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PROCESS OF PRODUCING BLISTER-FREE
COMPOUND METALSHarry R. Copson, Westfield, N. J., assignor to The
International Nickel Company, Inc., New York,
N. Y., a corporation of DelawareNo Drawing. Application January 14, 1939,
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The present invention relates to a process of producing compound metals, and more particularly to a process of producing cold rolled and annealed compound metals having a layer or core of foundation metal and an outer layer or coating of electro-deposited copper.

In the production of copper clad compound metals, it would have been advantageous in many instances to deposit a layer of copper by electro-deposition on the foundation or basis metal, and thereafter to work the compound metal to the desired size in which it was to be used in the trades or industry. Numerous difficulties have been encountered in commercial practice in producing satisfactory compound metal by this process. Among these difficulties have been particularly the problem of securing satisfactory adherence of the electro-deposited layer to the foundation metal, the problem of securing thick smooth electrodeposits of sufficient ductility to withstand cold work, and the formation of blisters during annealing of the cold worked compound metal. Processes have now been developed which assure satisfactory smoothness, and ductility of the electrodeposited copper layer and satisfactory adherence thereof to the foundation metal. The prevention of blisters, however, remained an outstanding and unsolved problem.

The blisters that formed during the annealing of cold worked compound metals comprising a layer of foundation metal and a layer of electro-deposited copper were of at least two types. The first type was made up of large irregular blisters from about $\frac{1}{8}$ " in diameter and larger. Formed at the plane of contact of the electro-deposited layer with the foundation layer or core, these large irregular blisters appeared to be related to poor adherence between these layers. Blisters of this type have been substantially eliminated by use of the aforementioned processes which assure satisfactory adherence of the electro-deposited layer to the foundation metal.

A second type of blister was made up for the most part of small, round blisters in the electro-deposited copper layer, varying in size from that of a pin point up to about that of a pinhead. Practically all of these small, round blisters were formed in the compound metal during an annealing step following cold rolling. The number of such blisters varied with the method of producing the sheets and also with the nature of the deposit. For example, no small blisters, or at most very few, were formed by annealing a compound metal sheet in the as-plated condition at temperatures up to about 1750° F. However,

after the compound metal plate or sheet had been cold rolled and subjected to high annealing temperature, numerous blisters were present in the copper layer. The largest number of blisters appeared after annealing at temperatures above about 1700° F., some being formed also at temperatures as low as about 1200° F. to about 1400° F. but in general few, if any, were formed at temperatures as low as about 900° F. It was also found that sheets which were plated in the same bath in substantially the same manner and thereafter rolled and annealed in identical ways exhibited varying number of blisters in the cold rolled and annealed condition, some having very few, if any, blisters and others having hundreds of blisters to the square inch. More of these blisters occurred near the outer surface of the electrodeposited layer than near the surface adjacent to the foundation metal. While these blisters ordinarily were distributed over the surface at random, they sometimes occurred in transverse rows across the sheet or clustered near the end of the sheet which passed through the rolls last. These last two phenomena appear to be related in some way with the cold rolling technique. The purity of the copper plating bath was not the cause of all the blistering because many blisters were obtained on deposits from a chemically pure, glue-free bath using lead anodes.

Various theories have been proposed to explain the cause of blistering. For instance, it has been suggested that hydrogen plated out with the electro-deposited metal might account for the blistering. Another theory was that oxygen in the form of cuprous oxide might be present as an impurity in the electrodeposited copper, and that upon annealing the hydrogen and oxygen combined to form steam under pressures high enough to produce blisters. Also it has been suggested that the blistering might be caused by occluded material, such as oxides, hydroxides, or even copper sulfate. These theories do not seem to explain all of the facts. It is difficult for example, under these theories to explain why blisters should be absent when the sheet is annealed in the as-plated condition when they are formed in large numbers by annealing cold worked material at the same temperature. Similarly, these theories fail to explain the occasional orientation of blisters in transverse rows or near the end of the sheet which passes through the rolls last. It will thus be seen that the theories which have been proposed for explaining the occurrence of blisters do not lead to a solution of the problem of devising a process for eliminating their occurrence.

Blisters of both of the aforementioned types are objectionable in finished sheets, wire, and other commercial shapes, and particularly so in sheets which are to be used, for example, in the manufacture of kitchen ware. Many attempts have been made to provide a process which would eliminate blisters from the finished product, but so far as I am aware no process has been developed which consistently produces satisfactory and acceptable cold worked and annealed compound metal shapes.

I have discovered a process of producing substantially blister-free cold worked and annealed compound metal sheets, plates, wires, and other commercial shapes comprising a layer or core of foundation metal and an electrodeposited copper layer, which process is capable of commercial operation on an industrial scale to produce satisfactory and acceptable compound sheets, plates, and the like.

It is an object of the present invention to provide a process of producing substantially blister-free compound metals comprising a foundation layer or core of metal and an electrodeposited copper layer.

It is another object of the present invention to provide a process of producing substantially blister-free cold worked and annealed compound metal comprising a metallic foundation layer and a relatively thick electrodeposited layer of copper.

A further object of the invention is the provision of a process for producing substantially blister-free cold rolled and annealed plates, sheets and other shapes of electrodeposited copper.

Other objects and advantages of the invention will become apparent to those skilled in the art from the following detailed description of the invention.

Generally speaking, the process of the present invention for eliminating the formation of blisters in a compound metal having a metallic foundation layer and an adherent electrodeposited copper layer comprises the steps of giving the compound plate, sheet, or other shape, a preliminary anneal at an elevated temperature; cold reducing the compound metal a relatively small amount; annealing the cold reduced compound metal at an elevated temperature; cold reducing the compound metal to finished dimensions with intermediate anneals, if necessary; and giving the finished cold reduced compound metal a final anneal at an elevated temperature. The layers of compound metals produced in this manner adhere tightly together and the electrodeposited layer is substantially free from blisters.

The temperature employed to anneal the compound metal after cold reduction to the desired finished dimensions is ordinarily the annealing temperature of the foundation metal. While not restricted to any particular metals or alloys, the foundation metals ordinarily used in the compound metals comprehended within the present invention will be stronger and harder than copper. Steels, such as plain carbon steel, low alloy steels, highly alloyed steels of the stainless types, and nickel and nickel alloys, are examples of metals and alloys from which the foundation metal is generally chosen. These metals and alloys harden during cold reduction and in most cases it is necessary to soften or anneal them before the compound metal can be utilized by the trades and industry. The temperature to which these metals and alloys must be heated to anneal

them, i. e., their softening temperature, lies above the annealing or softening temperature of copper, and as a consequence a compound metal of such a type must be heated to the annealing or softening temperature of the foundation metal. In most instances the annealing temperature will be over about 1500° F. It has been found preferable to use substantially the same temperature for the preliminary anneal, the intermediate anneals and the final anneal.

In order to give those skilled in the art a better understanding of the present invention, the following illustrative example is given:

EXAMPLE

COPPER CLAD ON NICKEL-CHROMIUM-IRON ALLOY

In this example, the foundation metal was in the form of a sheet about 0.02 inch thick made of nickel-chromium-iron alloy containing approximately 80% nickel, 14% chromium and 6% iron. The foundation sheet was thoroughly cleaned and pumice scrubbed until free from any water break. It was then immersed in a bath containing about 240 grams per liter of nickel chloride and about 37 grams of hydrochloric acid. It was made anode for about 2 minutes at 20 amperes per square foot and then made cathode for about 12 minutes at the same current density. The foundation sheet with the protective nickel coating was then rapidly transferred without rinsing to a copper plating bath containing about 200 grams per liter of technical copper sulfate and about 100 grams per liter of commercial sulfuric acid. The solution was continuously circulated through a filter press, being taken from the bottom and being returned at the top of the plating tank. Copper anodes enclosed in glass bags were used at a current density of about 20 amperes per square foot. A deposit of copper about 0.10 inch thick was produced.

Samples of the composite sheet were subjected to the following combinations of working and annealing operations:

Sample No. 1

One sample of the composite plate was annealed in the as-plated condition for about 15 minutes at about 1750° F. No blisters were formed in this treatment. The annealed composite plate was then cold rolled to effect about 10% reduction of the original thickness and thereafter annealed at about 1750° F. for about 15 minutes. It was then cold rolled directly to a thickness of 0.03 inch but if necessary intermediate anneals at 1750° F. for about 15 minutes each could have been used. The final anneal after cold reduction to finished thickness was also carried out for about 15 minutes, at about 1750° F. The final sheet was free from blisters and a satisfactory composite sheet for the fabrication of kitchenware.

Sample No. 2

Second sample cut from the same sheet was given the same treatment as Sample No. 1 except that the preliminary anneal was omitted. The final product in this case had some small blisters.

Sample No. 3

A third sample from the same sheet was given the same treatment as Sample No. 1 except that the preliminary 10% cold reduction was omitted. The final product in this case had some blisters.

Sample No. 4

A fourth sample from the same sheet was given the same treatment as Sample No. 1 except that both the preliminary anneal and the preliminary 10% cold reduction in thickness were omitted. On this sample approximately 1000 small blisters were found in the final product in an area of about 15 square inches.

Composite sheets produced by the processes employed for Samples No. 2 and No. 3 were far superior to sheets produced by the process employed for Sample No. 4, and in some instances satisfactory results have been obtained where either the preliminary anneal or the preliminary 10% cold reduction is omitted. The electrodeposited copper layers differ somewhat from each other in the tendency to form blisters. Where a sheet exhibits a strong tendency to form blisters, the process described in connection with Sample No. 1 is preferably employed as this process has produced satisfactory results in such cases. Where the tendency is less pronounced, the process described under Samples No. 2 or No. 3 may be employed to produce satisfactory blister free compound sheets and other shapes.

Two other samples from the same sheet were given the same treatment as Sample No. 1 except that the preliminary and intermediate anneals were carried out at about 900° F. and about 1300° F., respectively, instead of 1750° F. After a final anneal at about 1750° F. for about 15 minutes, products were found to have developed many small blisters in the copper layer. The annealing temperatures employed for the preliminary and intermediate anneals preferably approximate the temperature employed for the final anneal.

It will be seen from the foregoing description of the invention that a preferred procedure for uniformly producing satisfactory blister-free compound sheets, plates, bars, tubes, and other shapes, comprises subjecting the compound metal in the as-deposited condition to a preliminary anneal at a temperature within the range necessary to soften the final cold rolled compound metal; cold reducing the thus-annealed material a relatively small amount, e. g., about 10% reduction in cross-sectional area; subjecting the cold reduced compound metal to a second anneal within approximately the same temperature range as the preliminary anneal; cold reducing the annealed compound metal to the desired finished size; and finally subjecting the compound metal after the last cold reduction to an anneal within approximately the same temperature range as the preliminary anneal. This sequence of steps may be modified in certain instances as illustrated hereinabove where the compound metal being treated exhibits relatively slight tendency toward the formation of blisters. Thus, for example, intermediate anneals may be used, if necessary, during the cold reduction to the desired finished size within approximately the same temperature range as the preliminary anneal.

Although the present invention has been described in connection with certain specific illustrations thereof, it will be understood that modi-

fications and variations may be made therein as will be obvious to those skilled in the art. The process may be applied to plates, sheets, bars, tubes, wires and other structural shapes. Such modifications and variations are to be construed as within the scope of the invention as set forth in the following claims.

I claim :

1. The process of producing a substantially blister-free, cold worked, and annealed compound metal sheet, which consists in electrodepositing a layer of substantial thickness of copper on a foundation layer of an alloy of 80% nickel, 14% chromium, and 6% iron, subjecting said compound metal to a special heat treatment to about 1750° F. for about 15 minutes, cold rolling to effect a reduction of the order of 10%, heating at about 1750° F. for about 15 minutes, whereby the susceptibility to blister formation in the copper layer is overcome, cold rolling the compound material to the desired sheet gauge, and annealing the same whereby a substantially blister-free compound metal sheet is obtained.

2. The process of producing a substantially blister-free, cold worked, and annealed compound metal sheet, which consists in electrodepositing a layer of substantial thickness of copper on a foundation layer of an alloy of 80% nickel, 14% chromium, and 6% iron, subjecting said compound metal to a special heat treatment to about 1750° F. for about 15 minutes, cold rolling the compound material to the desired sheet gauge, and annealing the same, whereby a substantially blister-free compound metal sheet is obtained.

3. The process of producing a substantially blister-free, cold worked, and annealed compound metal sheet, which consists in electrodepositing a layer of substantial thickness of copper on a foundation layer of metal selected from the group consisting of steels, nickel and nickel alloys having a higher softening temperature after cold work than copper, subjecting said compound material to a special heat treatment at a temperature of at least 1500° F., cold rolling to effect a reduction of the order of 10%, heating at a temperature of at least 1500° F., cold rolling the compound material to the desired sheet gauge, and annealing the same whereby a substantially blister-free compound metal sheet is produced.

4. The process of producing a substantially blister-free, cold worked, and annealed compound metal sheet, which consists in electrodepositing a layer of substantial thickness of copper on a foundation layer of metal selected from the group consisting of steels, nickel and nickel alloys having a higher softening temperature after cold work than copper to produce a compound material, subjecting said compound material to a special heat treatment at a temperature of at least 1500° F., cold rolling the compound material to the desired sheet gauge, and annealing the same whereby a substantially blister-free compound metal sheet is produced.

HARRY R. COPSON.