

Dec. 6, 1949

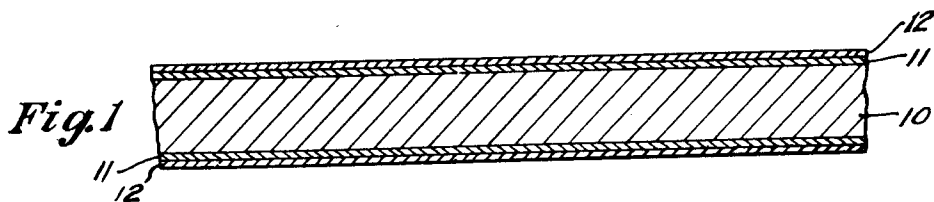
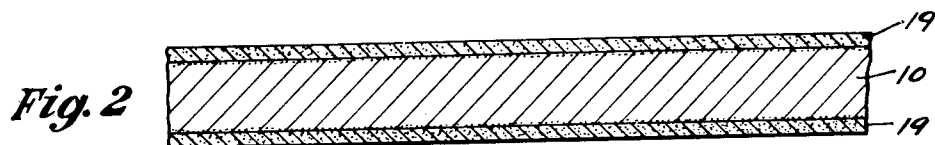
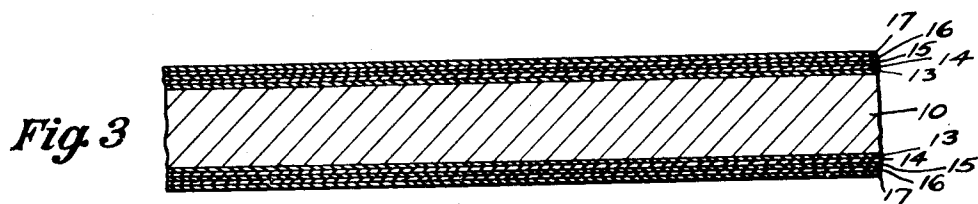
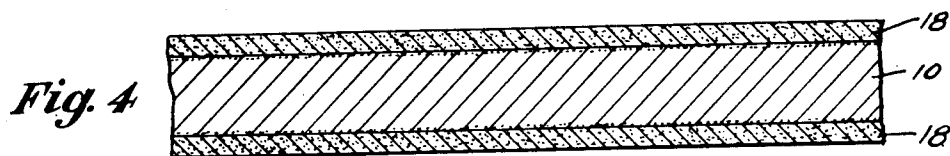
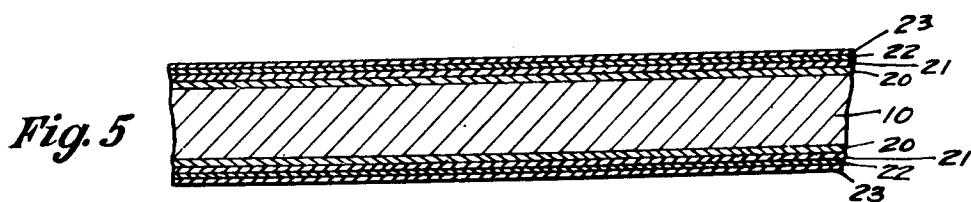
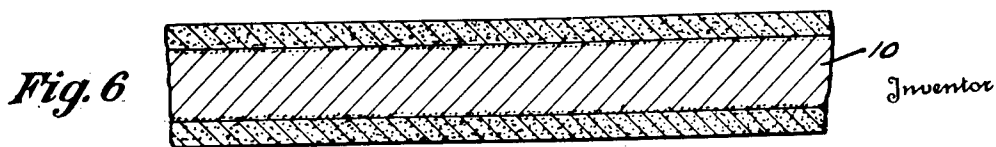
J. S. NACHTMAN

2,490,700

PRODUCTION OF ALLOY COATING ON BASE METAL MATERIAL

Filed Aug. 24, 1943

2 Sheets-Sheet 1



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PRODUCTION OF ALLOY COATING ON BASE METAL MATERIAL

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2 Sheets-Sheet 2

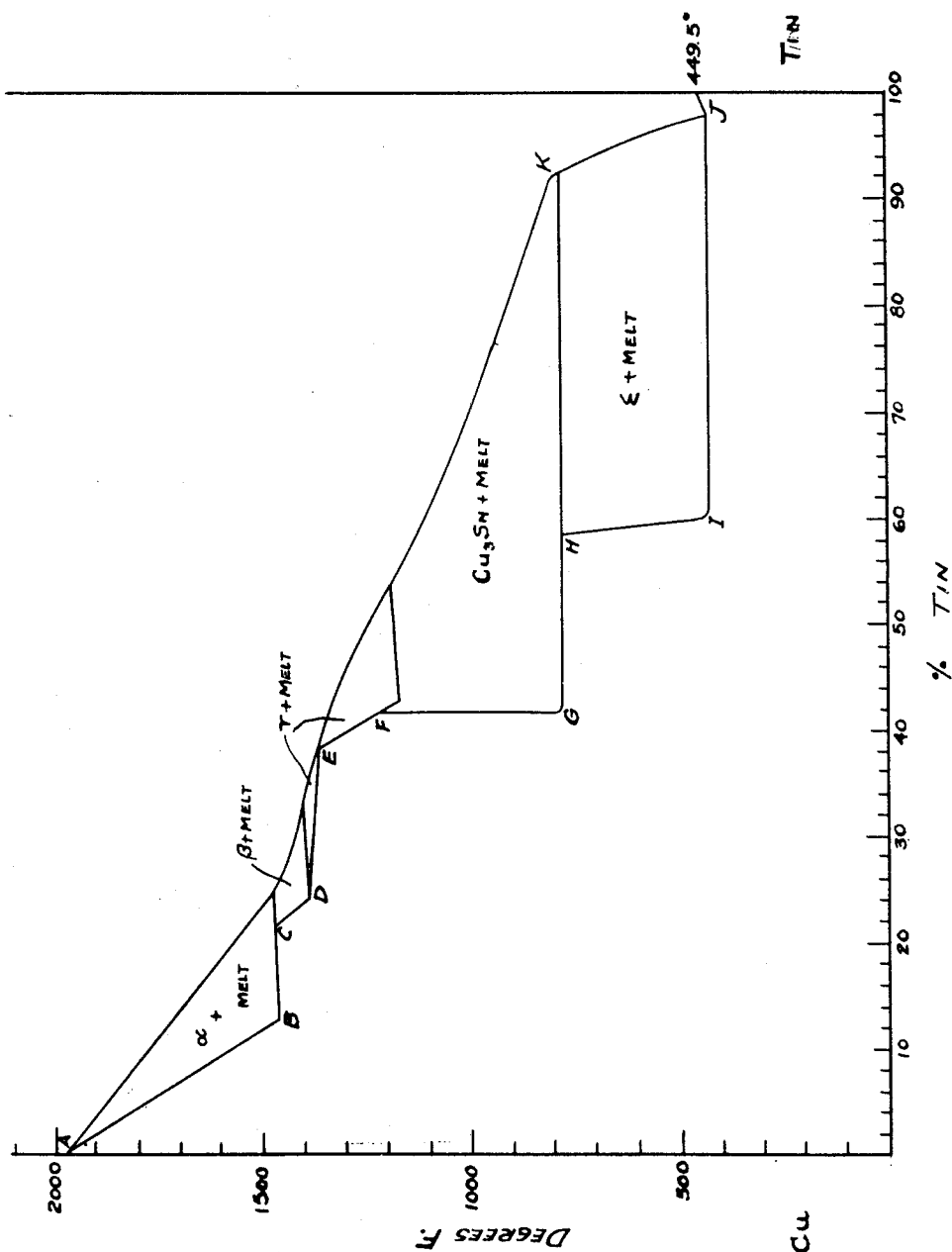


Fig. 7

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UNITED STATES PATENT OFFICE

2,490,700

PRODUCTION OF ALLOY COATING ON BASE METAL MATERIAL

John S. Nachtman, Youngstown, Ohio

Application August 24, 1943, Serial No. 499,835

2 Claims. (Cl. 204—37)

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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 co-pending application, Serial No. 311,930, filed December 30, 1939, and entitled Production of alloy coating on base metal material, and of my prior applications, Serial No. 55,917, filed December 23, 1935, and Serial No. 127,776, filed February 25, 1937, now Patent No. 2,266,330, granted December 16, 1941, of which the aforesaid application, Serial No. 311,930, was a continuation-in-part. Applications Serial Nos. 55,917 and 311,930 are now abandoned.

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 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

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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, homogenous, and adherent.

When the heat treatment is carried out over too long a time period, or at too high temperatures, or both, the inner copper layer of a copper alloy coating forms a copper-iron 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 subject 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.

I have discovered that in order to produce satisfactory, smooth, homogenous alloy coatings from separate layers, it is absolutely necessary to provide proper proportions of the alloying metals, to correlate the thickness of the layers and the time of heat treatment, and to correlate the heat treating temperatures, particularly starting temperatures, to the melting point of the lowest melting point coating metal, and to the lowest melting point of the alloy being formed in the coating.

Furthermore, I discovered that under such time conditions, the intermediate or inner layer of coating forms a copper-iron alloy which thus lessens the effective thickness of the base metal material and further destroys desired characteristics of the product in that this additional alloy layer has its own distinct characteristics. An important point is that the thickness of the base metal which must withstand the strain during the after-working or drawing operation is materially lessened and weakened. The time period involved tends to increase the size of the crystal structure of the base metal.

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.

These and many other objects will appear to those skilled in the art from the description herein, the drawings, and the appended claims.

In the drawings,

Figure 1 is a diagrammatic cross sectional view of a base metal piece coated with two thin electrodeposited layers to form a bimetal alloy coating;

Fig. 2 is a similar view showing the article of Fig. 1 after complete diffusion of the coating layers has taken place to form a relatively thin alloy coating;

Fig. 3 is a diagrammatic cross sectional view of a base metal piece coated with five alternate thin layers of two different metals to form a bimetal alloy coating which is thicker than that of Fig. 1;

Fig. 4 is a similar view showing the article of Fig. 3 after complete diffusion of the coating layers has taken place;

Fig. 5 is a view similar to Fig. 3, showing a base metal piece coated with thin individual layers of four different metals suitable for forming a bearing alloy;

Fig. 6 is a similar view showing the product of Fig. 5 after complete diffusion has taken place; and

Fig. 7 is a copper-tin constitution diagram.

Similar numerals refer to similar parts throughout the drawings.

As will be hereinafter shown, the principles of the present invention can be applied to the fabricating 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:

Brass (copper-zinc), bronze (copper-tin),terne metal (tin-lead), Monel metal (nickel-copper), and various other alloys such as are formed by the use of nickel-tin, chromium-tin, nickel-zinc, nickel-lead, nickel-chromium, nickel-iron, manganese-zinc, iron-tungsten, cadmium-copper, cadmium-iron, cadmium-lead, bismuth-lead, and bismuth-tin.

Examples of alloy coatings of more than two metals are tin-antimony-lead-copper, tin-antimony-nickel-lead-tin-copper, copper-zinc-tin, nickel-zinc-copper-silver-cobalt-copper, etc.

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.

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 oc-

cluded 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.

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.

In order to obtain the best results I have determined that the heat treatment should be started at a temperature which is below the melting point of the lowest melting point metal of the coating metals, and thereafter maintained at a temper-

ature below the lowest melting point alloy being formed in the coating until the coating metals are diffused into a homogenous alloy.

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.

In the drawings, 10 indicates the base metal material and in Fig. 1 the first or inner coating is indicated at 11 and the outer coating at 12. For example, the inner coating 11 may be copper applied electrolytically from a copper cyanide bath to a thickness of the order of .00005", and the outer coating 12 may be an electrolytically applied coating of zinc of the same thickness.

Such a coating can be heat treated in accordance with my invention in a relatively short time to produce complete diffusion of the copper and zinc layers and form a copper-zinc alloy coating of approximate composition 55.6% copper and 44.4% zinc.

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 greatly increase 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; and by starting and maintaining the heat treating temperatures below the melting point of the lowest melting point metal and of the lowest melting point alloy being formed, 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, homogenous 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 the 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 brass, for example, I preferably form at least three layers of the metals with a layer of the lower melting point zinc sandwiched between the layers of the higher melting point cop-

per, and with the higher melting point copper 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 copper, zinc, copper, zinc, copper, preferably with the higher melting point metal constituting the outer or exposed layer of the coating. In the case of bronze, the order preferably will be copper, tin, copper, tin, copper.

Referring to Figs. 3 and 4, of the drawings, the inner coating layer 13 may be copper, the next outer coating layer 14 tin, the next outer coating layer 15, copper, the next outer coating layer 16 tin, and the last outer coating layer 17 copper, constituting five relatively thin layers which after proper heat treatment provide a copper-tin alloy coating indicated at 18 in Fig. 4, which is thicker than the bimetal coating 19 in Fig. 2, but which becomes completely diffused in a relatively short time because of the intimate contact between the relatively thin layers of the coating metals.

Also, the amount of diffusion of the inner layer 13 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.

The heat treatment, according to my invention, in the case of a copper-tin alloy, coating for example, is carried out at temperatures determined by the copper-tin constitution diagram shown in Fig. 9. The melting point of pure copper is represented at A and the melting point of pure tin is represented at the other end of the curve. Therefore, in heat treating a coating composed of copper and tin layers, the heat treatment must start at a temperature below 449.5° F., which is the melting point of pure tin, and immediately dropped to below 440.6° F., which is represented by the line I, J, and which is the eutectic or lowest melting point temperature of the alloy being formed, in order to maintain the coating in a solid state.

As the heat treatment progresses, the tin and copper diffuse and form alloys which are richer in copper, representing the whole curve from A to J.

If the layer next to the base stock is tin and the outer layer is tin, the alloy first formed next to the base stock and on the outer surface contains a high percentage of tin, but as the heat treatment progresses further the temperature may be increased in accordance with the curve as the metals diffuse further and the percentage of tin in the alloy being formed decreases.

Between the line or curve A, B, C, D, E, F, G, H, I, and J, or A to J, and the line A, K, J, the alloys are in a mushy or semi-liquid form, so that if the layers of tin and copper are very thin and the tin is sandwiched between an inner and outer copper layer, then the heat treating temperatures may safely be carried between the lines A to J, and A, K, J, without danger of distortion, because the thin sandwiched layers of mushy alloys will be held in position between inner and outer solid layers of the higher melting point metal.

If the outer layer is tin and the heat treatment at any time exceeds the lowest temperature on the curve A to J represented by the alloys present in different percentages of copper and tin, a portion of the coating will melt and become rough.

Accordingly, while the heat treating tempera-

tures may vary during the alloying of the coating layers, the temperatures are determined by the constitution diagram and should not be raised to points such as to melt the coating metals or the alloys being formed and cause distortion and other disadvantageous results.

In the case of high melting point metal coating layers, such as copper and nickel, a further consideration is that the heating must not be for a long period within the temperature range, since the range for nickel and copper rises above the critical temperature of a steel base material. 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.

As indicated in Figs. 5 and 6, invention may be applied to a plurality of layers of different metals. For example, in Fig. 5 the inner coating 20 may be tin, the next coating 21 antimony, the next coating 22 lead, and the outer coating 23 copper. These metals are applied in proper proportions to form the desired alloy coating and then heat treatment is carried out in accordance with the constitution diagram of the metals involved, that is, the heat treatment is started below the melting point of the lowest melting point metal, and continued at temperatures below the melting points of the alloys being formed.

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, and the heat treatment is started and maintained at temperatures below the lowest melting point metal and the lowest melting point alloy being formed.

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 anneal-

ing 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, such as tin, 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.

Example 1

As an example of the method of carrying out my invention to produce a copper-tin alloy coating on ferrous base stock to give a total coating weight of .095 ounce per square foot of surface with the copper and tin in the proportions of 63% copper and 37% tin, I first plated a layer .000080 inch thick of copper from a copper cyanide bath at 48 amperes per square foot on the base stock. I then plated a layer of tin .000057 inch thick from an acid tin bath at 60 amperes per square foot onto the copper layer. These two layers were electroplated in accordance with regular practice.

The thus coated stock was heated up in a hydrogen atmosphere by raising the temperature 16° to 18° F. per minute to a temperature of 440° F., then maintaining the temperature of 440° F. for one half hour, and then raising the temperature 16° to 18° F. per minute to 900° F. where it was held for about ten minutes, after which the temperature was dropped to room temperature at the rate of 18° to 25° F. per minute.

The resulting coating was a completely diffused smooth copper-tin alloy, with no blistering or distortion of the coating, and no substantial alloy between the copper and base stock so as to weaken or affect the characteristics of the base stock.

It is apparent that the heating was held below the eutectic (440° F.) for a sufficient time and then raised in accordance with the copper-tin constitution diagram as the melting point of the lowest copper-tin alloy being formed increased, the heating temperatures always being maintained below that represented by the line which divides the liquid and solid state of the alloy being formed.

Example 2

Using the same thicknesses of two layers of copper and tin electroplated on ferrous base stock, as in Example 1, the coated stock was heated in a hydrogen atmosphere by increasing the temperature 16° to 18° F. per minute to 440° and holding that temperature for ten minutes. The temperature was then increased 16° to 18° F. per minute to 600° F. and held there for 20 minutes, and then cooled at 18° to 25° per minute to room temperature.

The resulting coating in this instance was only

partially alloyed, and a copper layer was exposed when the coating was sanded, showing that the heating time and temperatures were not sufficient to form complete diffusion of the two coating layers.

Example 3

A ferrous base stock was electroplated first with a layer of tin .000028 inch thick, then with a layer of copper .000080 inch thick, and then with a layer of tin .000028 inch thick according to regular practice, to give a coating having a total weight equal to that of the coatings in Examples 1 and 2, and in the same proportion of copper and tin.

The thus coated stock was then heated according to the exact times and temperatures given in Example 2.

The resulting coating was smooth and completely diffused into a copper-tin alloy so that no copper showed on sanding off a part of the coating, and the coating showed no blistering or distortion.

Thus, it is apparent that by using thinner coating layers, of the alloys desired, and by using three or more alternate layers of two desired coating metals, the heating time can be decreased and the temperatures lowered.

Example 4

A steel strip .010 inch thick was electroplated first with a layer of copper at .325 pound per base box, then electroplated with a layer of tin .350 pound per base box, and then electroplated with a layer of copper at .325 pound per base box, making a total coating of 1 pound per base box. The strip was then loosely wound in a 300 pound coil and placed with other like coils in a bell type furnace with a reducing atmosphere. The temperature in the furnace was raised from room temperature to 1100° F. in eight hours at a rate of 2° to 5° per minute, then held at 1100° F. for two hours, and then cooled at a rate of 10° to 15° per minute to room temperature.

The resulting coating was smooth without any blistering or roughness and the coating metals were completely alloyed to produce a 65% copper and 35% tin bronze coating.

Example 5

A steel strip .010 inch thick was electroplated first with a layer of nickel at .30 pound per base box, then with a layer of tin at .40 pound per base box, and then with a layer of nickel at .30 pound per base box, making a total coating of 1 pound per base box. The strip was loosely wound in a 300 pound coil and placed with other like coils in a bell type furnace with a reducing atmosphere. The temperature was raised from room temperature to 1100° in eight hours at the rate of 2° to 5° per minute, then held at 1100° F. for two hours and then cooled to room temperature at a rate of 10° to 15° per minute.

The resulting coating was smooth without any blistering or roughness, and the coating metals were completely alloyed to produce a 60% nickel and 40% tin alloy coating.

Example 6

Low carbon annealed steel strip was electroplated with a layer of copper .0000340 inch thick, then with a layer of tin .0000534 inch, then with alternate layers of copper and tin each .0000340 and .0000534 inch thick respectively until seven coating layers were produced with the outer and

inner layers being copper. The thus coated strip was heated slowly from room temperature to 440° F. at a rate of 16° to 18° F. per minute, and held at that temperature for ten minutes. The temperature was then raised at a rate of 16° to 18° per minute to 900° F. and held at that temperature for ten minutes after which the temperature was dropped at the rate of 18° to 25° F. per minute to room temperature.

The resulting coating was smooth without any blistering or roughness and the copper and tin were completely alloyed to provide a bronze alloy approximately 55% tin and 45% copper. This example shows the advantage of multiple alternate coatings providing a bimetal alloy of increased thickness without increasing the heating time and temperatures required during the heat treatment.

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. Hard steel unannealed is plated with copper, nickel, copper, nickel, copper, in continuous succession. The strip is then coiled without interrupting its movement and placed as a coiled length in an annealing furnace having a reducing atmosphere and held at a temperature of approximately 1100-1800° F. for a sufficient length of time to anneal the base stock. The number and thickness of alternate layers of nickel and copper should be such that these two metals are completely diffused to form a homogeneous alloy by the time the annealing of the base stock is completed.

Where one of the metals being plated to form the alloy has a melting point below the annealing temperature of the base metal, I preferably sandwich this metal in between layers of the higher melting point metal, and the annealing of the base stock is then carried out concurrently with the formation of the alloy coating, as explained above.

A hard unannealed steel strip is plated with nickel, tin, nickel, tin, nickel, tin, nickel, wound into a coil, and placed with other coils in an annealing furnace having a reducing atmosphere and a temperature approximately 1100-1800° F., for a sufficient length of time to anneal the base metal strip or stock. The number and thicknesses of the plated layers should be such that the diffusion between the layers is completed by the time the annealing is completed.

If the reverse order of plating is employed (not preferred), that is, a sequence of tin, nickel, tin, there is danger of fusing adjacent layers of the strip together if its temperature is raised to a point above the melting point of the lowest melting point metal, namely, tin, but I have discovered that the heat treatment in such case can be carried out at a temperature below the melting point of the tin for a sufficient length of time to alloy the outer layer of tin with its adjacent layer of nickel and then after this has been accomplished, the temperature will be increased to quickly anneal the base stock or strip.

In such a case, I preferably provide a relatively thin layer of tin immediately adjacent the base metal strip whose thickness is less than the other layers of tin so as to limit the formation of a steel-tin alloy.

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.

For deep drawing, stamping and forming stock I prefer to use steel strip with a carbon content of 0.15% or less. In providing a coating of copper-tin alloy, I obtain best results by keeping the total coating weight between $\frac{1}{4}$ and 10 pounds per base box and also if I keep the copper content between 80% and 35% and the tin content between 20% and 65% of the total coating weight.

Likewise, when producing a coating of nickel-tin alloy, I obtain best results by keeping the total coating weight between $\frac{1}{4}$ and 10 pounds per base box, with the nickel content between 80% and 35% and the tin content between 20% and 65% of the total coating weight.

Similarly, when producing a coating of lead-tin alloy on steel strip of 0.15% carbon or less for deep drawing stock, I obtain best results by keeping the total coating weight between $\frac{1}{4}$ and 10 pounds per base box, with the lead content be-

tween 32% and 40% and the tin content between 8% and 60% of the total coating weight.

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 in the examples, 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. In a method of forming a smooth homogeneous alloy coating on ferrous metal base stock, the steps of electroplating at least three layers of at least two alloying metals on the base stock, one of which metals has a melting point above the annealing temperature of the base stock and the other of which metals has a melting temperature below the annealing temperature of the base stock, and in such proportions that the higher melting point metal is in excess and is interposed between the lower melting point metal and the base stock, then heat treating the thus plated metals to start diffusion of the same by subjecting the plated strip under non-oxidizing conditions to an initial temperature below the melting point of the lowest melting point metal and then gradually increasing the heat treating temperature to a higher point above the melting point of the lowest melting point coating metal to the point of complete diffusion between the metal layers and to a temperature sufficient to anneal the base stock but maintaining the temperature below the melting point of the alloy formed.

2. In a method of forming a smooth homogeneous alloy coating on ferrous metal base stock, the steps of electroplating at least three layers of at least two alloying metals on the base stock, one of which metals has a melting point above the annealing temperature of the base stock and the other of which metals has a melting temperature below the annealing temperature of the base stock, then heat treating the thus plated metals to start diffusion of the same by subjecting the plated stock under non-oxidizing conditions to an initial temperature below the melting point of the lowest melting point metal and then gradually increasing the heat treating temperature to a higher point above the melting point of the lowest melting point coating metal to the point of complete diffusion between the metal layers and to a temperature sufficient to anneal the base stock but maintaining the temperature below the melting point of the alloy formed.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,364,051	Groff	Dec. 28, 1920
1,547,394	Hoyt	July 28, 1925
1,578,254	Bennett	Mar. 30, 1926
1,820,204	Wilkins	Aug. 25, 1931
2,196,002	Whitney et al.	Apr. 2, 1940
2,304,709	Rubin	Dec. 8, 1942
2,315,740	Schoonmaker et al.	Apr. 6, 1943
2,428,033	Nachtman	Sept. 30, 1947
2,428,318	Nachtman	Sept. 30, 1947