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MANGANESE ALLOY COATING ON FERROUS
BASE AND METHOD OF PREPARATION
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Fig. 1.

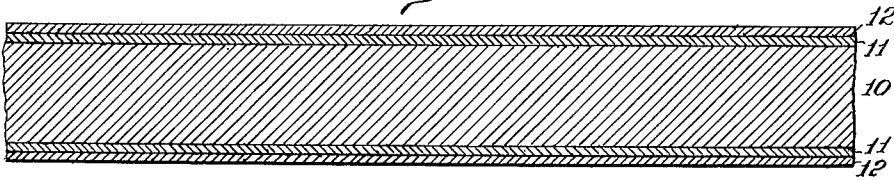


Fig. 2.



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MANGANESE ALLOY COATING ON FERROUS
BASE AND METHOD OF PREPARATION

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The invention relates to the provision of an alloy coating or ply on suitable base metal material, such as strip, sheet, wire, or articles, and more particularly to a new and improved procedure for providing an alloy coating on continuous strip; and this application is a continuation-in-part of my application, Serial No. 492,835, filed August 24, 1943, now Patent No. 2,490,700, granted December 6, 1949, which was a continuation-in-part of my co-pending application, Serial No. 311,930, filed December 30, 1939 (now abandoned), for Production of Alloy Coating on Base Metal Material, and of my prior applications, Serial No. 55,917, filed December 23, 1935 (now abandoned), and Serial No. 127,776, filed February 25, 1937, now Patent No. 2,266,330, granted December 16, 1941, and Serial No. 402,155, filed July 12, 1941, now Patent No. 2,402,834, granted June 25, 1946.

In one aspect, the invention deals with the production of an alloy coating or coatings on base metal material having improved characteristics.

I have determined that a number of factors and limitations hinder the provision of a satisfactory type of alloy coating. In the first place, the provision of an alloy coating by direct electroplating has not been entirely satisfactory from a commercial standpoint. Taking brass as an example, I will consider some factors involved in plating it as an alloy on a suitable base metal:

An alkaline bath containing the two metals, namely, copper and zinc cyanide, is employed. Such a bath can only operate at low current densities and also at low cathodic efficiency. As a result, the operation takes an extremely long time for coating an ordinary thickness of brass and even then the characteristics of the coating are far from satisfactory.

I am aware that the Rubin Patent No. 2,115,749 discloses electroplating separate coatings of desired metals on a ferrous article and subsequently heat treating the coated article in a reducing atmosphere to alloy the coated metals, but said patent teaches heat treating a copper-zinc coating at temperatures anywhere between 700° F. to 1500° F. for a period of about 10 to 30 minutes.

I have determined that heat treating such a coating by starting at a temperature within the given range, say at 850° F. and maintaining that temperature for 10 to 30 minutes, produces a rough and unsatisfactory surface because the outer layer of zinc starts to melt before alloying can take place. Moreover, I have determined that if the proportions of copper and zinc are

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such that the final alloy contains more than 60% zinc, as the heat treating temperature approaches 1500° F., the coating will melt on the surface of the base metal and produce a rough surface.

I am likewise aware that the Rubin Patent No. 2,304,709 discloses electroplating separate coatings of copper and tin on a ferrous article and then heat treating to alloy the coating metals, but said patent teaches that the heat treating can be started and maintained at a temperature anywhere from 400° F. to 2000° F. I have determined that heat treating a copper-tin coating at temperatures anything like 2000° F., according to the teaching of this latter patent, will produce a rough coating due to the melting of the outer coating layer of tin.

Since neither of these Rubin patents mentions obtaining a smooth coating, and the heat treating temperatures given obviously cause melting of the coating, it is apparent that the said Rubin patents were not concerned with the production of a smooth alloy coating.

It is an object of the present invention to provide an improved method of producing alloy coatings which are smooth, homogeneous, and adherent.

When the heat treatment is carried out over too long a time period, or at too high temperatures, or both, the inner layer of an alloy coating forms an alloy with the base metal, and this lessens the effective thickness of the base metal and reduces the ability of the coated metal base to withstand subsequent working or drawing operations.

Therefore, another object of the present invention is to provide an improved method of producing alloy coatings on ferrous material without reducing the effective thickness of the base metal or disadvantageously affecting its characteristics.

Accordingly, it is another object of the present invention to provide an improved method whereby two or more layers of two or more metals can be completely diffused to form a smooth and highly satisfactory alloy coating on a ferrous metal base material or strip.

Another object has been to solve the problems involved in the art relative to the provision of a suitable alloy coating on ferrous strip material.

A further object has been to provide a process for providing alloy coatings which can be carried out on a commercial basis, and more particularly in a continuous line operation.

As will be hereinafter shown, the principles of the present invention can be applied to the fabri-

cating of an alloy coating or coatings on a base metal material providing certain factors are present, and the invention is particularly valuable in providing improved bimetal alloy coating. Examples of such bimetal alloys are: manganese-zinc or manganese-zinc-manganese. Other metals that may be alloyed with manganese include iron, nickel, copper and chromium.

Broadly, any number of metals may be used as long as the metals are plated in the correct proportions of the total weight of the alloy desired to be formed, and the temperatures kept below the melting point of the lowest melting point alloy being formed.

Thus, the present invention involves a suitable method and order of coating individual metals which are applied in suitable proportions to provide the desired alloy type of coating.

These examples of bi-metallic alloys are illustrated in the accompanying drawing in which:

Fig. 1 is a diagrammatic cross section showing two thin metal layers on each side of a base metal piece; and

Fig. 2 is a similar view showing three layers on each side of the base metal piece.

Where a very thin alloy coating is desired, it may be sufficient to apply a thin layer of each alloying metal on the base, preferably with the higher melting point metal adjacent to the base, and then to heat treat according to my invention, because the heat treating time required for very thin alloy layers is not long enough to cause formation of any substantial amount of undesirable alloy between the inner layer and the base so as to weaken the same, and also because occluded gases which may be produced escape very rapidly and easily through the very thin layers. The rate of alloying thin layers is such that the temperature rise can be very rapid up to near the melting point of the alloy formed.

However, as the desired total thickness of the electroplated coating is increased, the allowable rate of heating up the coated strip is decreased, because the occluded gases in the strip have farther to travel to come to the surface and therefore tend to build up internal pressures and cause blisters or distortion in the coating. If a very thin bimetal alloy coating is desired, one layer of each metal may be sufficient; the heating-up rate may be relatively rapid and yet produce a satisfactory coating because the time necessary to form the complete alloy is short, but if a thicker layer of alloy coating is formed from two layers of electroplated metals, the heating-up time has to be increased because the alloying time for the thick layers is longer. However, the heating-up time may be short for a thick layer of alloy coating if the constituent metals are electroplated in thin alternate layers. Care must be taken, however, to permit the occluded gases to escape without causing damage to the coating due to internal pressure.

Thus, where a bimetal alloy coating of substantial thickness is desired, I preferably employ three or more alternate thin layers of the two metals, with a layer of the higher melting point metal preferably next to the base and another layer of said metal as the outer coating. By using a plurality of thin alternate layers, the heating-up rate is increased, and the total heat treating time is kept at a minimum while preventing the formation of any substantial amount of a so-called "bastard alloy" between the inner layer and the base metal, so as to weaken the base and decrease adherency of the coating.

It will thus appear that from a broader standpoint, my invention deals with the provision of two or more thin coated layers of two or more metals on a ferrous or steel base, and the greater number of layers the greater surface contact between the individual plated metals is provided, and the less distance the molecules of those metals have to travel while being diffused or alloyed. In the drawing 10 indicates the base metal material which is relatively thick with respect to the coatings that are electrolytically deposited on one or both opposite sides thereof. The first or inner coating is indicated at 11 in Fig. 1 and the second coating at 12. It is preferred that the inner coating be the higher melting point metal, which in the example given would be manganese; and the lower melting point metal zinc, in this example, would be deposited thereon.

Where three layers are to be applied as in Fig. 2, the same first and second layers 11 and 12 are used and a third layer of manganese as indicated at 13 may be applied thereover if desired. The number of layers and thickness thereof may vary according to the desires and the use of the strip.

I have determined that thin layers provide a more intimate contact between metals to aid diffusion between the metals and that penetration of the base metal by the adjacent coating metal is limited because of the increased speed of the alloying action.

Thus the provision of alloy coatings according to my invention provides a coated product which loses substantially no ductility or deep drawing quality due to the coating process, and which requires minimum time of heat treatment to provide complete diffusion of the alloy coating.

I have determined that a plurality of suitably spaced and alternated thin layers of two individual metals, or a plurality of thin layers of more than two individual metals, can be provided with distinct advantageous results and in such a manner as to make possible a quick and effective complete diffusion of alloying action within the time limit requirements of a continuous process as applied to an electroplating line, for example.

Although any suitable means may be employed for accomplishing the alloying action, I prefer to move the strip coated in accordance with the present invention, through a reducing atmosphere furnace, or through suitable liquid or oil treatment bath of a non-oxidizing or preferably reducing nature.

Such a coating can be heat treated in accordance with my invention in a relatively short time to produce complete diffusion of the manganese and zinc layers and form a manganese-zinc alloy coating.

As distinguished from the old process of using a cyanide bath to produce the alloy coating directly by an electroplating operation, I have been able to increase greatly the current densities for a copper plating operation, for example, to substantially 75 to 200 amperes per square foot in an acid bath, as compared to very much lower densities for a brass alloy cyanide bath.

The same applies with equal force to a zinc acid bath wherein a current density of 100 to 1000 amperes per square foot may be employed.

In addition, the resistance of an acid solution is lower than that of a cyanide solution, providing reduction in power consumption for equal current densities, and acid solutions can be operated at lower temperatures to keep the heat down and minimize fumes.

I have been able to solve the various problems involved in obtaining a successful and practical commercial alloying treatment of electroplated layers by applying very thin individual layers of the metals to be alloyed to a base metal or continuous metal strip in the proper proportions desired in the alloy coating; the thickness of each individual coating layer is maintained at a minimum, and increased thicknesses of bimetal coatings are obtained by providing alternate coating layers of the metals.

Thus a complete diffusion or alloying operation can be carried out continuously and in a minimum of time so as to produce a smooth, homogeneous and adherent coating without deleteriously affecting the base metal.

In applying alternate coatings of two different metals, I prefer to apply the higher melting point metal coating to the base material, then apply the lower melting point metal layer to such coating, and then apply another coating of the higher melting point metal, to in effect form a sandwich, with the lower melting point metal between two layers of the higher melting point metal; although the reverse order of plating can be used with certain limitations. Thus in forming an alloy such as manganese-zinc-manganese, for example, I preferably form at least three layers of the metals with a layer of the lower melting point zinc sandwiched between layers of the higher melting manganese, and with the higher melting point manganese first plated on to the base material.

It will be apparent that this sequence can be continued indefinitely, depending upon the desired thickness of the resulting alloy coating, and the order will continue manganese, zinc, manganese, zinc, manganese, preferably with the higher melting point metal constituting the outer or exposed layer of the coating.

Also, the amount of diffusion of the inner layer into the base is kept at a minimum because of the short time of heat treating, whereas if two layers only of the two coating metals were employed, having increased thickness, the required increased time of heat treatment would cause greater diffusion of the inner layer into the base metal.

In the case of high melting point metal coating layers, a further consideration is that the heating must not be for a long period within the temperature range. The heating is preferably carried out in a continuous furnace with a reducing atmosphere wherein the temperature of the piece can be quickly raised above and lowered below about 1750° F. to 1800° F. The ferrous base material, if it were subjected to prolonged heating above its critical temperature, would be subject to crystallization and other undesirable effects. Thus the sheet would be brittle and apt to break when subsequently cold drawn or worked.

It is apparent that in accordance with my invention a rapid rate of heat alloying treatment can be effected with thin coating layers of the metals to be diffused or alloyed, and consequently, where heating above the critical temperature for the base metal is required by the alloying metals, such heating need be carried out for a short time only so as not to substantially affect the base material.

Any desired number of layers of any desired number of metals may be heat treated to produce a satisfactory alloy coating which is completely diffused, as long as the metals are in thin layers

in the correct proportions of the total weight of the alloy coating desired.

Thus I have determined that a complete alloy diffusion may be accomplished between two or more layers of two or more coating metals by employing suitable thicknesses and relationships of the coating metals, and relationships between the heat treating temperatures and heat treating time periods with respect to each other and with respect to the base metal; and further, that a quick heat treatment will be sufficient to diffuse such metals into an alloy, and will not be sufficient to form any material amount of so-called "bastard alloy" between the base metal and the coating.

In accordance with my invention, such coatings may be applied and heat treated in a continuous line operation.

If hard, unannealed strip is employed, it may be desirable to anneal or normalize the strip after the alloying operation, or where the melting points of the alloying metals are sufficiently high the annealing or normalizing may be effected during the alloying operation, and such annealing may be carried out by coiling lengths of the strip and box annealing the coils in a well-known manner, or the normalizing may be carried out in a continuous furnace.

Where the lower melting point metal constitutes the outer layer, care must be taken, particularly in a continuous operation, to avoid contact with any solid material until the outer layer has cooled sufficiently to avoid scratching or other injury. However, as previously pointed out, I prefer to provide an outer layer of the higher melting point metal, and I have determined that where a coiled plated strip is alloyed, such an order of plating is preferable in order that the coils will not fuse together in the annealing box.

Thus, when coating metals are being alloyed, and one of them has a relatively low melting point, either continuous or coil annealing can be employed; and in the case of higher melting point metals, coil annealing is usually preferable because the alloying treatment requires more time and can be accomplished during the annealing operation.

Other combinations of other metal layers can be similarly treated according to my invention to produce a variety of alloy coatings, because each pair of metals alloyed has a constitution diagram from which the temperatures can be determined so as to always heat below the melting point of the alloy being formed. The time of heating at any temperature should be sufficient to alloy the metals without melting any appreciable part of the coating, and the heating times will obviously vary somewhat depending upon the thickness of the coating layers and the particular metals present.

Moreover, where one of the metals forming the alloy coating has a melting point below the annealing temperature of the base metal, and another metal or metals has a melting point higher than the annealing temperature of the base metal, I preferably sandwich the lower melting point metal between layers of the higher melting point metal, so that the annealing of the base stock can be carried out concurrently with the heat treatment of the coating.

If the melting point of the alloy being formed in the coating is below the required annealing temperature of the base stock, then the base stock must be annealed before the coating layers are applied.

In the case of applying coating layers to hard unannealed base stock, not only are the metals selected which will form an alloy having a melting point above the required annealing temperature, but the number and thickness of the coating layers is such that complete diffusion takes place in the coating by the time the annealing is complete.

From the foregoing description, it will be apparent that there are a number of factors to be controlled in order to obtain the improved results desired and to accomplish the objects of the present invention, as follows:

1. The sequence of an application of the metals that are to form the completely diffused alloy coating;

2. The number of layers or alternate layers of the different metals applied in succession as electroplated coatings to the base metal;

3. The time and temperature conditions of heat treatment which vary in accordance with the melting points of the coated metals and the alloys being formed in the coating;

4. The thickness of each layer and the thickness of the total coating as related to the time and temperature of heat treatment; and

5. The selection of hard (unannealed) or soft (annealed) base metal strip or stock upon consideration of the requirements of the heat treating operation and of the melting points of the individual plated metals and the melting points of the alloy being formed therefrom.

The invention is applicable to continuous strip base stock and also to other suitable shapes, such as wire, sheets, etc.

While certain coating metals and alloys have been specifically referred to for the purpose of illustrating my invention, it will be apparent that

such metals and alloys are representative of my invention and that other combinations of other metals and alloys may be used, and while ferrous or steel base metal has been referred to, it will be apparent that other base metal may be coated with appropriate alloy without departing from the scope of the invention defined in the claims, as long as the various factors enumerated are properly determined.

I claim:

1. The method of producing corrosion resistant coatings on iron or steel which comprises electrolytically depositing a plurality of layers of different metals on iron or steel, at least one of said metals being manganese, and heating the resultant coated iron or steel at a temperature below the melting point of the iron or steel but sufficient to cause at least partial diffusion of the electroplated metal layers.

2. An article of manufacture comprising iron or steel provided with an adherent corrosion-resistant coating formed by diffusion of electroplated metal layers, at least one of which is metallic manganese.

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