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PROCESS OF TREATING TIN BRONZE

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This invention relates to tin bronzes, and is directed particularly to the provision of an improved deoxidized tin bronze having a much higher endurance strength than it has been possible heretofore to attain in these alloys. Such bronze is produced, in accordance with the invention, by a method which involves subjecting it, after preliminary working and annealing operations, to severe plastic deformation, followed by a full recrystallization anneal at an exceptionally low temperature, and then by a moderate degree of cold working.

The tin bronzes to which the invention relates are deoxidized alloys of tin and copper which commonly contain a small residue of the deoxidizer, such for example as phosphorus, silicon, boron, sodium or lithium. The so-called Phosphor bronzes, in which phosphorus is the deoxidizer present in small residual amount, are perhaps the best known of these alloys. Phosphor bronze, like other deoxidized tin bronzes, is outstanding among non-ferrous metals for its combination of strength, hardness, resistance to corrosion, and fairly good electrical conductivity. Phosphor bronze is extensively employed for the manufacture of springs in the electrical industry, and it is also much used for making mechanical parts that are subjected to repeated flexure under corrosive conditions.

For many of the uses to which Phosphor bronze and other deoxidized tin bronzes are put, it is important that the metal have good endurance strength. As heretofore produced, the best grades of deoxidized tin bronze possess endurance strengths substantially less than 35,000 pounds per square inch at 10,000,000 cycles, and less than 30,000 pounds per square inch at 300,000,000 cycles. The ultimate endurance limit of the best commercial Phosphor bronzes heretofore made is probably less than 25,000 pounds per square inch.

In my copending application Serial No. 243,587, filed August 24, 1951 (of which this application is a continuation-in-part), I have described a method for producing deep drawn, cold headed, and similar brass articles by a method which involves applying suitable cold fabricating methods to an exceptionally fine grained brass produced by annealing severely worked metal at an unusually low temperature. I have now discovered that the method of preparing brass for deep drawing or cold heading, as described in my aforesaid copending application, can be applied to the manufacture of tin bronzes, and that deoxidized tin bronzes thus prepared (especially after being cold worked) have notably greater endurance strength than corresponding bronzes produced by the methods heretofore employed for their manufacture.

Based on the foregoing discovery, the present invention provides a method for making a deoxidized tin bronze having an endurance strength exceeding 40,000 pounds per square inch at 10,000,000 cycles, which comprises subjecting a bronze containing 1½% to 12% tin, 0.001% to 0.5% residual deoxidizer (phosphorus, silicon, boron, aluminum, manganese, magnesium, sodium and lithium are examples of suitable deoxidizers), and the balance

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essentially all copper, to cold working and then annealing at a temperature in the range from 500° C. to 600° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.045 mm., then subjecting the bronze to severe cold working sufficient to effect a reduction in cross-sectional area greater than 65%, then annealing the thus-worked bronze at a temperature of about 375° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.008 mm., and then subjecting the thus-annealed bronze at room temperature to substantial plastic deformation.

Preferably, in carrying out the method of the invention, the bronze is cold worked to effect a reduction in area of at least about 70% before subjecting it to the low temperature recrystallization anneal at about 375° C.; and the time of this low temperature anneal is kept short enough so that the average grain size is not increased to above about 0.005 mm. The final cold working of the thus-annealed bronze is advantageously sufficient to reduce its cross-sectional area by at least about 10%.

The cold worked deoxidized bronze product of the invention possesses a very fine grain structure corresponding to a ready-to-finish grain size averaging less than 0.008 mm., a yield strength of 0.1% offset exceeding 60,000 pounds per square inch, and a tensile strength above 65,000 pounds per square inch (above 70,000 pounds per square inch in the case of Phosphor bronzes generally and at least about 75,000 pounds per square inch in the case of Phosphor bronze alloys containing more than 0.1% phosphorus). The new product is particularly characterized by having a remarkably high endurance strength exceeding 40,000 pounds per square inch at 10,000,000 cycles, and at least about 40,000 pounds per square inch even at 300,000,000 cycles.

Any of the known deoxidized tin bronze alloys may be fabricated with advantage by the method of the present invention. These alloys in general may be defined as containing 1½% to 12% tin, 0.001% to 0.5% residual deoxidizer, and the balance essentially all copper. In the case of the commercially important Phosphor bronzes, the residual deoxidizer is of course phosphorus. Most commonly, the commercial Phosphor bronzes contain from 4½% to 8½% tin, from 0.1% to 0.35% phosphorus, and the balance essentially all copper. Typical commercial Phosphor bronzes are composed nominally of 5% or 8% tin, 0.25% phosphorus, and the balance copper of commercial purity.

By specifying that the bronze is composed of tin, residual deoxidizer, and the balance essentially all copper, I do not exclude the possibility that it may include minor amounts of additional metals, either by way of impurities or as intentional additions made to impart modified properties to the alloy. For example, 1% more or less of iron is sometimes included in these alloys. Alternatively (or additionally) the alloy may contain 1% or even more of lead to improve its machinability, or it may contain as much as 10% or 15% of zinc (especially when the tin content is low) to increase its strength and hardness. For purposes of this invention, these metals (in modest amounts) are the equivalents of a part of the copper. A fairly free-machining leaded Phosphor bronze composed nominally of 5% tin, 1% lead, 0.25% phosphorus, and the balance copper, and a low-tin Phosphor bronze containing 2% tin, 11% zinc, 0.25% phosphorus, and the balance copper, are examples of commercial phosphor bronzes normally containing metals in addition to tin, phosphorus, and copper to which the method of the invention may be applied. In addition to iron, lead and zinc, elements such as arsenic, nickel, selenium, and tel-

lurium are normal impurities in copper and may be present in the alloys of this invention in small amounts. The particular and detailed composition of the bronze alloy is not in itself a vital part of the invention, and the improved endurance strength which is attained by subjecting deoxidized tin bronze to the method of the invention can be secured whether or not these additional elements are present, as impurities or otherwise, in the alloy.

Preparatory to carrying out the method of this invention, the bronze is subjected to conventional rolling, drawing, or other primary working operations. The conventional working methods used for this purpose need not be described in detail. Generally they comprise melting the alloy, casting it into a wirebar, cake, or other suitable shape, and then reducing its cross-sectional area by rolling, wire drawing, or other conventional primary working operation. As the cross-sectional area of the metal is reduced by cold working, it becomes hardened and its capacity to be worked further is lessened. Accordingly, it is customary to anneal the metal from time to time during the course of the working operations, to restore it to a soft condition in which it can readily be further worked.

After the metal has been brought to the desired size, just before being reduced to its ready-to-finish size, it is given a somewhat lighter anneal than is customary by heating at a temperature in the range from 500° C. to 600° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the grain size to above 0.045 mm. (A full recrystallizing anneal of cold worked Phosphor bronze commonly is at a temperature of 700° C. to 800° C. for a time sufficient to effect grain growth to an average size of 0.050 to 0.090 mm.)

The term "average grain size" is used herein, in the manner customary in the art, to mean that the average diameter or equivalent dimension of a typical grain is of the size stated. The grains are of course very irregular in size and shape, but for the most part they are similar to one another in size and shape, and it is customary in referring to the average grain size to have reference to the most typical size that is found upon microscopic examination of the metal structure. In general, the estimation of grain sizes is herein contemplated to be in accordance with the methods set forth in A. S. T. M. Specification E79-49-T, entitled "Tentative Methods for Estimating the Average Grain Size of Wrought Copper and Copper Base Alloys."

The annealed metal, with its average grain size less than 0.045 mm., is then subjected to severe cold working (that is, to working at a temperature below the recrystallization temperature and generally at or near room temperature) sufficient to reduce its cross-sectional area by at least 65% and preferably by about 70% or more. The manner in which such cold working is effected is not in itself critical. It may be by rolling, or by drawing through dies, or by any other cold working method; and it may be performed in whatever number of successive rolling, drawing, or like operations is most convenient. However, it is done, its effect must be to reduce the cross-sectional area of the worked metal, without any intermediate anneals, by the amount stated.

At the conclusion of this cold working operation, the metal is at its ready-to-finish size and shape. Thus, if the metal has been prepared in sheet or strip form by a rolling operation, it will be at its ready-to-finish thickness when this cold working operation is completed; and if it has been prepared by drawing through dies, it will be in the form of rod or wire of the desired ready-to-finish diameter (or other dimension if the finished shape is non-circular).

The cold worked metal now is subjected to a very unusually light anneal by heating it at a temperature of about 375° C. for a sufficient length of time to effect substantially complete recrystallization of the metal, but to

do so without increasing the average grain size to above 0.008 mm., and preferably to do so without increasing the average grain size to above 0.005 mm. The time required for such annealing at the rather low temperature of 375°

C. is the same as is usually employed at a substantially higher temperature (say 500° to 550° C.) for full recrystallization of bronze to an average grain size of about 0.020 to 0.040 mm. Upon completion of this annealing operation, the bronze is found to have the tensile strength and hardness that is characteristic of cold finished metal rather than of annealed fully recrystallized metal. Its tensile strength is upwards of 55,000 pounds per square inch, and (especially in the case of Phosphor bronze alloys containing more than 0.1% of phosphorus) even above 60,000 pounds per square inch. Hardness of the alloy on the Rockwell "B" scale is above 50, and even 60 or higher in the case of alloys showing a tensile strength of 60,000 pounds per square inch or higher. The metal generally meets at least the minimum requirements of A. S. T. M. Specification B103-51 for phosphor bronze sheet and strip in the half-hard condition, even though it is fully recrystallized and has not yet been cold finished. It has, however, a substantially greater elongation than cold-finished metal, and is therefore substantially more ductile.

Following the above described low temperature anneal, the bronze is cold-finished by plastically working it sufficiently to reduce its cross-sectional area by at least 10%. Such cold finishing normally is accomplished by cold rolling (in the case of sheet or strip) or by wire drawing through dies (in the case of wire). The cold finishing operation results in markedly increasing the yield strength of the metal, to a value exceeding 60,000 pounds per square inch at 0.1% offset. For example, in the case of a commercial Phosphor bronze containing nominally 5% tin and about 0.25% phosphorus, the yield strength at 0.1% offset is about 46,000 pounds per square inch following the low temperature anneal, and is increased to above 70,000 pounds per square inch by cold rolling two B & S numbers hard. The tensile strength of the alloy also is increased by the cold finishing operation to a value of at least 70,000 pounds per square inch, and generally to a value of 75,000 pounds per square inch or more when over 0.1% residual phosphorus is present.

The resulting cold finished bronze is characterized by possessing an exceptionally high endurance strength. The endurance strength at 10,000,000 cycles exceeds 40,000 pounds per square inch, whereas a typical Phosphor bronze of substantially equal tensile strength and hardness produced in accordance with conventional rolling and annealing schedules has an endurance strength of only about 32,000 pounds at 10,000,000 cycles. At 300,000,000 cycles, the endurance strength of bronze produced in accordance with the invention is even more outstanding, being still at least about 40,000 pounds per square inch. A conventionally prepared Phosphor bronze of the same composition has an endurance strength of only 30,000 pounds per square inch, or less, at 300,000,000 cycles.

It appears that the S-N curve (prepared by plotting applied stress, as ordinates, against number of bending cycles required to produce fracture, as abscissae) for a typical Phosphor bronze prepared in accordance with the invention becomes substantially horizontal somewhere in the range between 1,000,000 and 10,000,000 cycles, at a stress value above 40,000 pounds per square inch. This indicates that Phosphor bronze produced according to the invention has a true endurance limit in excess of 40,000 pounds per square inch (that is, it seems capable of withstanding an indefinite number of reverse bends at an applied stress of 40,000 pounds per square inch). The S-N curve for a conventionally produced Phosphor bronze, on the other hand, does not show any tendency to become horizontal even at 300,000,000 cycles, so if such metal has any true endurance limit, it is probably less than 25,000 pounds per square inch.

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Following is a specific example of the production of Phosphor bronze strip in accordance with this invention: A Phosphor bronze alloy composed nominally of 5% tin, 0.25% phosphorus, and the balance copper was melted in the usual manner and cast into the form of a cake for rolling. Analysis of the cast cake showed it to contain 4.50% tin, 0.24% phosphorus, 95.07% copper, 0.15% zinc, and 0.04% of other impurities (this latter figure being obtained by difference). The cast cake was rolled, with intermediate anneals, in accordance with conventional rolling practice, to a bar having a thickness of 0.158 inch. At this thickness the bar was annealed at 550° C. for two hours. The grain size of the annealed metal was found to be 0.020 mm. The annealed bar was then cold rolled to 0.050 inch, a reduction in cross section of almost 70%. The thus severely cold rolled metal was then annealed for two hours at a temperature which was maintained as closely as practical at 375° C. and which did not at any time exceed 400° C. The metal was substantially completely recrystallized by this anneal, and after annealing was found to have a grain size of approximately 0.007 mm. The resulting lightly annealed metal, now at ready-to-finish size, was cold rolled approximately 2 B & S numbers to 0.040 inch (reduction in cross-sectional area of 20%). Conventional tensile and hardness tests made on the resulting product showed the metal to have a yield strength at 0.5% extension of 74,000 pounds per square inch, a tensile strength of 81,700 pounds per square inch, an elongation of 17% over a gauge length of two inches, and a Rockwell "B" hardness of 89. These strength and hardness values are about the same as for Phosphor bronze of the same composition which has been rolled in accordance with conventional rolling and annealing schedules, and has been finished by cold rolling 4 B & S numbers hard; but the elongation is considerably greater than for such conventionally prepared Phosphor bronze. Ten samples of the exemplary alloy, without any surface preparation of the mill-finished strip, were subjected at various applied stresses to fatigue tests in a cantilever beam type of testing machine, with a complete reversal of stress during each bending cycle. The test results, upon being plotted in a conventional S-N curve, indicated that the endurance strength of the metal at 10,000,000 cycles was approximately 42,000 pounds per square inch, and that the endurance strength at 300,000,000 cycles was substantially in excess of 40,000 pounds per square inch.

The uncommonly high endurance strength of deoxidized bronzes such as Phosphor bronze prepared in accordance with the invention renders them especially suitable for the manufacture of springs and similar parts which in normal service are subjected to repeated flexure. Such parts, when made of Phosphor bronze or other deoxidized bronze prepared as herein described, can be operated reliably for prolonged periods of time at higher stresses than have heretofore been possible. The high endurance strength of the new bronze also makes it eminently suited for the manufacture of parts which in normal service are subjected to extensive vibration. When such parts are made of bronze prepared in accordance with the invention, they can be notably more highly stressed without danger of failure than corresponding parts made from a corresponding bronze product prepared by methods heretofore known.

An incidental advantage to the fabricating mill of the method of preparing Phosphor bronze and other deoxidized bronzes according to the invention resides in the fact that less mechanical working is required in the cold finishing operation than is necessary to produce a deoxidized bronze of equivalent hardness and tensile strength by the fabricating procedures heretofore employed. In general, the cold finishing operation of the method of the invention need involve only about half the reduction in area that would have to be effected in order to develop the same tensile strength and hardness in a bronze of identi-

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cal composition prepared by the procedures heretofore conventional in the manufacture of Phosphor bronzes. Thus to produce a typical Phosphor bronze strip having a tensile strength of 80,000 pounds per square inch and a Rockwell "B" hardness of 85 to 90 by the rolling and annealing schedules heretofore customarily employed requires cold rolling, after the final anneal, sufficient to reduce the gage of the metal by at least 4 B & S numbers (i. e. to effect a reduction in area of at least about 37%). On the other hand, in preparing Phosphor bronze according to this invention, the metal after being given the full recrystallization anneal at about 375° C. would have to be cold finished by rolling only 2 B & S numbers (i. e. effecting a reduction in cross-sectional area of only about 20%) to develop substantially the same tensile strength and hardness. In consequence, the extent to which the metal must be handled in bold finishing in accordance with the invention is substantially simplified as compared with producing corresponding metal (but with lower endurance strength) by the methods heretofore conventionally employed.

I claim:

1. The method of producing a deoxidized tin bronze having an endurance strength exceeding 40,000 pounds per square inch at 10,000,000 cycles, which comprises subjecting a bronze containing 1½% to 12% tin, 0.001% to 0.5% residual deoxidizer, and the balance essentially all copper to cold working and then annealing at a temperature in the range from 500° C. to 600° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.045 mm., then subjecting the bronze to severe cold working sufficient to effect a reduction in cross-sectional area greater than 65%, then annealing the thus-worked bronze at a temperature of about 375° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.008 mm., and then subjecting the thus-annealed bronze substantially at room temperature to plastic deformation sufficient to reduce its cross-sectional area by at least 10%.

2. The method of making a deoxidized tin bronze strip having an endurance strength exceeding 40,000 pounds per square inch at 10,000,000 cycles, which comprises subjecting a bronze bar containing 1½% to 12% tin, 0.001% to 0.5% residual deoxidizer, and the balance essentially all copper to cold rolling and then to annealing at a temperature in the range from 500° C. to 600° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.045 mm., then subjecting said bar to severe cold rolling sufficient to effect a reduction in cross-sectional area of at least about 70%, then annealing the thus-worked bronze bar at a temperature of about 375° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.005 mm., and then cold rolling the thus-annealed bronze bar at room temperature to an extent sufficient to reduce its cross-sectional area by at least 10%.

3. The method of producing a deoxidized tin bronze wire having an endurance strength exceeding 40,000 pounds per square inch at 10,000,000 cycles, which comprises subjecting a bronze rod containing 1½% to 12% tin, 0.001% to 0.5% residual deoxidizer, and the balance essentially all copper to cold working and then to annealing at a temperature in the range from 500° C. to 600° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.045 mm., then subjecting said rod to severe cold drawing sufficient to effect a reduction in cross-sectional area of at least about 70%, then annealing the thus-worked bronze rod at a temperature of about 375° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.005 mm., and then cold

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drawing the thus-annealed bronze rod at room temperature to an extent sufficient to reduce its cross-sectional area at least 10%.

4. The method of producing Phosphor bronze having an endurance strength exceeding 40,000 pounds per square inch at 10,000,000 cycles, which comprises subjecting a bronze containing 1½% to 12% tin, 0.001% to 0.5% phosphorus, and the balance essentially all copper to cold working and then annealing at a temperature in the range from 500° C. to 600° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.045 mm., then subjecting the bronze to severe cold working sufficient to effect a reduction in cross-sectional area greater than 65%, then annealing the thus-worked bronze at a tem-

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perature of about 375° C. for a sufficient period of time to effect substantially complete recrystallization without increasing the average grain size to above 0.008 mm., and then subjecting the thus-annealed bronze substantially at room temperature to plastic deformation sufficient to reduce its cross-sectional area by at least 10%.

5. A deoxidized tin bronze prepared in accordance with the method set forth in claim 1.

6. A Phosphor bronze prepared in accordance with the method set forth in claim 4.

References Cited in the file of this patent

UNITED STATES PATENTS

2,676,123

Gregory ----- Apr. 20, 1954