Patented Apr. 1, 1941

2,237,243

UNITED STATES PATENT OFFICE

2,237,243

METHOD OF MAKING CORROSION RESISTANT METAL STRIP

Richard A. Wilkins, Rome, N. Y., assignor to Revere Copper and Brass Incorporated, Rome, N. Y., a corporation of Maryland

No Drawing. Application January 24, 1940, Serial No. 315,430

7 Claims. (Cl. 148—11.5)

My invention relates to methods of making cold rolled, corrosion resistant metal strips including slabs from which the strips may be formed by further cold rolling in the usual manner.

The invention is particularly concerned with making corrosion resistant strips of phosphor-bronze alloy which is so compounded, worked and heat treated that the metal has improved physical properties and a greater resistance to chemical corrosion than the metal of the original cast alloy, and, what is of particular importance, especially with thin strips within the range of commercial sizes, a greater resistance to stress corrosion than the metal of the original casting.

Heretofore copper has been alloyed with tin-bronzes to harden and toughen the copper. In connection with such alloys it has been common to add small amounts of phosphorus to the melt for deoxidizing it, the bulk of the phosphorus however burning off, or going off in the slag, so that in the cast alloys only such minute fractions of a percent of phosphorus remain as exert no appreciable effect on the chemical properties of the alloys. It also has been proposed to add higher amounts of phoshorus to tin-bronzes for improving the free flowing and casting qualities of the metal. In these latter castings it has been found, that although the phosphorus therein in itself tends to increase the corrosion resistance of the alloy, that resistance as a matter of fact is not increased.

Applicant has found that the above mentioned castings having relatively high amounts of phosphorus, even when consisting wholly of a mixture of copper, tin and phosphorus, contain one or more secondary mixtures, which latter, existing as crystals or other segregates of different chemical composition from the rest of the metal of the casting, reduce the resistance of the cast metal to corrosion, particularly when subjected to stress.

Applicant has found that these crystals or other segregates, which for the most part apparently are a brittle compound represented by the formula Cu_3Sn_8 and brittle compounds or mixtures containing a higher phosphorus content than other portions of the metal, form with the remaining tougher metal of the casting galvanic couples, which couples at the surface of the casting, when said surface is exposed to the action of corrosive media, form foci for initiation of corrosion of the metal, resulting, when the metal is subjected to vibration, bending, shock or other strains, in the corrosion working ino the metal along the boundaries of these crystals or segregates. This defect is so pronounced under such conditions that the alloy is markedly subject to pitting, and to breakage or other failure, when subjected to a combination of corrosive action and stress, particularly the stresses occasioned by the repeated bending or other flexure to which an article made of the metal is commonly subjected when in use.

Applicant however has found, that by properly proportioning the tin and phosphorus to each other and to the copper, the cast metal may be worked, by operations and treatments hereinafter described, into the form of strips and slabs in which these crystals or other segregates of different chemical composition from the rest of the metal are eliminated by dissolving them into the rest of the metal to form a single solid solution of copper, tin and phosphorus. By having all the metal in the form of such a solution, the above mentioned galvanic couple effects are entirely eliminated despite the metal, largely considered, being an aggregation of crystals, for when the deleterious crystals or segregates are eliminated all the crystals are of the same chemical composition and each is of uniform chemical composition. In this way full advantage may be taken of the action of the phosphorus in increasing the resistance to corrosion, and a metal obtained having a resistance to corrosion markedly greater than that of the cast ternary alloy.

This increase in the corrosion resistance obtained by eliminating the above mentioned deleterious segregates by dissolving them into the rest of the metal is particularly marked because, at the same time, the resistance of the strip to any stress to which it may be subjected also is increased by the working of the metal, which working acts to decrease the size of the "grains" or crystals of the metal and intimately interlock them. On account of its increase in resistance to stress and to chemical corrosion per se the improved product is particularly useful in situations where it is subjected to so-called "stress corrosion," that is to say, to stress and to the action of a corrosive medium under conditions such that the stress tends to cause the material mechanically to open up minutely and permit the corrosive medium gradually to eat into it.

The metal of the improved strips according to the invention contains approximately 5 to 10% tin, 0.1 to 0.5% phosphorus, with the balance substantially all copper. The addition of small amounts of other metals such as vanadium, lithium, calcium, boron, manganese and similar

scavenging and deoxidizing agents however is not precluded so long as they do not materially eliminate the characteristic corrosion resisting properties imparted by the combination of copper, tin and phosphorus.

The three constituents of the basic ternary alloy may be melted and mixed according to usual metallurgical practice, the phosphorus being introduced preferably in the form of phosphor-copper or phosphor-tin. To prevent burning off of the phosphorus, or it going off with the slag, the molten metal, while being handled, is preferably covered by a molten layer of neutral flux such as a mixture consisting of 50% each of fused borax and diatomaceous earth. In pouring the metal into the mold preferably the metal is poured in a known way from beneath this layer of flux so as to prevent the flux entering the mold.

Generally speaking, the present process consists in forming a casting of the above mentioned composition and hot extruding it materially to reduce its cross-sectional area and then alternately elongating the extruded shape and heat treating it, the elongating of the shape being performed by cold rolling it. The hot extrusion, which it has been found causes solution of a material part of the deleterious segregates, so conditions the metal that substantially complete solution of all these segregates may be effected with ordinarily no more than two cold rolling operations. Although applicant has found it is possible to cause this solution of the segregates wholly by alternate elongation and heat treatment, the present process effects marked economic savings over such operations in that it permits the solution to be effected with a minimum of working of the metal, and without the necessity of scalping or otherwise machining the surface of the casting to remove imperfections, and in many cases with less total reduction of the casting. These advantages will be appreciated from the fact applicant has found that when alternate cold rolling and heat treatment alone are employed not only is it necessary preliminarily to remove the surface imperfections of the casting but a total of at least six cold reductions, each of the same amount as with the present method, ordinarily will be necessary, which large number of reductions in some cases is economically prohibitive and in others mechanically impossible.

In making the strips according to the improved method, the metal mixture conveniently, but without limitation thereto, is cast in the form of a cylindrical billet, for example, but without limitation thereto, one about 6 to 9 inches in diameter and about 70 inches long. This billet may then be sawed into shorter lengths, for example about 12 inches, adapted for use in the extrusion press, the end portions of the original billet preferably being discarded. A short billet, so formed, may then be heated to about 1150 to 1250° F. (about 620 to 680° C.), and, while at that temperature, all but the outer surface portion and the butt end of the billet may be expressed through the die opening of the press, the shape of this opening preferably being such as to cause the extruded metal to be in the form of a slab of rectangular cross-section to adapt it for the subsequent cold rolling steps. At this temperature approximately maximum plasticity of the billet is secured, and most of the undesired segregates are at about their melting point or just under it, there being some tendency of the segregate considered as a whole to melt. The mass of the metal, being a solid solution of copper, tin and phosphorus of the composition represented by the proportions of these elements added to the melt, is well below its melting point although in a highly plastic condition.

To secure best results the size of the die opening of the extrusion press ordinarily should be such that the cross-sectional area of the extruded slab represents a reduction of about 60 to 92% in the cross-sectional area of the billet. For example, the billet may be reduced in this way to form a slab which in cross-section is about 1 inch thick and 4 inches wide, representing a reduction of about 89% in the cross-sectional area of a 7 inch diameter billet when all but a surface layer about 0.1 of an inch thick is expressed through the die. A reduction of 60 to 90% in the cross-sectional area of the billet will ordinarily result in solution of about 60 to 70% of the undesired segregates, apparently caused by the flowing of the metal through the die opening with the segregates at a temperature at or slightly below their melting point. Complete solution, however, it has been found cannot ordinarily be effected by any increase in reduction caused by reducing the size of the die opening within the limits possible to be employed.

The outer portions of the cast billet ordinarily are imperfect and liable to contain impurities, and thus by not expressing those portions through the die these impurities are eliminated from the extruded slab. Although it is possible, as hereinbefore mentioned, to remove these imperfections and impurities by scalping or otherwise machining the billet prior to extruding it, such operation because of its cost ordinarily would be economically undesirable.

The slab formed by extrusion may then be passed, while cold, through the rolls of a metal rolling mill. The particles of deleterious segregates present, which have been decreased in size by reason of the dissolving action on them during the extrusion process, are brittle at room temperature and thereabout, and the mechanical action of the rolls acts to crush and divide them and to elongate the metal, which elongation acts to diffuse or separate broken up particles. As a result of this breaking and diffusion of the brittle segregates their further solution may be effected as a result of subsequent heat treatment to which the slab is subjected before further cold rolling.

The slab after being cold rolled as above described may then be heated, preferably in an annealing furnace. The nature of the metal of the slab is such that it has been found it can be heated to a temperature which is above the annealing temperature of the bulk of the metal yet below, although close to, the melting temperature of the deleterious constituents, and that at that temperature the segregates will dissolve into the bulk of the metal. By heating it to that temperature and maintaining it thereat for a considerable period a large portion of the broken up and diffused segregates will be so dissolved and the slab will be annealed to condition it for further cold rolling.

By repeating the elongating and heat treating operations the segregates can be practically all dissolved, provided the metal is sufficiently reduced in thickness as a result of each elongating operation. Ordinarily, if the metal is reduced in thickness about 20 to 25% by the elongation effected by each cold rolling, only two such re-

ductions, each followed by a heat treating operation, will be necessary to secure complete solution. In no case that has come to applicant's attention will more than two such reductions be necessary if the reduction by hot extrusion amounts to about 80%, or more.

As a result of the above operations, the 1 x 4 inch slab coming from the extrusion press in the above example would be reduced to a strip or slab about nine-sixteenths of an inch thick if each of the two cold rollings sufficiently elongates the metal to reduce its thickness about 25%.

If desired, the metal, after the segregates are dissolved, can be readily reduced to form thinner strips by cold rolling, or alternate cold rolling and annealing, in the usual manner, but under such conditions much greater reductions in thickness may be made between anneals, say in the order of 65%, because of the absence of segregates which when present act to make the metal brittle. In other words, the nine-sixteenths inch strip or slab of the above example could be reduced to one about three-sixteenths of an inch thick by one pass through the rolls. In practice satisfactory strips about 0.02 of an inch thick have been made.

In performing the above mentioned cold rolling operations on the slab coming from the extrusion press the cross-section of the metal could be reduced to the maximum extent that can be secured without fracture of the metal, so as to secure a maximum breaking up or division of the segregates and their diffusion, it being understood that cold rolling causes embrittlement of the bulk of the metal and will cause it to fracture, especially along its edge portions. if too great a reduction in cross-section is attempted without annealing it to condition it for further cold rolling. However, the commercial significance of increasing the reduction by cold rolling over about 25% would be very slight, and two cold rollings in any ordinary case would be necessary to secure the desired results.

Geometrically the effect of cold rolling the slab longitudinally thereof is to increase its length without substantially increasing its width or reducing its volume. Ordinarily such elongation as will reduce the thickness of the extruded metal about 30% is the maximum that can be obtained during the first cold rolling with assurance that there will be no fractures in the metal, although a slightly greater reduction, say about 35%, can be made as a result of the second cold rolling. Preferably, for economic reasons, each reduction is made in one pass of the slab through the rolls. Smaller reductions in thickness than about 20% could be employed, but ordinarily they would necessitate a disproportionately unfavorable increase in the total number of cold rolling and heat treating operations, and reductions of less than about 20% do not seem effectively to break up the segregates throughout the entire thickness of the slab unless the latter is rather thin, in which latter case reductions as low as about 10% may sometimes be made. However, as above mentioned, it has been found, that after the copper-tin segregates are practically all dissolved, the strip can be reduced by cold rolling as much as 65% without fracture or it being necessary to anneal it to condition it for further cold rolling.

In respect to dissolving the segregates by heat treatment after each cold rolling effective results will be obtained if the rolled metal is heated to about 550 to 650° C. and maintained at that temperature from 60 to 90 minutes, the time depending upon the thickness of the cold rolled metal, the greater the thickness the longer the time necessary to secure maximum solution of the segregates. Longer times than 90 minutes do not seem to result in any increase in the amount of segregate dissolved. Shorter times than those specified could be employed in some cases, but would increase the total number of rolling operations necessary, and in many instances would make it impossible to secure practical total solution of the segregate especially if small reductions in the cross-sectional area of the slab were caused by the rolling operations.

The elimination of the segregates to a satisfactory degree can be determined by polishing and etching the surface of a specimen of the metal in the usual manner and examining it at 75 diameters with a metallurgical microscope. Absence of segregates when the metal is so examined indicates that it has been dissolved to a satisfactory degree even though traces of them may be observed at higher magnifications.

The strip made as above described, it has been found, possesses the requisite toughness, tensile strength, and shock and abrasion resisting properties to enable it to stand up when subjected to combinations of stress and corrosion. The solution of the segregates enables full advantage to be taken of the phosphorus in resisting corrosion, while the mechanical properties just mentioned act markedly to prevent any corrosion which may occur from working into the metal at its grain boundaries or along any minute cracks or surface scores that may exist therein, for example, those occurring as the result of abrasion. In all these respects the metal of the strip is markedly better than that of the casting, and may be machined with greater ease and less wear on the tools. Further, the strip may be cold worked by bending, pressing, etc., to form various machine parts and other articles, which cannot be done with the metal of the casting because of the segregates rendering it brittle and refractory.

It will thus be understood that the above described method readily adapts itself to the equipment and facilities commonly possessed by nonferrous mills, and that any of the above mentioned elongations made by rolling the strip need not be made in one operation, for example, if the equipment employed demands it, each elongation may be made, for instance, in two rolling steps, and the material in such case need not be heat treated until after each second step. It will also be understood that the elongating steps, if desired, may involve rolling the material to elongate it transversely as well as longitudinally, for example, if the extruded slab is 4 inches wide and a final strip 4.5 inches wide is desired, the first or first and second rolling operations may comprise passing the slab transversely through the rolls to cause it to be about 4.5 inches wide before it is further reduced by passing it longitudinally between the rolls, it being understood that the rolling operation, although elongating the slab or strip in the direction in which it is rolled, does not cause any material elongation in its dimension axially of the rolls. Each transverse rolling operation may be followed by the same heat treating operation as the longitudinal rolling operations, and preferably is followed by it if the transverse rolling involves reducing the material about 20 to 25%.

It will be understood that, within the scope of

the appended claims, wide deviations may be made from the forms of the invention above described without departing from the spirit of the invention. In these claims, both the strip and the slab made according to the improved method, from which slab the strip may be made by further cold rolling, or cold rolling and annealing, in the usual manner as above described, are for convenience in terminology called "strip."

I claim:

1. The method of making corrosion resistant phosphor-bronze strip from a cast metal containing 5 to 10% tin, 0.1 to 0.5% phosphorus, balance substantially copper, and having secondary mixtures of two or more of these constituents existing as segregates in the metal, which comprises die expressing the cast metal at elevated temperature through an opening of such size as will materially reduce its cross-sectional area, cold rolling the extruded metal to elongate it to such an extent as will materially reduce its cross-sectional area, heating the cold rolled metal to about 550 to 650° C. and maintaining it at that temperature for a substantial period of time, and repeating the cold rolling and heat treating operations specified until all the copper, tin and phosphorus in the metal exist substantially as a single solid solution.

2. The method of making corrosion resistant phosphor-bronze strip from a cast metal containing 5 to 10% tin, 0.1 to 0.5% phosphorus, balance substantially copper, and having secondary mixtures of two or more of these constituents existing as segregates in the metal, which comprises die expressing the cast metal at elevated temperature through an opening of such size as will reduce its cross-sectional area about 60 to 92%, cold rolling the extruded metal to elongate it to such an extent as will reduce its cross-sectional area about 10 to 35% without fracturing the metal, heating the cold rolled metal to about 550 to 650° C. and maintaining it at that temperature for a substantial period of time, and repeating the cold rolling and heat treating operations specified until all the copper, tin and phosphorus in the metal exist substantially as a single solid solution.

3. The method of making corrosion resistant phosphor-bronze strip from a cast metal containing 5 to 10% tin, 0.1 to 0.5% phosphorus, balance substantially copper, and having secondary mixtures of two or more of these constituents existing as segregates in the metal, which comprises heating the cast metal to about 620 to 680° C. and die expressing it while at such temperature through an opening of such size as will reduce its cross-sectional area about 80 to 92%, cold rolling the expressed metal to elongate it to such an extent as will reduce its cross-sectional area about 20 to 25%, heating the cold rolled metal to about 550 to 650° C. and maintaining it at that temperature for about 60 to 90 minutes, and repeating the cold rolling and heat treating operations specified until all the copper, tin and phosphorus in the metal exist substantially as a single solid solution as determined by absence of segregates when a polished and etched surface of the metal is microscopically examined at about 75 diameters magnification.

4. Forming strips by the method according to claim 1 comprising die expressing the cast metal through a die opening of such shape as will form a flattened slab adapted for passage through the rolls of a rolling mill.

5. Forming strips by the method according to claim 2 comprising die expressing the cast metal through a die opening of such shape as will form a flattened slab adapted for passage through the rolls of a rolling mill.

6. Forming strips by the method according to claim 3 comprising die expressing the cast metal through a die opening of such shape as will form a flattened slab adapted for passage through the rolls of a rolling mill.

7. Forming strips by the method according to claim 2 comprising die expressing the cast metal through a die opening of such shape as will form a flattened slab adapted for passage through the rolls of a rolling mill, the percentage of reduction effected by so die expressing the metal of the casting, and the percentage of reduction effected by each elongation of the slab by cold rolling, being such that the substantially single solid solution will be obtained as a result of the second heat treatment.

RICHARD A. WILKINS.