

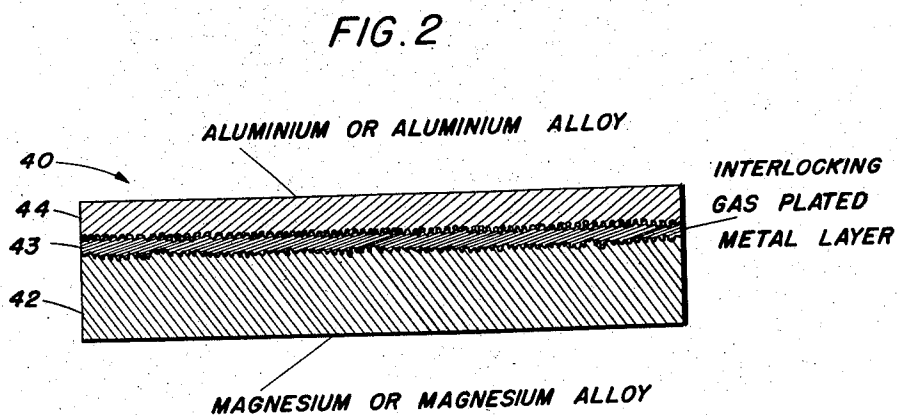
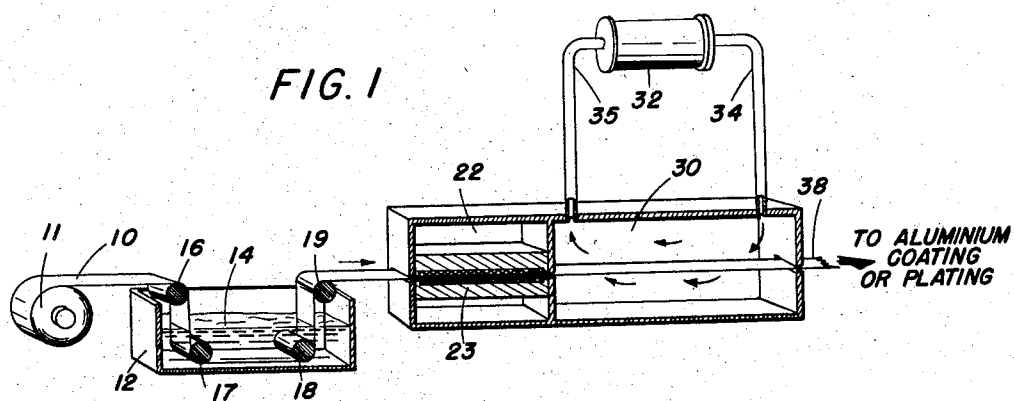
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ALUMINIZED MAGNESIUM PRODUCTS AND METHOD OF MAKING

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## ALUMINIZED MAGNESIUM PRODUCTS AND METHOD OF MAKING

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This invention relates to composite metal stock, and more particularly to composite metal bodies or products made of magnesium and aluminum.

It has been very difficult heretofore to produce satisfactory composite articles of magnesium and aluminum. This is principally due to the relatively weak bond formed at the interface of the metals, the magnesium-aluminum alloy layer product being brittle and easily fractured. Difficulty is also encountered in working with these light metals due to their chemical affinity with oxygen, tending to produce a film of oxide on the surface of the metals. Such oxide coatings inhibit the formation of tenacious bond between the metals.

The present invention overcomes these difficulties for all practical purposes and provides a composite magnesium-aluminum metal body which does not have a brittle bonding interfacial layer.

A principal object of the present invention is, therefore, to provide a composite magnesium and aluminum metal product wherein magnesium metal, or alloy thereof, is coated with aluminum, or alloy thereof, and wherein the intermediate bonding layer consists of metal deposited by gas plating.

It is another object of the invention to provide a composite metal product of magnesium and aluminum by a process which insures a substantially uniform bond throughout the interface of the metals.

Another object of the invention is to provide a method of coating magnesium with aluminum to produce a composite magnesium aluminum product which has the desired physical properties of magnesium and the chemical resistance of aluminum.

Another object of the invention is to provide a method for fabricating magnesium into a wide variety of articles and wherein the magnesium metal is protected from corrosive action by a layer of aluminum.

Another object of the invention is to provide a method of treating magnesium whereby it can be used, for example, in preparing anti-friction articles such as bearings, or friction type products, such as clutch plates, etc., and wherein magnesium metal is bonded to an outer layer of aluminum metal.

Another object of the invention is to produce aluminized magnesium products in the form of sheets or wires, etc., and such as used for electrical conductors, the aluminum being bonded to magnesium by an interlocking intermediate gas plated metal layer which provides a tooth-like surface for the reception of aluminum whereby a substantially integral magnesium-aluminum metal product is formed.

A still further object of the invention is to provide an improved method of bonding magnesium to aluminum by gas plating on the surface of the magnesium a metal layer, e.g. of copper, nickel, iron, chromium or the like, or alloys thereof, this intermediate metal layer being deposited in the pores and interstices of the magnesium and interlocking the base metal with the outer aluminum metal layer.

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Another object of the invention is to provide a magnesium-aluminum composite product having a metal bonding layer deposited by gaseous metal deposition, and wherein the metal is deposited in the pores of the magnesium forming an interfacial bonding layer which is strong and ductile.

Further objects and advantages of the invention will become apparent from the following description taken in conjunction with the accompanying drawing wherein:

Figure 1 illustrates diagrammatically one method and a suitable apparatus for aluminizing magnesium metal sheet material in accordance with this invention;

Figure 2 is a fragmentary sectional view, on an enlarged scale, illustrating a composite magnesium and aluminum product and showing the interlocking interfacial layer of gaseous metal plated structure bonding the two metals together.

In accordance with the present invention, magnesium metal or alloy metal is bonded to aluminum or alloy metal through an intermediate layer consisting of a gaseous metal deposited metal or alloy. Employing metal gas plating, a thin, relatively porous metal coating is deposited and diffused into the magnesium metal surface preparatory to receiving the protective outer coating of aluminum. Gaseous metal carbonyls such as copper carbonyl, nickel carbonyl, chromium carbonyl, iron carbonyl and the like, or alloy plating mixtures thereof, are suitable for this purpose. A suitable method of gas plating utilizing metal carbonyls and the like heat-decomposable metal compounds is described in more detail in the U.S. patent to Fink No. 2,475,601, and which is assigned to the assignee of the present application.

Referring to the drawings, there is illustrated diagrammatically in Figure 1, a method and apparatus for gaseous metal plating magnesium material preparatory for the application of aluminum metal thereto as a continuous process. As shown, a magnesium metal strip or wire 10, which is suitably drawn from a storage roll 11, is passed through a tank 12 which contains cleaning fluid 14 for thoroughly cleaning the surface of the magnesium strip. The strip 10 is preferably immersed in the cleaning fluid, being drawn over the roll 16 downward into the tank, and beneath the rolls 17 and 18 and outward over the roll 19.

The cleaning and degreasing solution in the tank 12 may comprise suitable chemicals, for example alkaline metal phosphate, phosphoric acid or the like as required to clean the magnesium metal strip. A suitable degreasing composition comprises by weight a 50-50 mixture of kerosene and trichloroethylene. If desired, electro-chemical cleaning methods may be utilized in the cleaning tank. Sandblasting may also be employed where it is only necessary to mechanically remove foreign matter from the surface of the magnesium metal. The particular degreasing and cleaning treatment employed in each instance is governed by the material to be removed from the magnesium body being aluminized.

After the cleaning operation, the metal magnesium strip 10 is then passed through a heating compartment 22 where it is moved along between a heating element 23, the same being preferably heated by electrical resistance means as shown. Preheating of the magnesium is effected out of direct contact with air or under atmospheric conditions conducive to oxidation, the chamber 22 being preferably filled with nitrogen or a mixture of nitrogen and 2 to 10% hydrogen. The temperature of the magnesium strip in chamber 22 is raised sufficiently to bring about decomposition of the gaseous metal carbonyl used in the gas plating operation which is carried out in chamber 30.

After heating the magnesium strip 10, it is advanced through the gas plating chamber 30, as indicated by the

arrows in Figure 1, the chamber being filled with the gaseous metal carbonyl to be plated out onto the strip. For this purpose nickel carbonyl, copper carbonyl, or a mixture of the two may be suitably employed. The heat decomposable gaseous metal compound is drawn from the generator 32 and circulated to the chamber 30 utilizing conduits 34 and 35, the gaseous metal carbonyl taking the general path as indicated by the arrows in Figure 1.

The heat-decomposable gaseous metal compound preferably comprises a carrier such as carbon dioxide, nitrogen, or the like, which is inert. Gas plating is effected by thermal decomposition of the carbonyl depositing a layer of the metal constituent onto the surface of the magnesium strip. Metal carbonyls for example of nickel, copper, iron, chromium or the like, or alloy mixtures thereof, may be used as aforementioned. The thickness of the metal deposit may be varied as desired by limiting the time the strip remains in contact with the gaseous metal compound. Metal deposits on the order of 0.0001 to 0.0005 inch thickness are suitable in most cases, but the amount of metal deposited may be increased or decreased as may be desired for different articles and uses.

After subjecting the strip to gas plating to provide an intermediate metal bonding layer, the strip coated with the bonding metal layer, being generally indicated at 38, is conducted to the aluminum coating or plating compartment where aluminum metal is applied over the bonding layer of gas plated metal.

In Figure 2 a finished composite metal strip is illustrated at 40. This product comprises a base or supporting metal core of magnesium or magnesium alloy 42 and having an intermediate bonding layer of gas plated metal 43, e.g. nickel, copper or the like, with an outer protecting coating 44 of aluminum.

The application of aluminum metal to the gas plated magnesium, may be carried out by different methods. For example, the aluminum coating may be done by spraying. In this method the so-called "Schoop" process of spraying metal for depositing the aluminum on the magnesium metal may be employed. Utilizing this method a small diameter aluminum wire is fed into a hot flame, for example oxyacetylene flame. A soft aluminum wire having an aluminum content of 99% or more is satisfactory for this purpose. The molten aluminum metal is broken up into small drops by an air blast and deposited upon the surface of the gaseous metal coated magnesium.

A suitably thick aluminum metal layer is thus built up to provide a sufficiently dense coating whereby infiltration of air is prevented. The aluminum metal coating may also be applied by electroplating or by dipping the gaseous metal plated magnesium body in molten aluminum metal. A relatively thick aluminum coating is applied which may be on the order of 0.01 to 0.10 inch or more depending on the product and its intended use.

The intermediate metal bonding layer as deposited by gas plating comprises a relatively thin porous coating, presenting a sandpaper-like surface which functions as a toothed structure for the reception of aluminum metal as illustrated in Figure 2. Aluminum metal is thus tenaciously bonded through the intermediate gas plated layer 43 to the magnesium metal 42.

A finished composite metal product or strip is produced which may be used for like purposes as aluminum metal in the fabrication of various products and articles. A very light metal product is thus provided which exhibits the desirable properties of magnesium particularly its light weight while possessing the corrosion resistance of aluminum.

In place of strips, sheets or wire, other articles and shapes made of magnesium or magnesium alloy may be aluminized by the application of a gaseous metal plated intermediate layer to provide a bonding metal for receiving the protective coating of aluminum.

Utilizing gaseous metal plating to provide the intermediate bonding metal layer, magnesium may be effectively aluminized, thus producing a composite metal product having the properties of both magnesium and aluminum. A bonding layer of copper, nickel, iron, chromium or the like, or suitable alloy thereof, provides a tenacious tooth-like interfacial metal structure which interlocks the magnesium and aluminum metal.

Utilization of gaseous metal plating to apply an intermediate bonding coating or layer of metal, in accordance with the process of this invention, provides a relatively simple and efficient method of producing continuous lengths of composite aluminum metal material in the form of strips, wires, or sheets, as desired. The process can be carried out at a high rate of speed inasmuch as an intermediate metal layer of metal of sufficient thickness to provide a bond may be deposited on the metal strip while the same is being moved along through the gas plating chamber. A flash coating of the bonding metal may be deposited in a manner of a few seconds to thus provide a tenacious metal bonding layer for the reception of aluminum metal.

In carrying out the gas plating, use may be made of heat-decomposable gaseous metal carbonyls as described or vaporized solutions of certain of the metal carbonyls may be employed. For example, metal carbonyls dispersed in readily vaporizable solvents such as petroleum ether may be used.

Illustrative compounds of the carbonyl type which are useful are nickel, copper, iron, chromium carbonyls and mixed carbonyls of these metals. Other useful substitute heat-decomposable compounds are the nitroxyls, such as copper nitroxyl; nitrosyl carbonyls, for example, cobalt nitrosyl carbonyl; and hydrides, e.g., antimony hydride, tin hydride; also metal alkyls, magnesium diethyl and carbonyl halogens, for example, osmium carbonyl bromide, ruthenium carbonyl chloride, and the like. Vaporizable metal compounds in the form of chlorides, bromides or iodides may be used, as well as metallic salts of organic radicals having less than six carbon atoms, e.g., tetraethyl tin, nickel or copper acetylacetonates and the like. Metallic halides may be obtained from sea water or formed as a by-product in processes utilizing brine-containing waters.

Each compound from which a metal may be plated out has a temperature at which decomposition is complete. However, decomposition may take place slowly at lower temperature while the vapors are being raised through some particular range. For example, nickel carbonyl completely decomposes at a temperature in the range of 375° F. to 400° F. However, nickel carbonyl starts to decompose slowly at about 175° F. and, therefore, decomposition continues during the time of heating from 200° F. to 380° F. A large number of the metal carbonyls and hydrides may be effectively and efficiently decomposed at a temperature in the range of 350° F. to 450° F. When working with most metal carbonyls we prefer to operate in a temperature range of 375° F. to 425° F.

Heating of the metal preparatory to plating is preferably carried out under non-oxidizing conditions and may be effected using radiant heating, electrical resistance heating, induction heating or the like.

Decomposition of the gaseous metal compound for plating may be accomplished by mixing the metal compound with hot inert carrier gas, e.g., carbon dioxide, concurrently while bringing the gaseous mixture in contact with the metal surface to be plated. Even a fine spray of liquid can be transformed from a liquid at a temperature of 100° F. to a vapor having a temperature of 325° F. in a fraction of a second, and the vapors decomposed by being brought into contact with a heated surface having a higher temperature, as aforementioned.

The invention provides an efficient, relatively low-cost method of aluminizing magnesium to give it heat and cor-

rosion protection. Besides pure aluminum metal, aluminum alloys such as aluminum-silicon can be used with the advantage of greater fluidity and better brazing characteristics. Iron-aluminum alloys which have a hardness of approximately 50 Rockwell C or better are also useful.

By employing gas plating in accordance with this invention, it is possible to envelop the material or article by a metal film or plate of any desired thickness, and which consists of substantially pure metal. A protective film is thus provided which film or plating does not have occluded foreign matter such as undesirable metals, salts, anode particles, bubbles and the like, which are inevitably plated out on the cathode along with the desired metal during ordinary electroplating methods.

Gas plating on the contrary, avoids these difficulties with respect to the impurities occluded by way of the electrolyte during electroplating, inasmuch as the gas plating works best, in most cases, in the absence of moisture or water vapor. Oxygen and oxidizable materials are also absent. The plating deposited by such gas plating method has been observed to produce a metal deposit which penetrates into the pores and interstices of the substrate metal but does not produce the undesirable brittle alloy effects as observed when such plating is applied by wet processes or molten metal plating methods. It is not known the exact reason for this, but it is believed that these beneficial effects are accounted for by reason of the freedom of the metal deposit from impurities, particularly metal impurities which produce the brittle alloy characteristic property. The metal deposit at the interstices of the substratum by gas plating produces a tenacious intermediate portion which remains ductile and tough so that the metal thus plated can be worked as desired. Any desired thickness of plating may be deposited by gas plating, for example, so thin that the metal area is actually transparent and when deposited on a transparent substratum, such as glass, produces a smoked glass. The metal plating may also be increased so as to provide a coating thickness such as  $\frac{1}{16}$  to  $\frac{1}{32}$ " if desired, or greater.

In the use of conduit, pipe and the like conveying corrosive material, it is desirable to coat or plate the interior of the pipe so that it will resist corrosion. This may be done by gas plating so that the inner wall is resistant to corrosion. Metal plating done in this manner is very superior to wet plating methods because it has been difficult to bring about uniform plating on the interior of hollow objects, especially conduits. Further, employing conventional wet electroplating methods there is always a certain amount, even though minor, of entrapment of electrolyte. While this may be imperceptible under ideal conditions, there is generally enough impurities plated out with the metal to ultimately cause deterioration of the plated article. Gas plating eliminates these difficulties because no electrolyte is present or required in order to carry out the process and is a prerequisite element in performing the wet electrolytic plating process.

Further, gas plating makes it possible to bring nacent pure metal in direct contact with chemically clean substrate surface on which the metal is to be plated, and due to the deposition of the metal from a gaseous state, the penetration of the same deeply into the pores and interstices of the metal is accomplished without the inclusion of impurities and such as will alter the physical characteristics of the metal so that the interstitial plate portions

function to actually enhance the physical characteristics of the base metal or substrate.

While a preferred procedure and suitable apparatus has been described for carrying out the invention, it is to be clearly understood that the same is not to be restricted thereto, as various changes and modifications may be made therefrom by those skilled in the art without departing from the spirit and scope of this invention and as more particularly set forth in the appended claims.

What is claimed is:

1. A method of forming a composite article comprising magnesium coated with aluminum which comprises depositing by gas plating a bonding metal layer onto the surface of magnesium to be united with aluminum, and applying over said bonding layer by gas plating a metal layer of aluminum to interlock said aluminum metal therewith, said bonding metal layer being selected from the group consisting of the metals iron, nickel, copper, chromium and alloys thereof.

2. A method of aluminizing magnesium to provide the same with a protective coating, said method comprising depositing by gas plating on said magnesium a bonding metal layer of metallic nickel by gaseous metal deposition, and applying thereover a layer of aluminum metal by the application of a deposit thereon to form a composite product of magnesium and aluminum with an intermediate bonding layer.

3. A method of aluminizing magnesium to provide the same with a protective coating, said method comprising depositing metal onto the magnesium by gas plating as a bonding layer of metal and heating the same, whereby to engage and diffuse said bonding metal layer into the pores of the magnesium, and applying a layer of aluminum metal by deposition of the metal onto said bonding layer whereby the same is interlocked with the bonding layer to produce a magnesium aluminum composite product, said bonding metal layer being selected from the group consisting of the metals iron, nickel, copper, chromium and alloys thereof.

4. A method of bonding aluminum metal to magnesium metal which comprises cleaning the surface of the magnesium to be bonded with aluminum, heating the cleaned magnesium, and gas plating the clean magnesium surface with metal by contacting the heated magnesium metal with a heat-decomposable gaseous metal compound to bring about decomposition of the same and deposition of an intermediate metal layer to which the aluminum metal bonds, said intermediate metal layer being selected from the metals of the group consisting of nickel, copper, iron and chromium and alloys thereof, and applying aluminum metal onto said bonding metal layers in the form of a metal deposit of aluminum to form a composite magnesium aluminum product.

5. A metal product made in accordance with the method set forth in claim 4.

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