

April 12, 1938.

F. L. ANTISELL
ELECTROLYTIC COPPER
Filed Dec. 4, 1935

2,114,161

3 Sheets-Sheet 1

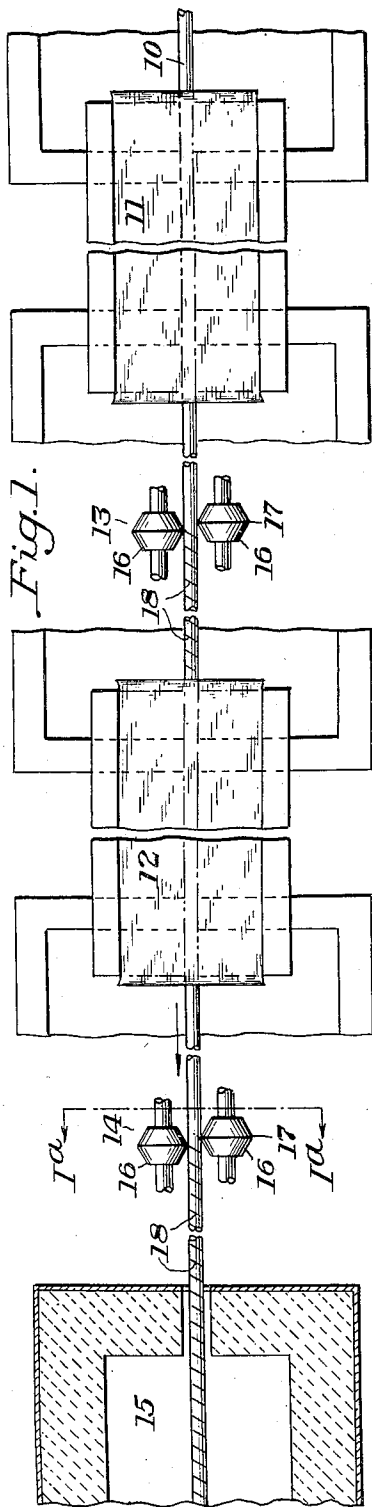


Fig. 1.

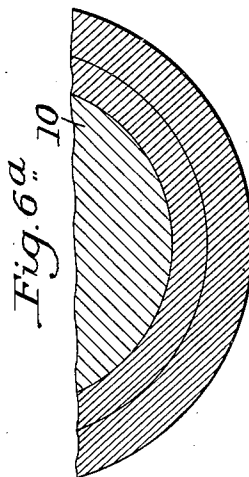
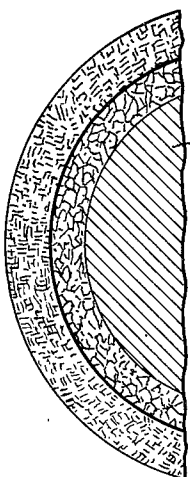


Fig. 6.

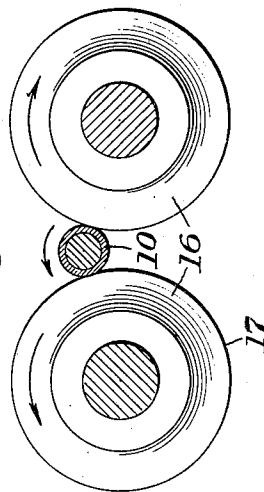


Fig. 1a.

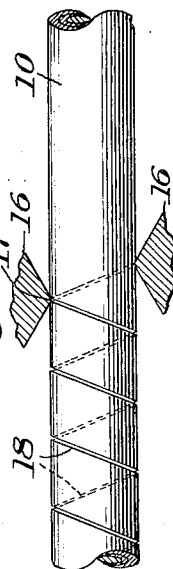


Fig. 1b.

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Fig. 2.

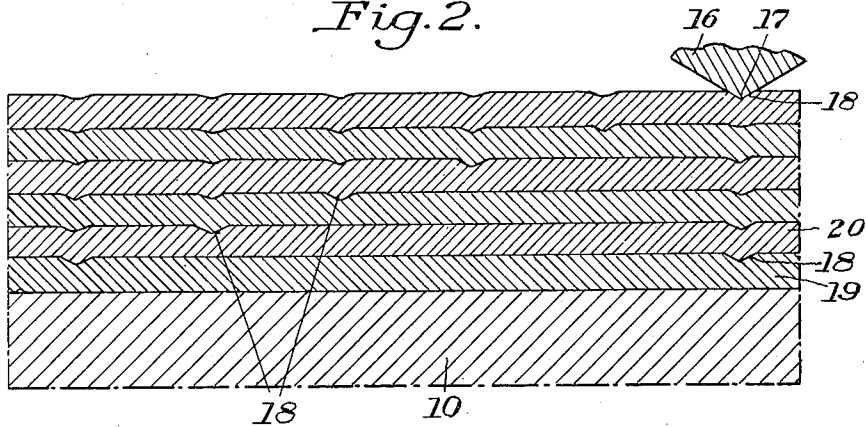


Fig. 7.

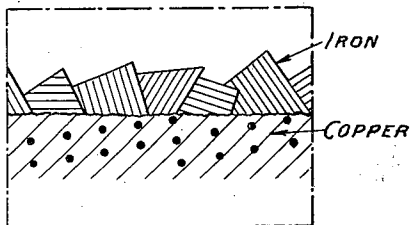


Fig. 8.

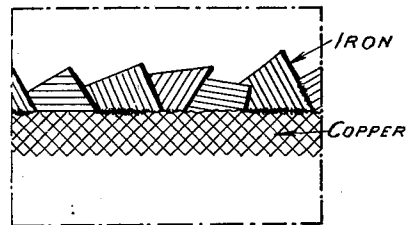
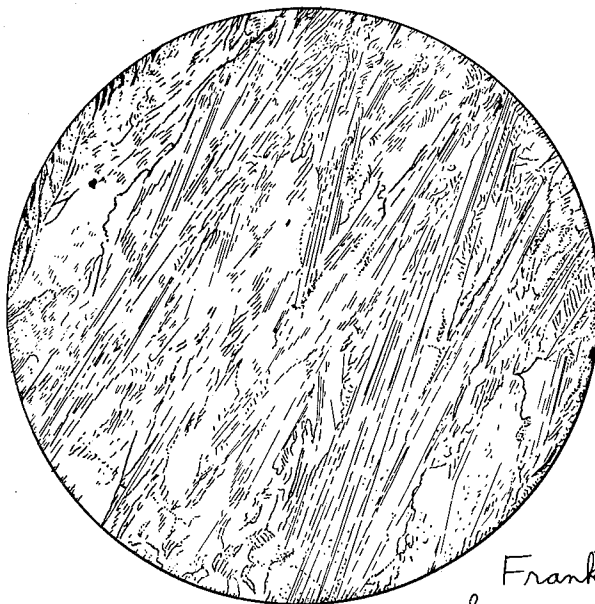


Fig. 3.



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Fig. 4.

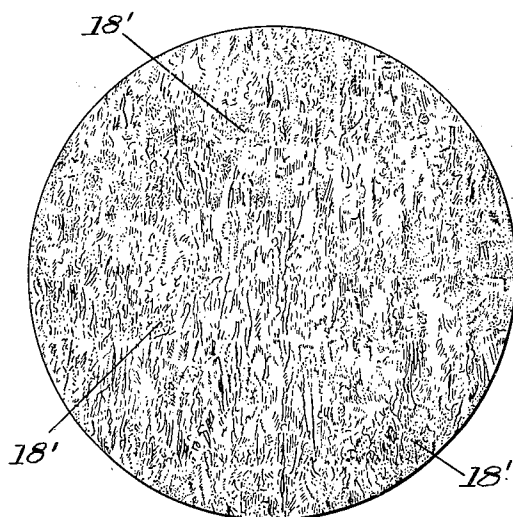
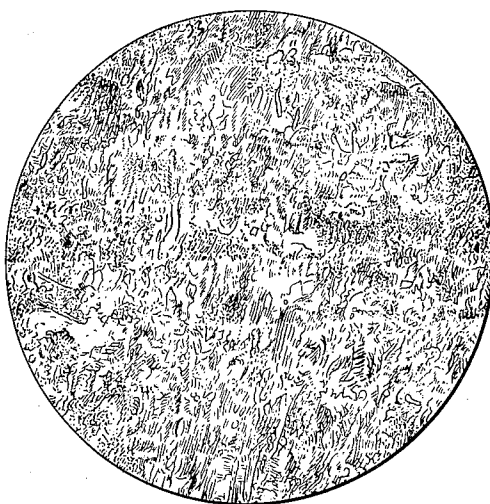


Fig. 5.



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UNITED STATES PATENT OFFICE

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ELECTROLYTIC COPPER

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Application December 4, 1935, Serial No. 52,799

2 Claims. (Cl. 204—10)

My invention relates to improved copper products electrolytically obtained, and in particular to products obtained by depositing copper electrolytically upon a base of copper or another metal such as steel, and to the formation of a firm bond between the deposited copper and the base metal, as well as between successive deposited layers.

It is well known that copper of an exceedingly high degree of purity, for example, 99.99 per cent, can be obtained by electrodeposition from commercial anodes which, themselves approach a purity of 99.95 per cent. The characteristics of the usual electrolytic copper, however, are not those which are most desirable in the commercial field. Electrolytic copper is ordinarily characterized by a fairly coarse grain structure, the size of the grains increasing with the building up of the deposited layer. The initially deposited layers may be of very fine grain structure but subsequently deposited layers show a marked increase in the grain size. The typical grain structure of electrolytic copper is shown in photomicrograph b of a plate opposite page 152 of "The Story of Copper" by Watson Davis, published in 1924 by the Century Company, New York, N. Y.

It has not been possible heretofore to improve the grain structure or physical characteristics of electrolytic copper by heat treatment. It has been found, for example, that the coarse grain structure characteristic of electrolytic copper has remained even after heating in hydrogen; and where electrolytic deposits as thick as those herein contemplated were attempted, the grain structure generally obtained was too coarse to be refined even by alternate hot and cold rolling. The bond heretofore obtained between electrolytically deposited copper and the base metal, furthermore, has not been entirely satisfactory.

I have obtained by my invention electrolytic copper which is characterized by an improved grain structure; and which is transformed by relatively low temperature heat treatment to a grain structure entirely different from that of the original electrolytic deposit, this transformed grain structure having numerous desirable physical characteristics, principally, high conductivity, with malleability and ductility. My improved product can be obtained by depositing successive layers of copper on the base metal, and subjecting this electrolytic copper to cold working operations under rolling pressure in spaced tracks as the electrolytic deposit proceeds layer by layer, to produce an amorphous constituent in these spaced tracks; and by subsequently heat treating

the built-up deposit of electrolytic copper at comparatively low temperatures well below the fusion point. The effect of the mechanical working during the growth of the deposit tends to refine the grain structure of the copper deposit, but the most unexpected effect of such cold working does not become apparent until after the heat treatment. Apparently this treatment causes an intrusion of the amorphous material produced by the mechanical working into the copper deposit and the base metal, forming a tight bond or weld with the latter and equiaxed fine grain structure of the metal in the former. Moreover, a remarkable decrease in the size of the grains of the deposited copper occurs during this subsequent heat treatment.

This application is a continuation in part of application Ser. No. 650,913, filed January 9, 1933, issued on January 7, 1936, as Patent No. 2,026,605.

According to one specific embodiment of my invention, I deposit copper electrolytically upon a base having the form of a rod or wire which may be steel or copper. I prefer to rotate the base and move it simultaneously through an electrolytic bath. Upon emergence from the bath, or even while still in the bath, I subject the rotating base with the coating of copper thereon, to the action of rolls disposed on axes substantially parallel to the base, provided with a slightly blunted or rounded edge which bears against the coated base. These edged rolls produce a spiral track on the coated base, the copper in the neighborhood of which is subjected to mechanical working under high pressures. This sequence of electro deposition and mechanical working is repeated until the desired thickness of copper has been deposited on the base. The coated base is then ready for heat treatment.

The heat treatment may be a separate operation, or may be preliminary to hot drawing the article to decrease its cross section. In either case the heating is a function both of the temperature finally reached and of the time taken to raise the temperature from about 450° F. (the temperature at which the improvement in grain structure begins to make itself apparent) to the maximum treating temperature. The product of the two is known as the time temperature value. Accordingly, if the maximum temperature is at or slightly above 450° F., the heat treatment should be long continued, and must be at least twenty-four hours long.

If the heat treatment is undertaken merely to improve the grain structure of the copper deposit, I prefer not to raise the temperature above 800° F.

In this case, the temperature should be quickly raised to 450° F. and the temperature then gradually raised to 800° F. during about ½ hour. While I have given 800° as the preferred maximum temperature, it will be understood that the conditions under which the heat treatment is carried out may be varied considerably, bearing in mind that for best results the heating should be continued at least long enough to attain the time temperature value above specified.

If the product has a steel core, and if the heat treatment is preliminary to hot drawing, I prefer that the bimetallic product reach a maximum temperature of 1200° F. just before passing through the die. But a short period of heating is required in such a case, and the desired results will be obtained by raising the temperature of the bimetallic product from room temperature to 1200° F. in about five minutes. However, if the drawing operation permits, the rise in temperature may take somewhat longer.

After heating, the coated base may be rolled at various temperatures as high as 1000° F., depending on the final temper desired, and/or it may also be drawn through dies.

The combined effect of the mechanical working at spaced zones on the deposit and the subsequent heat treatment is apparent in the product as a decrease in the size of grain structure of the copper. This is a most unexpected effect because in general, heat treatment of copper increases the size of the grains. The theory as to how this occurs, which I will now give, is the best explanation known to me for the phenomenon; but it is merely a theory; and in any event the results obtained do not depend upon the accuracy of my theory. In the grain structure of copper as pure as the electro-deposited metal here under discussion, the grains seemingly are separated by boundary material which must be almost entirely pure, i. e., metallic copper. Such copper is apparently in the form either of such minute crystals as to be merely a few atoms in size, or else in amorphous form. Ordinarily, an absolutely pure element is in but a single phase. Here, however, apparently the metallic copper exists both as grains and as grain boundary material. Under such conditions that a change in phase is possible, namely, for copper a temperature of about 450° F. or over, there is a tendency for the two phases to come into equilibrium. It is possible that to some extent the grain boundary material which is in amorphous condition or the like may coalesce to form grains. On the other hand, the grains of copper appear to be broken down into smaller sized grains. In any event, photomicrographs of copper, which has been subjected at spaced zones to mechanical work and has then been heat treated in accordance with my invention, disclose a smaller size grain structure in the heat treated copper than was found in the copper as deposited. The presence of the finely divided or amorphous copper resulting from the cold working has, therefore, an important effect in making it possible for the heat treatment to decrease the size of grain structure in the copper deposit. I interpret the function of this amorphous copper in the way of an intrusion effect. In other words, there is an intrusion of this amorphous copper into the grains, splitting the grains, and constituting the grain boundary material therebetween. My results show that without this amorphous copper there is not the tendency for the large size grains to break down into the smaller

grains such as characterize the grain structure of my improved product.

The increased adherence of the deposit to the base which results from the foregoing process is also caused, in my opinion, by an intrusive action of the amorphous grain boundary material of the copper into the intergranular spaces of the base metal. In the welding of wrought iron, mild steel, or other metals, an actual fusion of the metals must occur, accompanied by the formation of a bonding alloy, or the equivalent thereof. As heat treatment is carried out in accordance with my invention at temperatures well below the fusion temperature of either of the two metals being united, the bond between the two may most probably be explained on the basis of migration of grain boundary material only. If this be so, the identity and integrity of the grains, either of the base metal or the electro-deposited metal, are not changed. Such rearrangement of grain boundary material while the grains themselves are not disturbed is consonant with the relatively low temperatures at which the phenomenon takes place. It is found, as a matter of fact, that there is an interchange of material between the copper and the base at these low temperatures provided some at least of the deposited copper has been subjected to mechanical working. Accordingly, an excellent union of the two metals is obtained.

In accordance with my invention, therefore, it is possible to weld two pieces of the same metal or of different metals, by holding them in contact and subjecting them to a temperature much below the fusion point.

For a complete understanding of the invention and the theory I have evolved to account for the results produced thereby, reference is made to the accompanying drawings illustrating diagrammatically a preferred form of apparatus for producing my improved product, and the grain structure produced in the electrolytic copper by the invention, as observed in photomicrographs.

In the drawings:

Figure 1 is a diagrammatic illustration of the electrolytic coating baths, the working rolls and the continuous furnace by which the electrolytic copper is deposited on a base, wire or rod, subjected to mechanical rolling and finally heat treatment, in position thereon;

Figure 1a is a sectional view along the line IA-IA of Figure 1;

Figure 1b shows generally the appearance of the rod after the first deposit and mechanical working;

Figure 2 is a partial cross section to greatly enlarged scale taken axially through a copper-clad rod showing diagrammatically the physical effect of the cold working;

Figure 3 is a photomicrograph showing the grain structure of copper deposited in the laboratory on a rod revolving in a suitable electrolyte without any mechanical work being done thereon;

Figure 4 is a photomicrograph illustrating the effect of the cold working on the grain structure of the deposited layers;

Figure 5 is a similar photomicrograph showing the effect of heat treatment on the copper grain structure, both the photomicrograph of Figure 4 and the photomicrograph of Figure 5 being taken from the same sample;

Figures 6 and 6a are transverse sections showing the effect of the invention on a layer of electrolytic copper deposited on a cast copper base;

Figure 7 shows diagrammatically the crystalline state of the iron and the copper deposited thereon after the mechanical working; and

Figure 8 is similar to Figure 6 but shows the change in granular structure brought about by heating to temperatures below fusion.

Referring in detail to the drawings, I subject a base member 10, which may be a rod or wire of steel or copper, to treatment in electrolytic baths 11 and 12, each electrolytically deposited layer being subjected at spaced zones to mechanical working by sets of rolls 13 and 14. After emerging from the last set of rolls, the coated base passes into a continuous furnace 15 for heat treatment. Preferably I provide means for rotating the base during the progress of the electrodepositing and heat treating operations. The coated base may be wound upon a reel after treatment and the uncoated base unwound from another reel prior to introduction into the baths. Both the unwinding and winding-up reels may be rotated by suitably mounting them, and axial rotation of the rod is thereby effected.

The construction of the electrolytic baths 11 and 12 and the method of subjecting the base member to treatment therein are the subject of my Patents Nos. 2,075,331 and 2,075,332; and as the details thereof are not essential to the present invention, no description of them is given here. The sets of rolls 13 and 14 each comprise a pair of rolls 16 rotatably carried by suitable mountings, not shown. The rolls 16 are shaped so as to have a somewhat rounded or blunted edge 17 and the rolls of each set are mounted so as to be slightly offset as illustrated. The shape of the rolls 16 is similar to that resulting from placing a pair of truncated cones base to base. The rolls 16 of each set are preferably positioned in substantially the same horizontal plane (see Fig. 1a), and are adjusted therein so that the portions of the rolls of greatest diameter are separated by a distance slightly less than the diameter of the coated base. The weight of the coated base thus wedges it between the rolls and, because of the angular relation of the forces involved, the total pressure exerted on the coated member by the rolls is considerable.

Because of the shape of the rolls 16, the unit pressure to which the electrolytic copper is subjected is very high. It will be apparent that substantially the total pressure of the rolls on the coated member is transmitted through two spaced points, as shown in Figure 1a.

Since the rolls 16 of a single set are slightly offset in the direction of travel of the base, the result of the cold working in any set of rolls is to produce helical tracks 18 in the electrolytic layer deposited on the base, as shown in Figure 1b. Succeeding electrolytic treatments, however, cover the helical paths and all other portions of the initially deposited layer; and after the second layer is deposited, the mechanical work following thereupon again produces helical tracks.

In a particular instance, the dimension of the rolled mark on the wire was .009 inch wide, and the chord of contact was .011 inch, equalling an area of .000099 square inch, or say in round figures .0001 square inch, or a bearing area of one ten-thousandths of a square inch.

The total weight of wire on point contact is 2.2 pounds, and the resolution of force on this wire by reason of the wedge effect is 5 to 1, resulting in a component of pressure of $5\frac{1}{2}$ pounds, resulting finally in a pressure of 55,000

pounds per square inch on each of the two rollers, thereby compacting the copper completely.

Figure 2 illustrates a partial section of a length of the base member 10 having five electrolytic layers deposited thereon. The first layer, 19, has a well defined helical track 18 therein formed by the cold rolling after the first electrolytic deposit. The second layer 20 also has a helical track 18 but it is displaced axially of the base 10 relative to the track in the layer 19. It will be observed that the track 18 formed in the initial layer 19 is repeated to a decreasing extent in the succeeding layers. Repeated rolling and electrolytic deposition finally produce a coated base, the surface of which is lightly corrugated, showing a number of helical tracks one overlying the other.

Referring in particular to Figures 3, 4 and 5, I shall discuss the effect of the cold working on the grain structure of the deposited layers. As shown by Figure 3 and by the publication referred to above, electrolytic copper is ordinarily of comparatively coarse, columnar grain structure (although the layer next the base on which the deposition occurs is usually of finer grain structure than subsequently deposited layers). In Figure 4 is shown the grain structure of a portion of electrolytically deposited copper produced in accordance with my invention. The grain structure is modified from the columnar, comparatively coarse grain structure typical of the usual electrolytic copper. The mechanical working has compacted tracks (indicated diagrammatically at 18 in Figure 2) in the successive layers of copper and the high pressure of the blunt edges of the rolls has broken down the grain structure so as apparently to provide amorphous metal or particles of the order of a small multiple of the atomic diameter in size. These tiny particles are, of course, too minute to be seen in Figure 4, but the crushed grain structure is to be clearly seen at 18'. The portions of the copper other than the tracks resulting from the cold working exhibit the usual tendency to a columnar structure, but the grains are not so large in Figure 4 as in Figure 3 and there are indications of lamellae in the structure of Figure 4.

It is my theory that the amorphous metal or minute particles, while not individually visible in Figure 4, make their presence apparent when the deposited metal is heat treated, resulting in the grain structure shown in Figure 5. It is clearly apparent that the heat treatment, instead of causing grain growth as was to be expected, has effected a refinement of the grain structure and a decrease in the size of the grains. Seemingly, the heat treatment has caused the amorphous copper to split up grains of the copper as deposited copper, and the intrusion of this grain boundary material into the columnar structure of the deposited copper has resulted in a fine grained equi-axed structure, as illustrated in Figure 5.

As described, the helical tracks traced by successive sets of rolls, such as 13 and 14, are in general not superposed but somewhat displaced axially of the base member, and result in the formation of portions of compacted and crushed grain structure distributed throughout the mass of deposited copper, as indicated by the portions 18' of Figure 4. It will thus be apparent that each electrolytic layer is characterized by a helical band of compacted and crushed grain structure along the helical track formed by the rolls 16.

After a number of electrolytic depositions and 75

mechanical workings, which depends upon the thickness of the coating desired on the finished article, the latter is subjected to heat treatment in the continuous furnace 15. This heat treatment brings about a remarkable change in the grain structure of the deposited copper. Instead of separate portions in each layer having different grain characteristics, it is observed in Figure 5 that the grain structure of the entire deposited layer is quite fine and uniform. This result I attribute to the intrusive effect of the amorphous copper of the bands or tracks which have been subjected to cold working, which migrates as grain boundary material. The effect of this grain boundary material spreads through the deposited layers. Moreover, as above explained, there appears to be an intrusive action on the part of the amorphous or crushed copper effective for splitting the grains of the electrolytically deposited copper so as to produce the uniform, fine grain structure which is observed after heat treatment. This is best illustrated in Figure 5 in which it will be observed that the grain structure in the successive layers of deposited copper has been decreased in size due to breaking up of the deposited grains into finer grains. Between these smaller grains, as illustrated in Figure 5, the finely divided material resulting from the crushing of the grain structure (at 18' in Figure 4) by the mechanical working has made its way. This is the intrusive effect above referred to; and the finely divided copper is the grain boundary material which separates these grains. It is a remarkable characteristic of the structure of the copper shown in Figure 5 that the grain boundary material is composed substantially completely of metallic copper. In the electrolytic copper shown in Figure 3, there is substantially no grain boundary material. High grade cast copper (the prevailing purity of which is about 99.94%) is composed of grains separated by grain boundary material. This material is almost entirely composed of copper oxide and impurities. The finely divided metallic copper of which the grain boundary material of Figure 5 is essentially composed is present, I believe, solely because of the mechanically worked zones or paths which are distributed through the electrolytic deposit as it is built up.

Another feature of the grain structure of this heat treated layer of electrolytically deposited copper is the uniformity of the fineness of the grain structure from the initial deposit outwardly. Ordinarily, electrolytic copper varies in grain structure, as above pointed out, the grains of the initial deposit being finer than succeeding portions of the deposit. The intrusive action of the finely divided material appears to have an equalizing effect during the course of the heat treatment. There appears to be a tendency for the grain boundary material to come into equilibrium with the grains of the copper, resulting in uniform equiaxed grain structure. The uniform grain structure shown in Figure 5, of course, is highly desirable, since it gives rise to the physical characteristics required in commerce, namely, ductility and malleability; and provides an excellent bond between layers.

Upon emerging from the furnace 15, the coated base may be reduced in cross section either while hot or after cooling, and may thereupon be subjected to any further manufacturing operations desirable. As explained above, an improved bond between the copper sheath and the base is effected through the migration of amorphous material,

and accordingly it is not necessary or desirable to apply great welding pressures.

I have also observed that the intrusive action above mentioned is also effective in the case of, for example, a steel billet having a copper sheath cast thereon, and a second copper sheath deposited electrolytically on the first. By subjecting the electrolytic layer deposited on a cast copper sheath to combined mechanical working and heat treatment, as above described, however, I am able to convert the grain structure of the electrolytic copper to substantially the type shown in Figure 5 and to cause interchange of grain boundary material, resulting in a homogeneous grain structure throughout the copper layers, demonstrating the remarkable effects of the intrusive action of the amorphous constituent. Figures 6 and 6a show diagrammatically the grain structure of such electrolytic and cast copper layers before and after subjecting them to the process of my invention.

The effect of the treatment described upon the grain structure of the copper-iron boundary is best shown in Figures 7 and 8. In Figure 7, the iron (in the upper portion of the figure) has a fairly coarse grain structure and the copper (in the lower portion of the figure) has the grain structure illustrated more particularly in Figure 4. The solid circles in Figure 7 represent the amorphous constituent as shown in Figure 4 at 18'. On heating the composite article to a temperature between 400° and 800° F., however, the grain structure is converted into that shown in Figure 8. In Figure 8, the iron base is unaltered as to grain orientation. The heat treatment has not been carried to a temperature sufficiently high to rearrange the grains or cause grain growth. The copper grain structure has become equiaxed. The amorphous constituent of the copper has disappeared, and apparently this amorphous copper has penetrated all grain boundaries of the iron. Moreover, there is reason to believe that an interface penetration or, more strictly speaking, inter-crystalline penetration of the Neumann bands that appears to be, in effect, interface penetration by the amorphous copper has occurred. It is apparent that the grain boundary material of the copper has penetrated into the intergranular spaces of the iron and that, simultaneously, the grain structure of the copper has been considerably refined. There is an annealing effect upon the iron grain structure characterized by the introduction of Neumann lines. The interlocking grain boundary material, of course, effects a very strongly adherent union between the copper and the iron. The net effect of the electrodeposition accompanied by mechanical working and followed by heat treatment at about 800° F., seems to be that a weld between the metals is produced at a temperature much below the fusion point. There appears to be a critical temperature, at about 450° F., at or above which this result occurs.

It will be apparent from the foregoing description that the invention provides electrolytic copper which, after being subjected to heat treatment, has improved physical characteristics including electrical conductivity, malleability and ductility. It also affords superior qualities as to the bond with the base. My invention makes it possible to obtain a marked improvement in the characteristics not only of electrolytic copper, but also of other metals of similar properties, by a simple heat treatment and hot working pre-

ceded by the mechanical working after the deposition of each layer, as described above.

The dimension of the unit of amorphous material is of the order of a small multiple of atomic diameters. The ordinary grain boundary is from one to one-hundred thousand times that size and provides, therefore, a space for many millions of the amorphous units when the metal is below the temperature at which grain growth prevails.

On subjecting the metal to temperatures above the critical temperature above mentioned, penetration herein spoken of as intrusion takes place. When the time temperature value is approached, the tendency to form solid solutions within the matrix, as well as the inherent tendency for the amorphous material to recrystallize the grain units, will bring the intrusive action to an end, especially if the grain size of the grain boundary material becomes larger than the grain boundaries of the adjacent metal. While the size of the amorphous units must approximate only a fraction of the dimensions of the grain boundary, the so-called interface penetration (which may be, in fact, intrusions in the Neumann bands) must be of the order of atomic diameters. If interface penetration is effected, it must follow that not only is the grain boundary material amorphous but the treatment has been carried out under such time and temperature conditions as to extend the time of intrusive action to the point where the adjacent metals are saturated.

The amorphous constituent may be provided in ways other than that already described. As an example, I may wash the coated rod with nickel, arsenic or other solutions, as it emerges from the electrolytic baths, thus introducing a foreign constituent of .001%.

Although I have illustrated and described herein but one preferred embodiment of the invention including apparatus adapted thereto and the preferred manner of practicing the invention, it will be obvious that modifications in both the apparatus used and the method of obtaining my improved product may be resorted to without departing from the scope of the invention or the spirit of the appended claims.

I claim:

1. Electrolytic copper comprising lamellae of undistorted grain structure having spaced tracks highly compressed by rolling pressure during deposition of the lamellae so as to produce amorphous copper through the crystalline structure of the matrix of the copper, said lamellae also having substantially uncompressed portions between said tracks, said electrolytic copper having the property of being transformed by relatively low temperature heat treatment to a grain structure having a size smaller than that of the original electrolytic deposit.

2. A composite metallic article comprising metallic copper deposited on a base metal in successive lamellae by electrolysis, said lamellae having spaced tracks highly compressed by rolling pressure during deposition thereof so as to produce amorphous copper through the crystalline structure of the matrix of the copper, said lamellae also having substantially uncompressed portions between said tracks, said metallic copper having a grain structure of a size produced by relatively low temperature heat treatment and smaller than that of the copper as originally deposited.

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