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2,196,002

METHOD OF TREATING ELECTRODEPOSITED METAL

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2 Sheets-Sheet 2

Fig. 9.

Fig. 10.

Fig. 11.

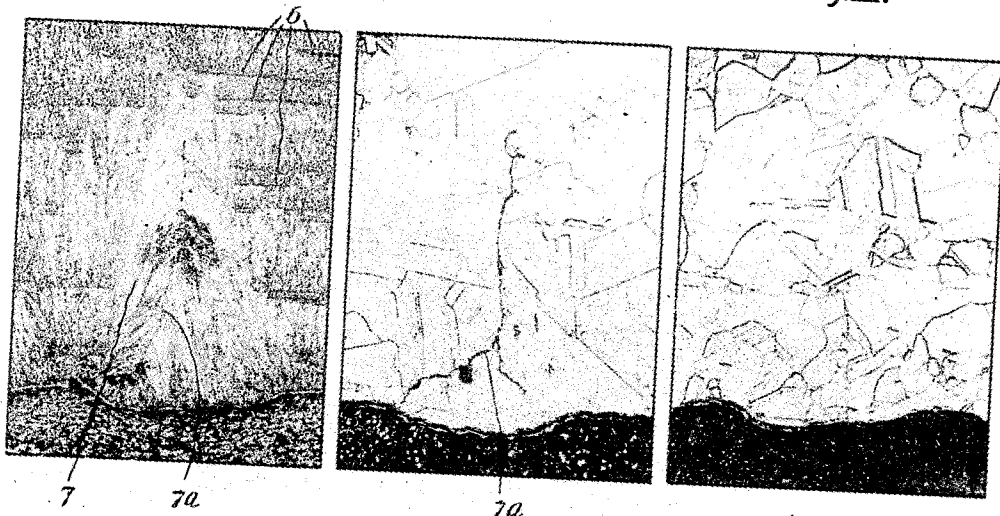


Fig. 7.

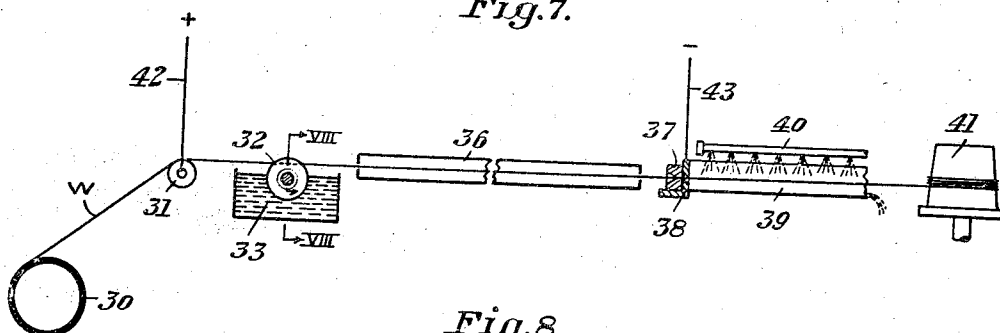
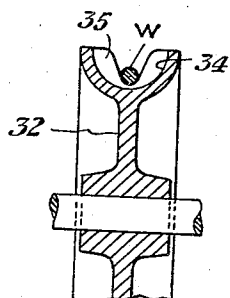


Fig. 8.



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METHOD OF TREATING ELECTRO-
DEPOSITED METAL

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7 Claims. (Cl. 29—188)

This invention relates to the treatment of electro-deposited metal and is herein particularly described as applied to the manufacture of a bimetallic wire or rod. Specifically, it is illustrated and described as applied to the manufacture of a bimetallic rod or wire having a steel core and a copper coating, although the invention has numerous other applications.

This is a continuation-in-part of our copending application Ser. No. 649,529, filed December 30, 1932, for Manufacture of electrodeposited metal.

A bimetallic wire having a steel core and a copper sheath combines high strength with protection against corrosion and is used in many places where this combination of properties is desirable. Such wire also has the property of high electrical conductivity compared with ferrous wires. It has been proposed to make wire of this character by a wide variety of processes the most conspicuously successful of which has been the molten process wherein molten copper has been poured around a specially prepared steel billet, the bimetallic ingot thus formed being rolled and drawn into wire. An outstanding advantage of such process is that a permanent union between the copper and the steel is formed, but it also has certain disadvantages, among them being the fact that it is impossible by the use of molten copper to produce a sheath of as great purity and high electrical conductivity as is desired. It is also difficult, particularly where the percentage of copper in the wire is high, to obtain concentricity of the core and the sheath.

These difficulties, which are inherent in the older processes, argue for the manufacture of bimetallic wire by a process of electrodepositing the copper over a steel core, but while many attempts have been made most of them have resulted in failure because of a number of difficulties which arise out of the step of electrodepositing a relatively thick coating of the copper or other sheath metal.

It has been proposed to draw the steel wire to its final size and deposit the copper thereover. This, however, is not satisfactory for a number of reasons. It is desirable to subject the bimetallic body to cold work in order to develop the proper physical properties. The copper in the "as deposited" condition is porous. It is difficult if not impossible to obtain merely by electrodeposition a continuously extending and permanent bond between the copper and the base metal. If the copper deposit is of any substantial thickness (and such thicknesses are essen-

tial in many of the products), the grain structure of the copper is unsatisfactory. The copper which is first deposited is fine-grained, but as the thickness of the coating increases, the grains become much larger and are columnar in character. Because of this columnar structure, the copper tends to crack if the wire is flexed in any material amount, thus reducing or destroying the corrosion-resistant and other physical properties.

For the foregoing reasons, it is commercially desirable to form a bimetallic article of considerably larger cross sectional dimensions than the final product and to work this article down to the final size. Unfortunately, this procedure merely emphasizes a number of the defects above enumerated. The absolute thickness of the copper deposited must be considerably greater on such a starting body than is the thickness of the copper in the final product in order to get the desired thickness of copper therein, and the defects arising from columnar structure are emphasized.

Other difficulties also arise. Process heat treatments are frequently necessary. It may be necessary, for example, to anneal the material while in process in order to permit of further wire drawing, or it may be desirable to anneal, normalize, or otherwise heat treat the final product in order to develop the desired physical properties. During such heat treatment, blisters or other porous zones are likely to develop, particularly with a thick coating. These blisters are probably due to the presence of foreign matter which expands or forms a gas upon heating, or they may be due to interruption in the crystal growth and consequent lines of weakness in the metal. However, we do not limit ourselves to either of these theories. The fact remains that blisters and porous zones are manifested upon heating of a thick commercially produced electrodeposited body of metal, especially where the same has been put on in successive layers, as, for example, by passing it through a series of coating baths. Once the blisters or porous zones have developed subsequent drawing of the wire in the ordinary fashion does not heal them and a defective product results.

Considerable difficulty also arises due to lack of proper adherence of the copper to the base metal. Even when the greatest care is employed, difficulties arise on this score. Attempts to draw wire made in this fashion, particularly where blisters or porous zones have developed, result in flaking or peeling of the copper and consequent damage or spoilage of the wire.

Attempts have been made to overcome these defects by heat treatment, but these have not proved satisfactory. A thin coating of copper may by heat treatment be made to adhere fairly well to the base metal, but the difficulties of porosity are still present.

The difficulty of blistering upon heating has been recognized and it has been attempted to overcome the same by careful control of the heating conditions. However, such proposals have not worked out satisfactorily in practice. If it is attempted to limit the heating of the metal to such low temperature that the blisters do not develop, it is frequently impossible to obtain the desired results, and such operation requires so much time as to render it commercially impractical. Furthermore, such prolonged heating is conducive to the growth of very large grains, which grain structure is frequently undesirable.

We have found that these difficulties may be overcome and a superior product obtained by going contrary to established practice and deliberately heating the metal, and in some cases in an amount sufficient to develop porosity, and then working it under such conditions as to compact and homogenize the porous metal. We prefer to carry out these steps on the electrodeposited metal preliminary to any further reduction thereof and have discovered that by so doing the metal is put in such condition that it can be readily worked and can be subsequently heat treated without any danger of blisters or other porous zones developing. We have found that there are certain limitations as to the temperature to which the electrodeposited metal is heated and the extent of the hot drawing to which it is subjected. Specifically, the deposited metal must be heated to a temperature of about 1000° F. or higher and subjected to a reduction in sectional area by hot drawing of at least 5%.

We prefer to carry out the steps of our process in a continuous manner, preferably passing the metal continuously through a heating zone and hot working it as it is delivered from such zone.

We have found that it is important to maintain the metal during the heating and hot working steps in an atmosphere which inhibits the formation of undesirable compounds of the electrodeposited metal. It is definitely undesirable, for example, to allow the formation of oxides of the metal. If the metal is blistered or cracked, the formation of oxides opposes the healing of the surfaces during the hot work which follows the development of such porous zone. We have successfully employed an atmosphere of hydrogen.

The use of our process gives as a new and improved product a metal body characterized by the purity of electrolytic metal and a grain structure of the character of annealed wrought metal. Stated in another way, the metal has the purity of electrolytic metal and it has been homogenized by heat and pressure. Such metal is particularly desirable as a sheath for a bimetallic article.

In the accompanying drawings, illustrating our invention as applied to the manufacture of bimetallic wire with a steel core and a copper sheath:

Figure 1 is a side elevation of a bimetallic wire broken away to show the successive layers;

Figure 2 is a side elevation of a wire which has been heated to such temperature as to develop blisters;

Figure 3 is a transverse section of the blistered wire shown in Figure 2;

Figure 4 is a diagrammatic view illustrating one form of apparatus by which our process may be carried out;

Figures 5 and 6 are diagrammatic views illustrating further steps in the manufacture;

Figure 7 is a view similar to Figure 4 showing the preferred practice of the invention and, diagrammatically, the apparatus used therein;

Figure 8 is a partial sectional view taken along the plane of line VIII—VIII of Figure 7;

Figure 9 is a photomicrograph showing the structure of the copper as deposited;

Figure 10 is a photomicrograph showing the electrodeposited copper after heating only; and

Figure 11 is a photomicrograph showing the electrodeposited copper after heating and hot-working.

The bimetallic wire shown in Figure 1 comprises a core 2 of drawn steel. We have successfully employed simple steel wire .375" in diameter. The carbon content is immaterial and will be determined by the physical properties desired. It will be obvious, of course, that alloy steel wires may also be employed if need be. The core 2 is covered with a continuous sheath 3 of acid copper. The copper may be deposited directly on the steel, but we have found it advantageous to use an intermediate layer 4 of nickel. It will be understood, of course, that instead of nickel, alkaline copper, electrolytic tin, zinc or iron, or other metal may be used, or if desired, the wire, prior to the deposition of copper, may be subjected to a chemical dip of arsenic trioxide in hydrochloric acid and water.

The percentage of copper in the final product will vary according to the requirements of the user. Bimetallic wire is usually rated according to the percentage relation which its conductivity bears to a solid copper wire of the same diameter. Thus a "30% conductivity wire" is one whose ratio of steel to copper is such that the wire will have a conductivity 30% of the conductivity of a solid copper wire of the same diameter. In order to make 30% conductivity wire from a bimetallic starting body having a steel core .375" in diameter, it is necessary to electrodeposit sufficient copper to make the diameter of the starting body .432". 40% conductivity wire may be made from a starting body having a steel core .375" in diameter and a diameter, with the copper sheath, of .467". The above examples require copper deposits of .028" and .046", respectively. These deposits are very much heavier than those employed in commercial electroplating and introduce the difficulties above referred to. The ordinary commercial electrodeposit for purposes of surface protection is measurable only in ten-thousandths of an inch, whereas we are concerned with electrodeposits very much thicker. For example, even a wire having a copper sheath whose cross section is 5% of the total cross section of the wire will have a thickness of .005" on a core .375". These heavy deposits, when heated to the temperatures required for heat treating the metal, are very likely to develop blisters. We have shown blisters at 5 in Figure 2.

Figure 3, which shows the wire in cross section, illustrates a blister 5a within the boundaries of the copper and a blister 5b at the interface between the copper and the steel. The blisters when developed are likely to lead to very serious difficulties either in subsequent manufacturing

operations or in use. As stated, great difficulty is encountered in processing blistered wire. There is danger also that a discontinuity in the metal, originally manifested as a blister, may, by reason of after operations enlarge and extend down to the base metal so that the sheath is discontinuous. This provides a starting point for rapid corrosion in the product.

While it may be possible under carefully controlled laboratory conditions to obtain a deposit wherein a minimum of blisters and porous zones will develop upon heat treatment, we are of the belief that it is difficult if not impossible to avoid them entirely and have found that they are of frequent occurrence in commercially deposited copper. Figure 9 is a photomicrograph of a commercial deposit magnified to 90 diameters, showing an etched section of a test specimen with the steel core below a layer of cyanide copper and a main deposit of acid copper above. It will be noted that, as viewed under the microscope, the acid copper shows distinct lines of interruption, as indicated at 6 in the drawings. This particular sample was formed by a succession of deposits, the article passing through a series of electrolytic baths. The columnar structure, indicated at 7, is very marked in the drawings and is characteristic of heavy deposits. The grain boundary lines extend in a direction generally perpendicular to the axis of the wire and form lines of weakness which may cause cracking of the copper on flexing or bending of the wire, or an attempted reduction thereof as by drawing. A radial crack appears at 7a, and is found to extend a considerable distance along the length of the test specimen.

The deposited copper may be recrystallized by heat treatment. For example, Figure 10 shows an etched section of a specimen cut from the same piece and adjacent the same point in the piece as that illustrated in Figure 4, after being heated in a reducing atmosphere to 1400° F. for 30 minutes and allowed to cool in air. It will be noted that the copper has recrystallized into very large grains. Such grains may be objectionable in certain cases and the heating time is commercially excessive. The radial crack has been enlarged.

It is desired to obtain a structure which is free of excessively large grains and radial cracks and yet reduces the heating time to a minimum. We effect this result and homogenize the copper by combined heating and working.

Figure 4 illustrates diagrammatically one form of apparatus which we have successfully employed for this purpose. In Figure 4, a bimetallic wire W having a wrought steel core and an electrodeposited sheath and of the dimensions given above is fed from a coil 8 through a water seal 9 to a hollow heating tube 10. The tube is contained largely within a furnace 11 heated in any desired manner, as by burners 12. The tube 10 is kept filled with hydrogen supplied from a source H through a reducing valve 13 and a tube 14 communicating with the pipe 10. In the passage of the wire W through the pipe 10, it is raised to the desired temperature and is then in condition to be subjected to hot work. This is accomplished in the example shown by a wire die 15. The delivery end of the pipe 10 projects beyond the end of the furnace 11 and is tapered as indicated at 16. The delivery end of the pipe 10 is very close to the die 15 and within the die holder 17. The small space between the die 15 and the open end of the pipe 16 is packed by

the drawing lubricant, as indicated at 18. The lubricant employed is graphite mixed with grease, which is a reducing compound, and it is placed around the end of the tube so as to seal it off from the atmosphere as well as to provide lubrication for drawing. The wire is drawn through the apparatus by a drawing block 19 of usual construction.

The highly desirable final structure obtainable by our process is shown in Figure 11, which is a photomicrograph of an etched section of a specimen cut from the same piece and from the same location therein as that illustrated in Figures 9 and 10. After heating, as before described, this specimen was given a 9% reduction by hot drawing through die 15 and cooled under a water spray. It will be noted that the copper has been homogenized by heat and pressure so as to give a grain structure of the character of annealed wrought metal. At the same time, it has the purity of electrolytic metal and is free of porosity. The heating to which the wire was subjected was sufficient to cause blisters and porous zones, but tests of the metal show it to be free of these defects. The radial crack 7a which originally extended through the several specimens, has been fully closed.

It will be further noted that the structure illustrated in Figure 11 is not of the columnar form which characterizes the deposited copper shown in Figure 9. The grains are smaller than in Figure 10, more uniform in size, and definitely equi-axed. Another important advantage is that a very firm union between the steel and the copper is effected. This union is so perfect that it successfully resists the severe tests hereinafter described.

The product shown in Figure 11 may be subsequently worked either hot or cold and heat treated without danger of developing blisters or porous zones. In Figures 5 and 6, we have diagrammatically illustrated such further treatment. The wire W₁ is shown in Figure 5 as being cold worked by drawing through a die 20 and thereafter passed through a heat treating furnace 21, as shown in Figure 6. This subsequent cold working and heating further improves the product.

Figures 7 and 8 illustrate a modified form of apparatus which we now prefer for practicing the method of our invention. As therein shown, a wire W similar to that indicated in Figure 4 is unwound from a reel 30 onto a guide sheave 31. From the sheave 31, the wire passes over a coating sheave 32, partially immersed in a bath of die lubricant 33, composed of engine oil and graphite. As shown in Figure 8, the sheave 32 has a large peripheral groove 34 divided into segments by notched, radial vanes 35. The latter insure the picking up of sufficient die lubricant to thoroughly coat the wire.

From the coating bath 33, the wire passes through a muffle 36, a die 37, mounted on a support 38, and a cooling tank 39 provided with water sprays 40, after which it is wound up on the usual drawing block 41. The water sprays quickly cool the material to room temperature and make it possible to operate at drawing speeds higher than would otherwise be possible. Electrical connections 42 and 43 extend from a suitable source of heating current to the sheave 31 and support 38, respectively. By means of these connections, electric current is passed through that portion of the wire between the sheave 31 and support 38 to heat it to the de-

sired temperature, say 1400° F. By making connection through the die, perfect contact with the material is obtained. This heating not only affects the change in grain structure already referred to, but also causes the die lubricant to be baked onto the wire. This heating also creates a reducing atmosphere within the muffle.

Test specimens of material produced according to the procedure just described may be conveniently made up as follows:

To provide specimens having different conductivity percentages (viz., 40%, 30%, and 20%), short lengths of steel rods having diameters of .500", .535", and .585" are subjected to electrodeposition sufficient to build them up to a common diameter of .650". For greater accuracy, these specimens are then turned down to a slightly smaller diameter such as .632", and then etched in nitric acid to a final diameter of .630". The test rods are then subjected to heating, for example, to 1000° F., for a period of 30 minutes in a reducing atmosphere. After heating, the rods are hot drawn through dies which would normally produce various percentages of reduction in sectional area, e. g., 5%, 15%, 25%, and 35%. The pull required to draw the material through these dies, however, results in drafts of approximately 10%, 19%, 28%, and 38%.

After heating and hot drawing, a short length is cut out of the mid portion of the rods and the steel core drilled through from end to end. The drilled sections are then placed in a hot 10% sulphuric acid bath to dissolve out the remainder of the steel core, leaving the copper in the form of a tube.

While we prefer to heat the material to 1000° F. or higher, to insure removal of all defects, it is possible to obtain an improvement of the physical properties of the deposited metal by heating to a somewhat lower temperature. Tensile tests on tubular specimens indicate that the maximum increase in ductility may be obtained by heating to the temperatures indicated below, if the electrodeposition has been carried out under optimum or ideal conditions:

	Percent conductivity of specimen	Temperature, ° F.	Percent hot reduction
50	20.....	600 to 800 or the practice 1000 to 1200.....	18 10 to 13
	30.....	800 to 1000 or the practice 1200.....	10 to 38 10 to 28
	40.....	800 to 1000.....	10 to 18

If the electrodeposition has been carried out under somewhat less favorable conditions, such as prevail in ordinary commercial practice, it has been found that a higher temperature say from 1400° F. to 1600° F. will produce the maximum improvement in physical properties of 30% conductivity material with a hot reduction of 10%.

Tubular specimens 1" long may readily be tested for ductility and local defects, such as the radial crack 1a shown in Figures 9 and 10, by driving a conical plug into one end, forcing the ends to "bell out." The specimens which have been subjected to heating only, without hot drawing, and those heated only to 1000° F. or below, regardless of the amount of hot reduction (up to a maximum of 29%) show definite local failure as by cracking or splitting axially. Specimens which have been heated to temperatures above 1000° F. (up to a maximum of 1800° F.) and hot drawn to reduce them by from 9% to

29%, all show uniform "belling out" with corresponding thinning of the edges, but without any localized failures such as cracks or longitudinal splitting. This confirms the conclusions drawn from Figures 9, 10, and 11 as to the healing of defects such as radial cracks in the copper sheath by the combined heating and hot drawing.

Our investigations show that the temperature to which the copper-steel body above described should be heated in carrying out our process is between 600° F. and 1900° F. As the maximum temperature is approached, care must be exercised to make sure that the copper does not flow and become eccentric to the steel. If it is attempted to operate below the minimum temperature above given, it will be found difficult or impossible to carry out the process successfully. It is preferred to use a temperature at least as high as that of any subsequent treatment to which the copper-steel body may be subjected and to follow this with the hot working at any temperature within the limits described above.

The reduction effected by the die should be sufficient to insure that its influence is felt throughout the copper. This is best insured by providing a sufficient reduction by the die to reduce the cross sectional area of the base as well as to work the copper. Generally speaking, the thicker the copper, the more mechanical work should be done in order to insure satisfactory results.

We have herein described our invention with particular reference to a bimetallic wire having a steel core and a copper sheath. However, the invention is of general applicability and may be used in the manufacture of bimetallic bodies of other forms, such as rods, sheets, strips, and shapes. It may also be used for the manufacture of bimetallic or multimetallic bodies other than copper on steel, as for example, nickel on copper, nickel on iron, chromium on copper, copper on nickel, etc. The invention is also useful in the manufacture of bodies of a single metal, as for example, copper may be deposited on a copper core, or the invention in certain aspects may be used for rendering workable commercial cathode copper which heretofore has been considered mechanically unworkable. It will be understood, therefore, that while we have illustrated and described a present preferred embodiment of the invention, in addition to an alternate practice, it is not so limited, but may be otherwise embodied or practiced within the scope of the following claims.

We claim:

1. In the method of making a bimetallic body, the steps consisting in electrodepositing a thick layer of copper over a steel base, heating the body and hot drawing it under non-oxidizing conditions which inhibit the formation of undesirable compounds of the electrodeposited metal to reduce the bimetallic body by a single pass through a die to a thickness approximating the original thickness of the base, thereby to compact and homogenize the copper.

2. In the method of making a bimetallic body, the steps consisting in electrodepositing a thick layer of copper over a steel base and hot drawing the bimetallic body under non-oxidizing conditions which inhibit the formation of undesirable compounds of the electrodeposited metal to reduce it by a single pass through a die to a thickness substantially equivalent to that of a bimetallic body formed from a base of the same original thickness as the base of the body in question, and

having a coating of copper of such thickness that a firm bond between the steel and the copper can be secured by heating alone.

3. In the method of making electrodeposited copper, the steps consisting in electrodepositing a layer of copper, heating the metal, drawing the metal while hot through a die, and lubricating the metal during drawing by a reducing substance.
4. In the method of making a bimetallic wire, the steps consisting in electrodepositing copper on an elongated steel core such as a rod or wire, heating the bimetallic body and drawing the bimetallic body while hot through a die, and lubricating the body during drawing by a reducing substance.
5. In the method of making a bimetallic wire, the steps consisting in electrodepositing a sufficiently thick layer of copper on an elongate steel core such as a large wire or rod as to produce a conductor of about 30% conductivity, heating the bimetallic body and reducing it while hot by from 5% to about 40% by a single pass under non-oxidizing conditions through a die.
6. In a method of making a composite metallic article including a core and a sheath, the steps

including electrolytically depositing the sheath on the core to a thickness such that the sectional area of the sheath is a substantial fraction (e. g. about one-tenth or greater) of the sectional area of the core and altering the grain structure of the sheath as deposited to render the article capable of being drastically cold worked, by heating the article to a temperature suitable for hot working and reducing the sectional area of the article at least 5% by drawing while at substantially such temperature.

7. In a method of making bimetallic wire comprising a ferrous core and a copper sheath, the steps including electrolytically depositing copper on a ferrous core to a thickness such that the sectional area of the copper is a substantial fraction of that of the core, and altering the grain structure of the copper as deposited to render the wire capable of being drastically cold drawn by heating the wire to a temperature suitable for hot working and reducing its sectional area at least 5% by drawing while substantially at said temperature.

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