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F. E. DRUMMOND
DUPLEX METAL SHEET OR ARTICLE

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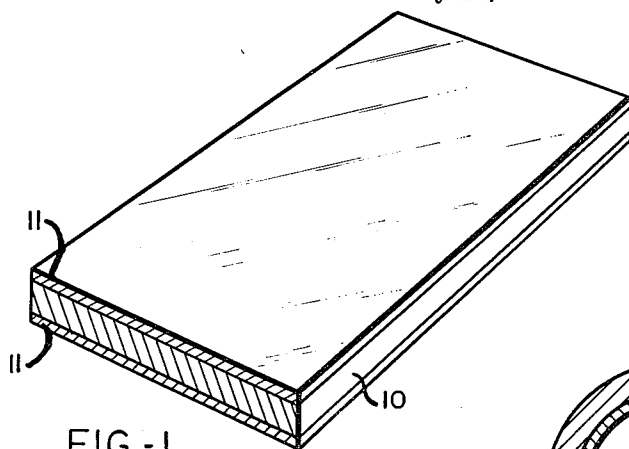


FIG-1

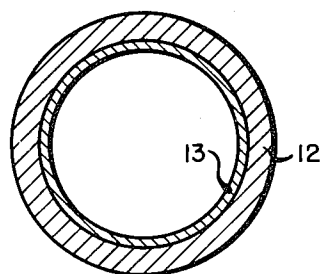


FIG-2

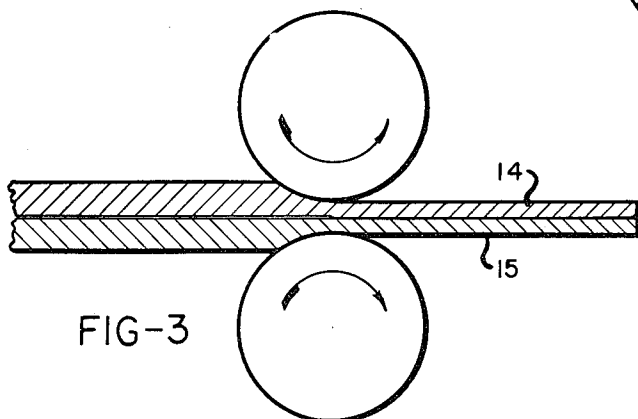


FIG-3

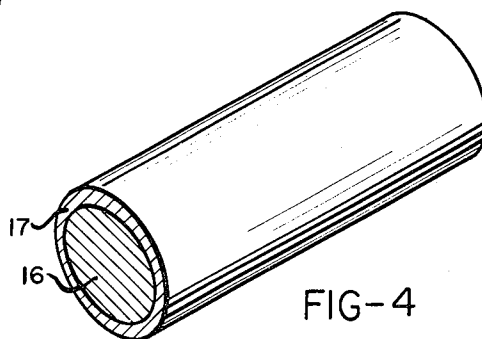


FIG-4

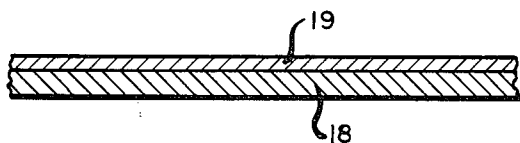


FIG-5

INVENTOR.
FOLSOM E. DRUMMOND
BY *Toulmin & Toulmin*
ATTORNEYS

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2,746,134

DUPLEX METAL SHEET OR ARTICLE

Folsom E. Drummond, Washington, D. C., assignor to Commonwealth Engineering Company of Ohio, Dayton, Ohio

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4 Claims. (Cl. 29—191.2)

This invention relates to duplex metal articles, and more particularly is concerned with the production of a duplex metal sheet or the like comprising a base of magnesium metal, or a magnesium alloy, having a layer of corrosion-resistant metal or metal alloy thereover which is highly resistant to corrosion.

It has been proposed heretofore to produce magnesium alloy sheets comprising a core of magnesium or magnesium alloy provided with a coating consisting of pure magnesium or a magnesium alloy which is more resistant to corrosive attack than the core metal. Such duplex metals, however, have not been generally satisfactory because they possess the disadvantage that at any point where the core or base metal is exposed in contact with the coating metal, as, for example, along a cut edge of the sheet, or where the coating has been perforated, an electrolytic type of corrosion is set up which causes a preferential attack on the base metal resulting in an impairment of its structural properties.

This preferential or selective corrosive attack on the core metal will occur when the core metal has an electrode potential greater than that of the outer metal. Under these conditions a voltaic action may be set up between the two metals in contact with the corroding medium and the resultant electrolytic action tends to dissolve the core metal. This type of corrosive action seriously restricts the use of magnesium and certain of the magnesium alloys as a core or base metal in the fabrication of duplex metal articles.

The preferred metal or alloy used is titanium, zirconium or alloys thereof wherein titanium or zirconium or both are the chief constituents. Other metals of group IV of the periodic table of elements, e. g. hafnium, thorium, etc., may be substituted for all or a part of the titanium or zirconium, the high melting point metals of group IVA being preferred. The A subgroup of group IV comprises the elements titanium, zirconium, hafnium and thorium.

It is an object of this invention to provide a duplex metal article consisting of a metal or alloy which corrodes readily (e. g. when subjected to boiling glacial (99.5%) acetic acid, and which is protected against this corrosive action by being provided with a sheath coating or covering of the metals or alloys of titanium, zirconium, hafnium and thorium.

Another object of the invention is to provide a duplex metal article in which the core or base metal is magnesium or magnesium alloy which is enclosed in a protective outer casing of a corrosion-resistant metal or suitable alloy thereof, the same being preferably welded or gas-plated, or otherwise secured to the base metal so as to form a unitary laminated metal product.

Another object is to provide a corrosion-resistant duplex metal article in which magnesium or various magnesium alloys may be used as the base, or core metal, and wherein the surfaces of the core metal are protected by a sheath comprising said corrosion-resistant metal or metal alloy, and wherein there is provided a light-weight metal article having the structural properties of the combined metals or

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alloys. A magnesium sheet or article is thus provided having improved corrosion-resistant properties over magnesium metal or its alloys.

Briefly, the invention comprises a composite metal body, which may be in the form of a sheet, tube or rod or the like wherein the base metal or core comprises magnesium metal or a suitable alloy thereof and the sheath or covering layer of a corrosion-resistant metal as its principal constituent. The sheath or covering layer may constitute from about 8% to 60% of the weight of the composite metal sheet, rod or bar, but for most purposes the preferred proportion is about 10 to 25% or less of the weight of the composite product.

One method of making a bonded composite sheet or rod is by coating the surface of the magnesium surface to be sheathed with molten metal, e. g., spraying molten metal such as zinc, cadmium, or alloys thereof, and then applying thereto a sheet or layer of titanium or zirconium metal. The magnesium sheet and corrosion-resistant sheet being superimposed one upon the other with the sprayed molten metal film at the interface, the superimposed sheets being heated to a temperature of about 600 to 700° F. or above, but below the melting point of the interface bonding metal. The superimposed sheets while still hot are passed one or more times between rolls adjusted to produce a substantial reduction in the thickness of the composite sheet. There results a magnesium base sheet having a sheath of corrosion-resistant metal strongly bonded thereto.

Using crushed sponge titanium metal, which is cheaper than titanium alloy metals, a suitable bonding agent such as molten metal may be employed to form the composite product. In this method crushed and screened titanium sponge metal (300 mesh or finer) is distributed as a powdered layer over the cleaned surface of the magnesium or magnesium alloy sheet and bonded therewith by the use of molten zinc, cadmium or a suitable alloy thereof, as described above. Where titanium alloy particles are used which have a sufficiently low sintering temperature, the same may be united to the magnesium metal surface by sintering. Titanium metal in a pure state has a melting point of around 1800° F., so that the lower melting point of titanium is preferably used for sintering purposes.

Zirconium metal, as produced by electrolysis of its double alkali metal fluoride salt, or by reduction of the oxide with calcium metal, may be used. Hafnium is used associated with zirconium from which, if desired, it may be separated by fractional crystallization of the complex fluorides. Thorium metal may be prepared by the action of alkali metal on the halide, e. g. thorium chloride.

The corrosion-resistant metals are amphoteric and possess the common characteristic of raising the electrode potential of the magnesium with which they are alloyed. The reason why this particular group should exhibit this effect is not entirely clear, but probably has some relationship to their relative position in the periodic table. These metals raise the electrode potential of the magnesium in varying degree, depending, first, upon the particular metal or metals used and, second, upon the particular amounts which may be added to the magnesium. The choice of the proper magnesium alloy to be used as the coating material in combination with any given magnesium metal base depends upon a predetermined knowledge of the electrode potential of the base metal in question.

The coating magnesium alloys containing one or more of the class of metals above described should have an electrode potential greater than that of the base metal. These different potentials are readily measured in accordance with methods long known in the art against a standard electrode. If the potential of the base metal is elec-

tronegative with respect to the standard electrode, it is not necessary that the coating metal be electro-positive with respect to the standard electrode, but only that it be less electronegative than the base metal in order to be satisfactory for the purpose of my invention. Therefore, throughout this specification and claims, where it is said that the electrode potential of the coating metal should be higher than that of the base metal, it is meant that the coating metal should be more electropositive with respect to the standard electrode than is the base metal. While no fixed potential difference is required between the electrode potential of the base metal and that of the coating metal, a substantial protection may be given any base metal by a coating metal of higher electrode potential. It is generally desirable that there be a relatively wide difference in the electrode potential of the two metals, since it has been found that with greater differences in potential there usually occurs less attack on the base metal, and by suitable adjustment of the potential difference it is possible to afford the base metal complete protection for all practical purposes.

A convenient standard electrode for measuring the potential difference mentioned may be readily selected from those now in regular use for similar measurements. For the purpose of this description of the invention, a calomel electrode has been selected as a standard. In measuring the electrode potential in question, the magnesium metal to be tested is made one element of an electrolytic cell; the calomel is made the other element. The electrolyte is a normal solution of sodium chloride containing 0.3 per cent by weight of hydrogen peroxide. The circuit is closed and the potential difference of the elements is measured on a potentiometer.

Titanium metal powder useful in practicing this invention may be obtained from any suitable source and produced by different processes. One method of producing titanium metal is by the reduction of titanium tetrachloride with magnesium. The resultant titanium metal is recovered in the form of a spongy mass which is crushed to produce metal particles of suitable size for incorporating into the coating composition.

Although a titanium alloy of aluminum and chromium is set out in an example illustrating the invention, it will be understood that other alloys of titanium may be employed. Titanium alloyed with up to 10% of other metals, e. g. molybdenum, tungsten, nickel, vanadium, copper or iron, are illustrative of alloys which may also be used.

The term "corrosion-resistant" metals, as used in the specification and claims, is intended to include the metals and their alloys of the IV group of the periodic table and mixtures of metal particles wherein the metals of this group constitute the major constituent.

The addition of one or more of the elements above described to the corrosion-resistant metal for the purpose of forming the protective coating or alloy may be made and in any suitable amount necessary to attain the desired electrode potential so long as other desirable properties of the magnesium itself are not materially impaired; and, likewise, other elements not deleteriously affecting the desired potential properties and other desirable characteristics of the magnesium may be added. In general, the following amounts of the metals of the class above described best serve the general purposes of this invention in producing the electrode potential desired without materially impairing other desirable properties of the magnesium metal.

The base or core metal, that is to say, the layer or body of metal from which the duplex metal article of my invention derives its principal structural properties, may be any magnesium metal having the properties which it is desired to obtain in the finished article. Various known alloys possessing known combinations of properties may be used, such as a magnesium-base alloy comprising 6 to

7% aluminum, and less than 1% zinc, the remainder being magnesium. Other magnesium-base alloys commercially available which may be used besides magnesium are alloys containing tin (5%), zinc (4%) and manganese (1%), remainder magnesium. Also magnesium metal containing 1 to 3 manganese, with or without tin.

In the drawing:

Figure 1 is a perspective view of a duplex article or sheet having a core 10 of magnesium metal and an outer covering or layer 11 of titanium metal or alloy.

Figure 2 is a view in cross-section, illustrating a duplex metal article in the form of a tube, and comprising a base metal 12 of iron, magnesium or the like with an inner layer or liner 13 consisting of titanium metal or alloy containing chiefly titanium.

Figure 3 is a cross-sectional view of showing two sheets of metal 14 and 15 being rolled and reduced in thickness while bonding the pair of metal sheets together, one of the sheets as at 14 being designated as magnesium and reference character 15 representing titanium, zirconium or the like metal.

Figure 4 illustrates in perspective and sectioned, a solid rod having a core 16 of magnesium having an outer protective layer 17 of a suitable corrosion-resistant metal.

Figure 5 is an enlarged cross-sectional view of a magnesium-base alloy sheet 18 having a layer 19 of titanium, zirconium or the like metal, which may be applied by spraying the metal thereon.

As an alternative method of applying the corrosion-resistant metal over magnesium metal surfaces, the same may be deposited by gaseous metal deposition. This may be accomplished by employing a heat-decomposable carbonyl or hydride or an equivalent gaseous compound of the metal to be deposited and effecting the deposition as described in the U. S. patents to F. E. Drummond, see for example Nos. 2,332,309 and 2,344,138.

In forming the duplex article of my invention, any of the known methods of forming such duplex metal articles may be used. One method which has been found particularly useful is to roll together the coating alloy and the base alloy in sheet or slab form as illustrated in Figure 3. It is satisfactory to cast the base alloy in an ingot mold lined with the coating alloy. The article may then, if desired, be mechanically worked, as for example, by rolling or drawing or other suitable operation to form the particular type of duplex article desired, such as sheet, rod or other form of material. The working with intermediate heating incident to such forming operations tends to improve the bond between the coating metal and the base metal. Duplex material may also be produced by spraying, gas plating or the like so as to provide the magnesium metal with an adherent coating of corrosion-resistant metal or alloy. This method may be used to advantage where irregular shapes such as castings are to be coated.

The duplex articles of the invention may be provided on any one or all exposed surfaces with the protective coating alloy, as for example are shown in Figures 1 and 2 of the drawing. Figure 1 shows a duplex article comprising a base 1 of a magnesium metal provided on its top and bottom surfaces with a magnesium alloy coating. In Figure 2, a duplex metal article in tubular form comprising a base metal having an inner layer or coating of titanium metal. This type of material is useful, for example, in the manufacture of pipes used to conduct a material to magnesium metal.

What is claimed is:

1. A corrosion resistant duplex metal article comprising a core of magnesium metal and a bonding layer thereover of a metal selected from the group consisting of zinc, cadmium and alloys thereof, and a layer of metal over said bonding layer of metal selected from the group consisting of titanium and zirconium.

2. A corrosion resistant duplex metal article comprising a core of magnesium metal and a bonding layer of zinc

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metal disposed thereover, and a layer of zirconium metal over said zinc metal.

3. A corrosion resistant duplex metal article comprising a core of magnesium metal and a bonding layer of zinc metal disposed thereover, and a layer of titanium metal over said zinc metal. 5

4. A corrosion resistant duplex metal article comprising a core of magnesium metal, a bonding layer of zinc thereover, and a layer of fine titanium metal particles sintered to said bonding layer of zinc. 10

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