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2,707,323

METHOD OF PRODUCING COPPER CLAD STEEL PLATES

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No Drawing. Application May 7, 1951,
Serial No. 225,066

6 Claims. (Cl. 29—470.9)

The present invention relates to the manufacture of copper clad steel plates; and more particularly it relates to a method for making copper clad steel plates from large masses of the metals, that is, from steel slabs or ingots, as distinguished from steel plates or sheets, and from copper plates as distinguished from copper sheeting or foil.

The manufacture of copper clad steel sheets, and of articles therefrom, such as cooking utensils, is well known. Such sheet ware is normally prepared by pressing together at high temperatures, a copper sheet or foil and a steel sheet to cause the welding of the copper sheet or foil to the steel sheet. Cooking utensils can readily be fabricated from such sheet ware. It has also been suggested to clad the copper sheet or foil to the steel sheet by a hot rolling operation, whereby in addition to welding of the copper to the steel, some slight reduction in thickness of the composite article may take place. While the cladding of copper sheets or foils to steel sheets by such procedures presents problems, they are relatively minor in view of the thinness of the stock being worked.

The manufacture of copper clad steel plates from large masses of the metals, that is from copper plates and from steel slabs or ingots, however, is an entirely different matter. Aside from the large size of the material being worked which gives rise to handling problems and difficulties during hot rolling, the large mass of metals being worked gives rise to other difficulties which, heretofore, have made it impossible to obtain satisfactory bonding between the copper and the steel. In the first place, it was found during early work, that blisters formed at the bond resulting in a defective product. Possible reasons for this will be set forth hereinafter. At any rate it has been found that by using copper plates made from a special type of copper, this formation of blisters is eliminated. In the second place, it was found that, in attempting to manufacture copper clad steel plates from large masses of copper and steel of the stated type, by a hot rolling procedure, the strength of the bond between the copper and the steel was very much less than that of even the copper itself. While this is believed to be due primarily to the difficulty of forming a copper-steel alloy at the bond interface, it is also believed to be aggravated by the tremendous strains set up during hot rolling due to the widely differing physical properties between the copper and the steel at the rolling temperatures. (The normal hot rolling temperature for carbon steel is 2300–2400° F. Yet, ordinary copper melts at several hundred degrees below this range, and is a relatively soft metal even at ordinary temperatures. Thus, at temperatures suitable for rolling copper, the steel is very much less ductile, and with standard rolling procedure for steel the copper tends to take up most of the strain from the rolls causing it to be squeezed out beyond the edges of the steel.)

Moreover, in hot rolling during cladding of large masses of metal the only practical way initially to se-

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cure the copper plate to the steel slab or ingot, or to secure a plurality of such composite assemblies into a "sandwich" or pack, is by welding around the peripheral edge of the assembly or pack. However, due to the wide differences in deformation characteristics between the copper and the steel at rolling temperatures, the copper, under normal rolling techniques, would, as stated, be caused to be squeezed beyond the edge of the assembly rupturing the initial weld. In addition, while weld metal is sufficiently ductile at normal steel rolling temperatures, i. e., at 2300–2400° F., to withstand the strains of rolling without breaking, it tends to rupture, under normal hot rolling technique, at the temperatures usable for copper cladding of steel, thereby rendering the assembly unfit for further rolling.

The foregoing are a few of the many problems encountered in attempts to produce copper clad steel plates from large masses of the metals, and have been cited to show that such manufacture represents a field entirely different from that where copper clad steel sheets, or other clad steel sheets, are prepared from thin metal stock such as sheets or foils, by pressing or hot rolling involving but slight reduction in thickness.

It is an object of the present invention to provide a method for the manufacture, by hot rolling, of copper clad steel plates from large masses of the metals, that is, from copper plates and steel slabs or ingots.

Another object is to provide a process of the type described whereby, in the product formed, the strength of the bond between the copper and the steel is equal to or greater than the strength of the copper itself.

Still another object is to provide a process of the type described whereby, in the product formed, the bond between the copper and steel is free from blisters or other defects.

A further object of the invention is to provide a process of the type described wherein the danger of rupturing the initial sealing welds during rolling is eliminated.

A further object is to provide a process of the type described wherein a plurality of copper clad steel plates may be produced during one operation.

Other objects will be apparent from a consideration of the following specification and claims.

In accordance with the present invention a series of novel steps and features, each dependent on the other, are combined in a novel correlated manner to provide a process by which the above-stated objects may be realized. The process comprises electrodepositing a layer of nickel on a face of a plate of oxygen-free copper; securing the copper plate to a steel slab or ingot with the nickel-plated surface of the copper plate in face-to-face contact with the steel slab or ingot; heating the resulting composite assembly uniformly throughout to a temperature between about 1550 and about 1800° F.; and subjecting the hot assembly to pressure rolls to reduce its thickness to between about one-fourth and about one-twenty-fifth of the thickness of the original assembly, the reduction in thickness of said copper-steel assembly during any one pass through the rolls being no greater than about one-eighth of an inch. In accordance with the preferred embodiment of the process, the reduction in thickness of the copper-steel assembly per pass during the first series of passes is no greater than about one-eighth of an inch, as stated. Then, when the copper-steel assembly is within 10% of the desired final thickness, the reduction in thickness of the copper-steel assembly per pass is no greater than about one-sixteenth of an inch.

By the above-described process it has been found that the difficulties which previously rendered the manufacture of satisfactory copper clad steel plates from large masses of the metals impossible, are eliminated, and that consistently excellent copper clad steel plate products are

obtained. By the use of oxygen-free copper it has been found that the blisters, which form when ordinary copper is used, are not encountered. It is believed that the freedom of the copper from dissolved oxygen is directly responsible for this. Ordinary copper contains about 0.04% oxygen. When ordinary copper is used, it is believed that, at the high temperatures to which the large mass of metal must be subjected in order to heat it throughout to the rolling temperature, a gas, which may be oxygen, carbon dioxide or steam, or mixtures thereof, forms at the bond line. Carbon dioxide may form by reaction of the oxygen with carbon in the copper or steel, or with carbon monoxide in the reducing atmosphere of the soaking pit; and steam may form by reaction between the oxygen and hydrogen from the furnace atmosphere or liberated from the steel during heating. At any rate the formation of the gas results in blisters at the bond providing a defective product. As stated, when oxygen-free copper plates are used there is no formation of blisters. By the present process, moreover, the bond provided between the copper and the steel is very strong, and, in fact, shear tests have shown that the strength of the bond is even greater than that of the copper itself. The use of oxygen-free copper in conjunction with the electrodeposition of nickel on the copper plate is believed to account for this. Apparently steel alloys more readily with nickel than with copper. Thus, the initial electrodeposition of the nickel on the copper facilitates the subsequent alloying of the copper and nickel at the interface during hot rolling. The nickel readily alloys with the steel during hot rolling, providing ultimately, due to hot rolling, a strong bond between the copper member and the steel member. The formation of this bond is also facilitated by the particular rolling procedure recited, where the maximum reduction in thickness per pass is only one-half to one-third of that conventionally employed in hot rolling during cladding of steel with other metals. In addition to this, it has been found that by the particular rolling procedure recited, even reduction in thickness of the steel as well as the copper takes place, and there is no extrusion of the copper beyond the edge of the steel, which would break the initial securing weld and otherwise disrupt the rolling procedure. Moreover, it has been found that by such a rolling procedure, even at relatively low temperatures employed as compared to conventional cladding operations, the initial sealing weld is not ruptured in spite of its low ductility.

Referring to the copper used as the starting material in accordance with the present process it is, as stated, oxygen-free copper in the form of a plate, that is, it will have a thickness of at least one-eighth inch and it may have a thickness up to about one inch. Oxygen-free copper, as it is known in the art, is copper prepared under conditions preventing the retention of the normal amount of oxygen therein. For example, such copper may be obtained by electrodeposition followed by melting, as in an electric furnace, under an inert atmosphere such as nitrogen. During pouring, the molten copper is also protected from the atmosphere. Such copper may also be obtained by treating copper, during conventional manufacturing procedures, for the removal of oxygen with an agent, such as phosphorus, manganese, and the like. Such copper is also known in the art as "de-oxidized" copper. The copper prepared by any of the procedures described above is substantially free of oxygen but may contain minute traces thereof. Such copper is referred to herein and in the claims as "oxygen-free" copper, and such term is used herein in the sense it is used in the art to refer to a copper containing no more than a trace of oxygen and to distinguish from ordinary copper which contains about 0.04% oxygen. While any oxygen-free copper may be employed in accordance with the present process, the preferred form is the de-oxidized

copper; referred to above, particularly phosphorus de-oxidized copper.

The steel body which is employed in accordance with the present process for cladding with copper is, as stated, in the form of a slab or ingot. An ingot is the form of the steel as it comes from the ingot mold, while a slab is prepared by rolling the rough ingot, to reduce it somewhat in thickness and to provide a smoother surface. The steel body, whether slab or ingot, employed in the present process will be at least two inches in thickness, and the thickness thereof may run up to about fifteen inches. With respect to the steel itself it may be any carbon steel or low alloy steel, that is, a steel containing less than about 6% of alloying materials. Such low alloy steels are steels in which relatively small amounts of other metals (such as nickel, titanium, chromium, molybdenum, manganese, and the like, and various combinations thereof, such as nickel and titanium; nickel and chromium; nickel, chromium and molybdenum; and the like), are incorporated in the steel to enhance the physical properties thereof, mainly tensile strength, as distinguished from chemical properties such as corrosion resistance.

The surface of the steel slab or ingot to which the copper is to be clad is preferably substantially free of oxide scale. Thus, one face of the steel slab or ingot may be, and preferably is, treated to remove oxide scale as by grit blasting, pickling, and the like, before the copper plate is secured thereto. Grit blasting is particularly advantageous in this regard.

The surface of the copper plate which is to be clad to the steel is provided, as stated, with a layer of electrodeposited nickel. In order to obtain satisfactory plating of the copper by the nickel it is desirable that the surface of the copper plate be clean and free from oxide. Thus, it is desirable to clean the surface of the copper plate by pickling, such as in a hydrochloric acid bath. Before pickling, the surface may be preliminarily cleaned in an electrolytic caustic bath containing, for example, an aqueous solution of caustic soda, or of caustic soda and sodium carbonate, after which the plate may be washed with water. Imperfections in the surface of the copper plate may be removed by buffing.

The provision of the nickel coating is conveniently accomplished by immersing the copper plate, after cleaning in the manner stated, in a nickel electroplating bath to provide an electrolytic deposit or coating of nickel on the surface of the plate. To prevent nickel from being plated on both surfaces of the plate, one side may be coated with a strippable film-forming material which prevents plating of the nickel on the surface to which it is applied, and, after plating, this film can be readily stripped from the unplated surface. While this coating may be provided by any strippable, film-forming material which is relatively unaffected by acids or bases, the use of a liquid composition which dries to a non-adhesive film and which is compounded from modified halide polymers, condensation resins and diene derivatives (known as "Tygon Temprotec," which is a registered trade-mark) is particularly advantageous. The electroplating bath will comprise a soluble nickel salt, such as nickel chloride, nickel sulfate, and the like, and a strong mineral acid such as hydrochloric acid, sulfuric acid, and the like, and a nickel anode or anodes may be provided. The electroplating of nickel on copper is in itself well known, and thus the provision of the nickel coating on the surface of the copper plate will present no problem to one skilled in the art. Insofar as the present process is concerned, however, the electroplating procedure will be controlled to provide a nickel coating having a thickness between about 0.001 "and about 0.020," a coating having a thickness between about 0.002 "and about 0.005" being preferred.

After the nickel coating has been deposited on the surface of the copper plate, and after the strippable film,

if used, has been removed from the other surface of the copper plate, the nickel-plated copper plate is positioned with respect to the steel slab or ingot so that the nickel coating is in face-to-face contact with the steel body. The copper plate will have a length and width somewhat smaller than that of the steel body to provide a margin of from about 1 inch to about 4 inches between edges of the copper plate and the edges of the steel body.

The copper plate and the steel body are then firmly secured together in the stated position. When the entire assembly to be rolled for cladding is to consist of one copper plate and one steel slab or ingot, a steel plate or slab may be placed over the copper plate and secured to the steel slab or ingot, thus holding the copper plate firmly against the base steel slab or ingot. The steel cover plate or slab may be secured to the steel slab or ingot by welding at the marginal edges; or advantageously steel spacer bars are placed in the gap between the cover plate or slab and base steel slab or ingot and these in turn are welded to the cover plate or slab and to the base steel slab or ingot to provide a compact unitary article. A weld-preventing material may be incorporated between the steel cover plate or slab and the copper plate to prevent welding thereof together during hot rolling. In accordance with the preferred embodiment of the invention, a plurality of copper plate-steel slab or ingot assemblies are secured into a single pack so that more than one copper clad steel plate may be produced in a rolling operation. For example, two copper plates may be sandwiched between two steel slabs or ingots, the nickel-coated face of each copper plate being in face-to-face relationship with the respective steel body to which it is to be clad. A weld-preventing material may be provided between the copper plates to prevent welding thereof together. The resulting sandwich or pack may be rigidly secured into a unitary structure by welding around the marginal edges, steel spacer bars advantageously being provided in the marginal gap between the steel bodies in the manner stated above.

Reference has been made above to a weld-preventing composition to prevent welding, during hot rolling, of the copper plate to the steel cover plate or to the adjacent copper plate in the event a plurality of copper plate-steel slab or ingot assemblies are assembled into a pack or sandwich. While any weld-preventing composition may be employed for this purpose, a particularly advantageous weld-preventing composition is that disclosed and claimed in co-pending application Serial Number 130,598 filed December 1, 1949, by Thomas T. Watson and Albert Riggall. The weld-preventing composition of this stated co-pending application comprises a finely-divided refractory inorganic material in a liquid vehicle comprising a very small amount of cellulose ether or ester dissolved in a volatile solvent.

The composite assembly or pack secured into a unitary structure as described above is then heated uniformly throughout to the rolling temperature. Heating preferably takes place in a "soaking pit" where the assembly can be subjected to high temperatures for extended periods. The temperature to which the assembly is heated will not exceed about 1800° F., and may be as low as about 1550° F. However, it is preferred to heat the assembly to a temperature between about 1600° F. and about 1725° F.

The hot assembly is then subjected to pressure rolls to provide pressure for welding the copper plate to the steel slab or ingot and to reduce the composite article to the desired thickness. As stated above, the amount of reduction in thickness of the assembly per pass is critical, and must not exceed about one-eighth inch for each copper plate-steel slab or ingot assembly. Thus, where two copper plate-steel slab or ingot assemblies are rolled in the form of a pack or sandwich in accordance with the preferred embodiment of the present in-

vention, the reduction in thickness per pass of the pack should not exceed about one-fourth inch. This is a marked departure from normal hot rolling procedures for cladding where the amount of reduction in thickness per pass is more than two to three times this amount. Rolling is continued in the manner stated until the desired reduction in thickness is obtained, which, as stated, will normally be where the assembly or pack is between about one-fourth and about one-twenty-fifth its original thickness, preferably between about one-sixth and about one-twelfth of its original thickness. This will provide, in view of the size of the starting materials, copper clad steel plate.

In accordance with the preferred form of the process, when the assembly or pack has been reduced in thickness to within about 10% of the desired final thickness, the reduction in thickness per pass for each copper-steel assembly will not exceed about one-sixteenth of an inch. This procedure insures the advantageous results obtained in accordance with the present process.

Following rolling, the product may be treated as desired. Rough edges may be cut evenly and initial weld metal sheared away. When a plurality of assemblies has been rolled in the form of a pack, the resulting copper-clad steel plates can be readily separated from each other by shearing around the edges to remove weld metal.

The operation of the present process will be more readily understood from a consideration of the following specific example which is given for the purpose of illustration and is not intended to limit the scope of the invention in any way.

Example

In this example two copper plates and two steel slabs are rolled together in the form of a pack to produce simultaneously two copper clad steel plates. The copper plates are of phosphorus deoxidized copper and 74" long, 48" wide and $\frac{3}{8}$ " thick. The steel slabs are carbon steel slabs 78 $\frac{3}{4}$ " long, 52 $\frac{3}{8}$ " wide and 3 $\frac{3}{8}$ " thick.

Steel lugs are first welded to one edge of each copper plate to facilitate handling. The plates are then pickled in hydrochloric acid and rinsed with water, and imperfections on the surfaces of the plates are removed by buffing. To one face of each of the plates is applied a strippable organic film. The plates are then electrically cleaned in a caustic tank, sprayed with water to remove traces of the caustic solution, and then pickled in hydrochloric acid and rinsed with water.

The thus-cleaned plates are then immersed in a Watts bath for nickel plating. A current density of 50 amperes per square foot is employed to provide a nickel coating 0.003" thick on the face of each copper plate which is not protected by the organic film.

Following plating the copper plates are rinsed with water, and the strippable organic film and handling lugs are removed. A weld-preventing composition is applied to each of the non-plated faces.

One face of each of the steel slabs is grit blasted to remove oxide scale. The two copper plates are then sandwiched between the two steel slabs so that the weld-preventing composition is between the copper plates and so that the nickel-coated face of each copper plate is in face-to-face contact with a grit-blasted face of the steel slab to which it is to be clad. The smaller copper plates are centered on the steel slabs to provide a margin between the edges of the plates and the edges of the steel slabs. Steel bars are then laid in the gap between the steel slabs, and the bars and the slabs are welded together to secure the metal members into a unitary pack.

The pack is then placed in a soaking pit where it is held until heated uniformly throughout to 1700° F. The pack is then transferred to a rolling mill where it is repeatedly passed between the rolls until it is reduced to a thickness of one inch. The rolling mill is adjusted so that the reduction in thickness of the pack per pass through the rolls during the first series of passes is

about $\frac{3}{16}$ ". Then when the pack is reduced in thickness to about $\frac{1}{4}$ ", the rolls are adjusted so that the reduction in thickness per pass is about $\frac{3}{32}$ ", and two passes are made at this adjustment. Then the reduction in thickness is gradually reduced further until the final one inch thickness is reached.

After rolling, the weld metal at the edges of the composite product is sheared away leaving two 10% copper clad steel plates 240 inches long, 80 inches wide and $\frac{1}{2}$ inch thick.

The shear strength of the resulting plate at the bond is 25,000–27,000 p. s. i. when tested by the standard A. S. M. E. shear test, whereas the shear strength of the deoxidized copper itself is 22,000 p. s. i. Copper clad steel plates made following the same procedure but without nickel plating the copper plates had a shear strength at the bond of only 17,000–19,000 p. s. i.

Considerable modification is possible in the selection of the particular techniques to be followed in carrying out the process of the present invention without departing from the scope thereof.

I claim:

1. The method of manufacturing copper-clad steel plates that includes the bonding of one face of an oxygen-free copper plate and a steel slab or ingot wherein the former varies from $\frac{1}{8}$ " to 1" in thickness as the latter varies from 2" to 15" in thickness, which method comprises electrodepositing a layer of nickel on one face of said copper plate; securing the copper plate to a steel slab or ingot with the nickel-plated surface of the copper plate in face-to-face contact with the steel slab or ingot; heating the resulting composite assembly uniformly throughout to a temperature between about 1550 and about 1800° F.; and subjecting the hot assembly to pressure rolls to reduce its thickness to between about one-fourth and about one-twenty-fifth of the thickness of the original assembly, the reduction in thickness of said copper-steel assembly per pass through the rolls being no greater than about one-eighth of an inch, and, when the thickness of the assembly is within about 10% of the desired final thickness, the reduction in thickness of said copper-steel assembly per pass through the rolls being no greater than about one-sixteenth of an inch.

2. The method of claim 1 wherein the assembly is heated uniformly to a temperature between about 1600° F. and about 1725° F. and wherein the assembly is rolled until its thickness is reduced to between about one-sixth and about one-twelfth of its original thickness.

3. The method of manufacturing copper-clad steel plates that includes the bonding of the faces of oxygen-free copper plates and steel slabs or ingots wherein the former vary from $\frac{1}{8}$ " to 1" in thickness as the latter varies from 2" to 15" in thickness, which method comprises electrodepositing a layer of nickel on one of the faces of each of two copper plates; securing the nickel-plated copper plates between two steel slabs or ingots, the nickel-plated face of each copper plate being in face-

to-face contact with a steel slab or ingot to form a unitary pack; applying a weld-preventing material between the juxtaposed faces of the copper plates; heating the pack uniformly throughout to a temperature between about 1550° F. and about 1800° F.; and subjecting said pack to pressure rolls to reduce its thickness to between about one-fourth and about one-twenty-fifth of the thickness of the original pack, the reduction in thickness of said pack per pass through the rolls being no greater than about one-fourth of an inch.

4. The method of claim 3 wherein said pack is heated uniformly throughout to a temperature between about 1600° F. and about 1725° F.

5. The method of manufacturing copper-clad steel plates that includes the bonding of the faces of oxygen-free copper plates and steel slabs or ingots wherein the former vary from $\frac{1}{8}$ " to 1" in thickness as the latter varies from 2" to 15" in thickness, which method comprises electrodepositing a layer of nickel on one of the faces of each of two copper plates; securing the nickel-plated copper plates between two steel slabs or ingots, the nickel-plated face of each copper plate being in face-to-face contact with a steel slab or ingot to form a unitary pack; applying a weld-preventing material between the juxtaposed faces of the copper plates; heating the pack uniformly throughout to a temperature between about 1550° F. and about 1800° F.; and subjecting said pack to pressure rolls to reduce its thickness to between about one-fourth and about one-twenty-fifth of the thickness of the original pack, the reduction in thickness of said pack per pass through the rolls being no greater than about one-fourth of an inch, and, when the thickness of the assembly is within about 10% of the desired final thickness, the reduction in thickness of said pack per pass through the rolls being no greater than about one-eighth of an inch.

6. The method of claim 5 wherein said pack is heated uniformly to a temperature between about 1600° F. and about 1725° F. and wherein the pack is rolled until its thickness is reduced to between about one-sixth and about one-twelfth of its original thickness.

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