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2,912,346

METHOD OF COATING FERROUS ARTICLES WITH MAGNESIUM AND MAGNESIUM-BASE ALLOYS

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No Drawing. Application December 16, 1957 Serial No. 702,774

17 Claims. (Cl. 117—51)

This invention relates to a method of coating ferrous 15 articles such as iron and steel with magnesium and magnesium-base alloys. It more particularly concerns an improved method of applying a coating of magnesium or magnesium-base alloy in the molten phase to the surface of a ferrous article without the use of a flux.

Some of the applications for this invention are in the field for which aluminum coatings on steels have been, and presently are, used. An important advantage of magnesium bonded to steel, over aluminum bond to steel, is that no brittle interlayer of compounds with the iron is 25 formed, as is the case with aluminum. In applications where it is necessary to flex the steel, or the article, magnesium presents a coating of greater integrity, adherence, and resistance to damage.

fluxes in processes in which ferrous articles are coated with magnesium to protect such articles from oxidation and obtain a cleansing action on such articles essential to obtaining a bond between the magnesium and ferrous considerable advantages to the process. First of all, the fluxes are quite expensive and difficult to obtain in commercial grades. Also, in employing fluxes there is always present the difficulty of removing the adhering flux salts after processing. Washing and scraping operations may damage the magnesium coating which is easily corroded by cleaning acids, and which is soft enough to be readily abraded during scraping operations. Furthermore, in fluxing procedures, a dipping temperature of from 750° C. to 800° C. is ordinarily necessary to produce suitable fluidity in the flux layer, whereas lower temperatures in the vicinity of that of melting for magnesium and alloys would be desirable. It is therefore another object of this invention to eliminate the necessity for a flux in the process for coating ferrous articles with magnesium or magnesium-base alloys. Other objects and advantages will appear as the description of the invention proceeds.

Broadly stated, the present invention relates to a process for coating ferrous metal articles with magnesium or magnesium-base alloys which comprises enveloping a surface of said ferrous article with an atmosphere of an inert gas, said surface having a thin coating of metal soluble in magnesium or magnesium-base alloy and suitable for coating ferrous metals, and contacting said surface of said article with magnesium or magnesium-base alloys in the molten phase for a period of time sufficient to permit the molten magnesium or magnesium-base alloy to dissolve said thin coating of said metal soluble in magnesium metal and wet the surface of said ferrous article.

In carrying out the method, if the surface of the ferrous article to be coated is not already substantially free from foreign matter, it may be cleaned in any suitable manner such as by pickling, wire brushing, or sand blasting. Pickling is the preferred form and may be accomplished by a dipping in a 15 percent aqueous solution of hydrochloric acid, although other ways are known which may 70 he used.

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The cleaned ferrous metal surface may then be plated or coated with a thin coat of metal soluble in magnesium, such as copper, nickel, tin, zinc, aluminum, beryllium, cadmium, cobalt, lead, silicon or silver, by an electroplating or other suitable coating operation. This coating provides an area of increased solubility with respect to the magnesium whereby the ferrous base is left clean to form a bond with the molten magnesium by virtue of the solution activity on said coating.

In the present process, the surface of the ferrous metal article to be coated is maintained in inert gas atmosphere immediately before and during the time it is contacted with the molten magnesium or magnesium-base alloy. The inert atmosphere is also maintained during the period the magnesium, or magnesium-base alloy is cooled. It has been discovered that the use of such inert atmosphere in such steps eliminates completely the necessity for using any flux in the process. The inert atmosphere may be an inert element, for example, a noble gas, such as argon, helium, neon, krypton or xenon. The inert gas may be maintained at atmospheric pressures, although in some instances it is desirable to employ super-atmospheric, or sub-atmospheric pressures.

In carrying out the coating step batchwise, in one embodiment, the ferrous metal article having a thin coat of copper, nickel, tin, zinc, aluminum, beryllium, cadmium, cobalt, lead, silicon or silver, is placed in a suitable chamber contained within a suitable heating means, such as a furnace. The air is removed from such chamber and In the past, it has been necessary to employ special 30 replaced with an atmosphere of inert gas. A portion of the vessel contains a pool of molten magnesium or magnesium-base alloy. The ferrous metal article to be coated is introduced by a suitable remote control device into the pool of magnesium and after a brief dwell, removed from metal. Elimination of the necessity for a flux presents 35 the pool into the inert atmosphere portion of the chamber without contamination of the inert gas with air. After removal from the pool, the article is permitted to cool sufficiently in the inert atmosphere to a temperature which will permit the article to stand exposure to air with out objectionable oxidation. After cooling, the ferrous metal article is further processed or removed from the said chamber.

> In another embodiment of the invention, the interior surface of a steel tube is coated with magnesium. The tube, previously plated with a thin coat of copper or other magnesium soluble metal, is removably connected to a vessel containing magnesium in the molten phase. After the tube is filled with an inert gas, the inert gas pressure is reduced, which draws the magnesium into the tube. The magnesium is then allowed to flow back into the vessel, and replaced by an inert gas, leaving a coating of magnesium on the inside of the tube.

The process may also be carried out in a continuous method in which the ferrous articles are moved continuously, such as by a conveyor, into the chamber containing the inert gas, into the molten pool, and then withdrawn from the molten pool into an inert atmosphere where they are cooled. In such a continuous method, air locks are provided at the entry and exit of the chamber so that the ferrous articles may be introduced into and removed from the chamber without contamination of the inert gas atmosphere with oxygen from the air.

In the present process it is only necessary to bring the temperature of the molten coating metal to a temperature at or slightly above the melting point of the magnesium or magnesium-base alloy, namely, in the case of magnesium not higher than about 650° C. The greater viscosity of the coating bath at such a relatively low temperature is a distinct advantage in that much thicker adhering coatings may be obtained. This temperature also presents the advantage of being subcritical to steel transformation whereas the flux process (750 to 800° C.)

takes the steel to a temperature above the critical transformation range.

In the case of magnesium alloys, the melting temperature will, of course, normally be lower than that for the pure magnesium. The primary requisite is to raise the temperature of the coating metal to a temperature at or slightly above the melting point. Obviously, the melting point of the coating metal represents the lower limit of the useful temperatures, and, generally speaking, the temperature need not be raised very far above that point.

While the present process is directed primarily to the elimination of the use of a flux in the coating step, it is further intended that the present invention shall provide an improved process for the fabrication of special composite structures including, for example, the steps of 15 actual working and forming of the material under the protection of an inert gas.

The following example is given by way of illustration of the process in question:

Pre-coat cleaning

A. The magnesium coating of stainless and carbon steel screens and perforated sheets was carried out successfully without the aid of a prior flux treatment by:

(1) Degreasing with trichlorethylene, followed by:

- (2) A mild alkaline anodic and cathodic cleaning with a water rinse;
- (3) A 60° Baumé sulphuric acid (H₂SO₄) cleaning with a water rinse;
- (4) Copper plating for 10 minutes at 20 amperes per 30 square foot in copper cyanide (.0002 copper); and

(5) A water rinse and dry.

B. Alternatively,

- (4) Plating in Watts nickel bath (13 ounces per gallon of nickel) for ten minutes at 20 amperes per square 35 foot (.0002 nickel).
 - (5) Water rinse and dry.

(The amperage, of course, is relative to the size of the piece intended to be plated.)

C. In both methods, upon completing the above, a 40 that said inert element is helium. hot hydrochloric acid (HCl) bath (50 percent by weight) dip for approximately 30 seconds.

Coating

The cleaned ferrous materials were then introduced into a sealed argon protected retort and subsequently dipped in magnesium metal (held at 1400° F.) for one minute or longer, depending upon the thickness of the piece to be coated. Pieces .028 inch in thickness were held for one minute while those approximately .125 inch in thickness were held for five minutes, for example.

Pieces were then raised to the comparatively cool retort zone (approximately 400° F.) and held for one to three minutes depending upon the thickness (.028 inch to .125 inch) of the part to be coated. Direct removal was then made from the retort.

This application is a continuation-in-part of application Serial No. 458,011, filed September 23, 1954, now abandoned.

In the specification, there has been set forth a preferred embodiment of the invention, and although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation. Changes in the form and in the proportions, as well as the substitution of equivalents are contemplated, as circumstances may suggest or render expedient, without departing from the spirit or scope of this invention as further defined in the following claims.

I claim:

1. The process for coating ferrous metal articles with 70magnesium and magnesium-base alloys which comprises enveloping a surface of said ferrous article with an at-

mosphere of an inert element, said surface having a thin coating of metal soluble in magnesium and suitable for coating ferrous metals, and contacting said surface of said article with a coating metal selected from the class consisting of magnesium and magnesium-base alloys in the molten phase for a period of time sufficient to permit said molten coating metal to dissolve said thin coating of said metal soluble in magnesium metal and wet the surface of said ferrous article.

2. The process of claim 1, further characterized in that said metal soluble in magnesium is selected from the class consisting of copper, nickel, tin, zinc, aluminum, beryllium, cadmium, cobalt, lead, silicon, and silver.

3. The process of claim 1, further characterized in that said metal soluble in magnesium is copper.

4. The process of claim 1, further characterized in that said metal soluble in magnesium is nickel.

5. The process of claim 1, further characterized in that said inert element is argon.

6. The process of claim 1, further characterized in that said inert element is helium.

7. The process of claim 1, further characterized in that said inert element is a mixture of argon and helium.

8. The process of claim 1, further characterized in that said inert element is a noble gas.

9. The process for coating ferrous metal articles with a coating metal selected from the group consisting of magnesium and magnesium-base alloys without the use of a flux which comprises introducing a ferrous article having a thin coating of metal suitable for coating ferrous metals and soluble in magnesium into a pool containing molten magnesium, and holding said article in said molten pool for a period of time sufficient to permit the same to dissolve said coating metal and wet the surface of said ferrous article, said molten pool being under an atmosphere of an inert element.

10. The process of claim 9, further characterized in that said inert element is argon.

11. The process of claim 9, further characterized in

12. The process of claim 9, further characterized in that said inert element is a mixture of argon and helium.

13. The process of claim 9, further characterized in that said soluble metal is copper.

14. The process of claim 9, further characterized in that said soluble metal is nickel.

15. The process of claim 9, further characterized in that said soluble metal is selected from the class consisting of copper, nickel, silver, aluminum, cadmium, 50 cobalt, zinc, tin, beryllium, lead, and silicon.

16. The process of claim 9, further characterized in that said inert element is a noble gas.

17. The process for coating ferrous metal articles with magnesium and magnesium-base alloys which comprises 55 enveloping a surface of said ferrous article with an atmosphere of an inert element, said surface having a thin coating of a metal soluble in magnesium and suitable for coating ferrous metals, contacting said surface of said article with a coating metal selected from the class consisting of magnesium and magnesium-base alloys in the molten phase for a period of time sufficient to permit said molten coating metal to dissolve said thin coating of said metal soluble in magnesium metal and wet the surface of said ferrous article, and cooling said 65 coated ferrous article surface under the atmosphere of an inert element.

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