly adherent to said intermetallic layer and composed essentially of aluminum of commercial purity containing a small amount but less than 5% of silicon.

10. An aluminum coated ferrous metal article comprising a cold worked bright smooth-surfaced outer layer composed of aluminum of commercial purity containing a small amount of silicon but less than 3.5% thereof, an intermetallic layer underlying and tightly adherent to said aluminum layer, said intermetallic layer being composed essentially of 50% to 60% by weight of iron, 40% to 50% by weight of aluminum, and 0.1% to 1% by weight of one of the metals zirconium and titanium, the proportion of said last-mentioned metal to aluminum in the intermetallic layer being at least twice as great as the proportion thereof to aluminum in the aluminum layer, and a cold worked ferrous metal base underlying and tightly adherent to said intermetallic layer.

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