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3,287,180<br>METHOD OF FABRICATING COPPER BASE ALLOY George H. Eichelman, Jr., and Irwin Broverman, Cheshire, Conn., assignors to Olin Mathieson Chemical Corpora-No Drawing. In the Hon, a corporation of Virginia<br>No Drawing. Filed Dec. 5, 1963, Ser. No. 328,184<br>13 Claims. (Cl. 148-11.5)

The present invention relates to improved aluminum<br>bronze alloys and to the preparation thereof. More parbronze alloys and to the preparation thereof. More particularly, the present invention resides in novel and inexpensively prepared alloys containing from 9.0 to 11.8 percent aluminum and the balance essentially copper, said alloys being prepared in such a manner as to be characterized by physical properties heretofore unattain of the present invention attain surprisingly high tensile strengths combined with high ductility. This combina tion of properties provides superior toughness and form ability. In addition, the novel alloys of the present invention have reasonably good electrical conductivity plus good brazability, solderability, weldability, corrosion resistance, stress corrosion resistance, and fatigue strength. able in alloys of this type. For example, the novel alloys <sup>15</sup> 20

The novel and inexpensively prepared alloys of the present invention readily attain a combination of strength present invention readily attain a combination of strength  $25$ <br>and ductility heretofore unattainable in these alloys, for example, tensile strengths ranging from 110,000 to  $120,000$  p.s.i. and yield strengths ranging from  $44,000$  to  $52,000$  p.s.i. at 0.2 percent offset in combination with elongations ranging from 9 to 12 percent. In addition, electrical conductivity values ranging from 14 to 16 percent I.A.C.S. are attained. Properties of this type approximate those provided by the relatively expensive<br>beryllium-copper alloys. A lower cost series of alloys<br>exhibiting properties similar to the relatively expensive<br>beryllium-copper alloys, such as provided in accordance with the present invention, would therefore, find wide application in a wide variety of fields, as a replacement for beryllium-copper in the manufacture of electrical springs, contacts, and diaphragms. In fact, considerable  $_{40}$ effort has been expended in the art, heretofore unsuccess ful, to develop such a lower cost substitute for beryllium copper. 30 35

Alloys exhibiting the foregoing properties would also tend to replace lower cost copper base alloys having lower strengths. In addition, these alloys would tend to replace a variety of other copper base alloys which are in a lower price range than beryllium-copper, e.g. Phosphor bronze.

The alloys of the present invention are extremely versa tile and have a wide variety of other uses exemplificative  $50$ of which are: corrosion resistant parts, such as condenser tubes and valves; metal bellows; heat resistant parts in which resistance to corrosion at high temperature is re quired, such as parts for internal combustion engines; wear resistant parts; and metal forming dies. 55

Accordingly, it is an object of the present invention to provide new and improved aluminum bronze alloys and methods for the preparation thereof.

It is a further object of the present invention to provide properties heretofore unattainable in alloys of this type, and especially possessing a greatly improved combination of yield strength, tensile strength and ductility. an alloy as aforesaid which is characterized by physical  $60$ 

It is a still further object of the present invention to provide an alloy as aforesaid which attains these greatly improved physical properties without degradation of other properties so desirable in alloys of this type. 65

It is a still further object of the present invention to provide an alloy and process as above conveniently, ex

Further objects and advantages of the present invention will appear hereinafter.

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In accordance with the present invention it has now been found that the foregoing objects and advantages of the present invention may be readily accomplished. The process of the present invention comprises: hot working an alloy containing from 9.0 to 11.8 percent aluminum and the balance essentially copper at a temperature of from  $1850^\circ$  F. to  $1000^\circ$  F.; and cold working said alloy at a temperature of below 500° F.<br>The improved aluminum bronze alloy of the present

invention contains from 9.0 to 11.8 percent aluminum and the balance essentially copper. In addition the im proved alloy of the present invention has a metallographic structure containing from 5 to 95 percent beta phase and the remainder alpha phase. The present alloy also has a uniformly fine metallographic grain structure with a grain size less than 0.065 mm.

The alloys of the present invention contain from 9.0 to 11.8 percent aluminum and the balance essentially copper. The aluminum content must critically be within the aforementioned range and preferably is within the more limited range 9.4 to 10.4 percent aluminum and optimally is between 9.8 and 10.0 percent aluminum. The remainder or balance of the alloy is essentially copper, i.e., the alloy may contain incidental impurities or other materials which do not materially degrade the physical characteristics of the alloy. Examples of such elements which can be present include tin, zinc, lead, nickel, silicon, silver, phosphorus, magnesium, antimony, bismuth, and arsenic.

The alloy of the present invention is prepared in accordance with the foregoing critical combination of steps to provide the surprisingly improved composition of the present invention.

45 from entrained aluminum oxide. The first critical step in the process of the present inven tion is the hot working step in the aforementioned critical temperature range. Preparatory to the hot working step the alloy may naturally be melted and cast in a suitable bar or ingot form using conventional practices to insure compositional and structural homogeneity. For exam ple, cathode copper may be induction melted under a charcoal cover. High purity or commercial aluminum in the requisite quantity may then be added and the melt thoroughly stirred to insure adequate mixing. The molten charge may then be cast by any commercial method which will insure a sound cast structure that is essentially free

The foregoing is, of course, intended to be illustrative and not restrictive. It is only necessary that there be provided a homogeneous, sound and clean aluminum bronze alloy satisfying the foregoing compositional re quirements, i.e., containing from 9.0 to 11.8 percent alu

minum and the balance essentially copper.<br>As stated above, the alloy is hot worked in the fore-As stated above, the alloy is hot worked in the foregoing temperature range. The term hot working is employed in its conventional sense, although, in accordance with the present invention hot rolling is the preferred operation and the present process will be described in more detail with reference to this preferred mode of operation. Naturally, other methods of hot working will readily suggest themselves to those skilled in the art, e.g., forging and extrusion.

The manner of bringing the material into the hot roll ing temperature range is not critical and any convenient heating rate or method may be employed.

The temperature of hot rolling is, as stated above, from 1850° F. to 1000° F., with it being preferred to utilize a narrower temperature range of from  $1650^\circ$  F. to  $1000^\circ$ F.

In the process of the present invention, the as cast ma terial may simply be heated up to the starting temperature. The time at temperature is not critical and generally the casting is simply held long enough to insure

uniformity of temperature. We then may hot roll direct ly from this temperature. During rolling of the ingot, some cooling occurs through natural causes. It is not necessary to maintain the ingot at any one starting temperature. In fact, it is preferred not to maintain the ingot  $\overline{B}$ perature. In fact, it is preferred not to maintain the ingot at any one starting temperature since, as the material cools alpha phase continuously precipitates and the series of reductions at progressively lower temperatures results progressively in structural refinements. In other words, progressively in structural refinements. In other words, it is preferred to commence the hot rolling at the more 10 elevated temperatures in the hot rolling temperature range and gradually decrease the temperature in order to refine the grain structure.

The length of time of hot rolling is not critical. The alloy may, if desired, be hot rolled until reaching the 15 lower temperature in the hot rolling temperature range, i.e., 1000° F.

It is an advantage of the alloy of the present invention that the hot rolling characteristics thereof are at least as such as 70-30 brass, i.e., with respect to, for example, power consumption and amount of reduction per pass. good as those of much lower strength copper base alloys, 20

Subsequent to hot rolling the alloy contains the maximum amount of alpha phase possible as governed by the phase equilibrium for the particular composition. This 25 is accomplished by insuring that the alloy, either during or subsequent to hot rolling, is held in the temperature range of 1050 to 1100° F. for at least two minutes. This may be done in a variety of ways either during the hot rolling or by a thermal treatment subsequent thereto. For 30 example, the alloy may be cooled slowly through this tem perature range during the normal course of hot rolling or reheated to a temperature of from 1050 to 1100 $^{\circ}$  F. upon completion of hot rolling and held there for at least<br>two minutes and preferably longer. 35

Subsequent to the hot working step the alloy is cold worked at a temperature of below  $500^{\circ}$  F., and preferably from 0 to 200° F.

The term cold working is employed in its conventional sense, although, in accordance with the present invention 40 cold rolling is preferred and the present process will be mode of operation. Naturally, other methods of cold working will readily suggest themselves to those skilled in the art, for example, drawing, swaging, and cold forging 45

It is especially surprising and unexpected that the alloys of the present invention can be readily cold worked, for example, within the optimum compositional range (9.8 to 10.0 percent aluminum) cold rolling reductions as high as 50 percent are attained, and even higher reductions of 50 over 50 percent aluminum are attained within the broad compositional range (9.0 to 11.8 percent aluminum) toward the low aluminum end.

This surprising and unexpected ability permits the in utilizing this composition. Particularly important is that these alloys can now be made commercially available in light gage, coiled strip or sheet form. Such products fill a significant commercial need and have heretofore not 60

The particular method of cooling the alloy to cold rolling temperature is not critical and any convenient method may be employed at any convenient cooling rate, for ex ample, the alloy may be spray quenched, cooled in water or air cooled.

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The reduction effected during the cold rolling step is dependent upon many factors. If no additional rolling steps are to be performed, the alloy may be cold rolled to final gage. The exact percentage reduction in the cold rolling is not critical, with the percentage and number of 70 cold rolling steps dependent upon manufacturing econom ics. If desired, in order to minimize the cold rolling reduction, the alloy may be reheated within the specified hot rolling range and be further reduced to a smaller thickness for cold rolling.

If desired the alloy may be supplied in this cold rolled form, i.e., temper rolled.

After the desired reduction has been effected in the cold rolling step, the alloy may be annealed at a temperature of from  $1000^\circ$  F. to  $1400^\circ$  F., preferably from  $1000^\circ$  F. to 1100° F. and optimally from 1050° F. to 1100° F. As the annealing temperature is increased, the amount of beta phase increases and if subsequent cooling doesn't precipitate the maximum amount of alpha phase, the amount of reduction on subsequent cold rolling is reduced.

The particular method of reheating the alloy to this ele vated temperature is not especially critical and any convenient heating procedure may be employed. The alloy should be held at this elevated temperature for at least two minutes.<br>In the preferred embodiment the cold rolling and an-

nealing steps are repeated, preferably a plurality of times.<br>Optimum results have been found at three cycles of cold rolling and annealing. The practice of the present invention, and in particular the three cycles of cold rolling and annealing, effectively develops a fine grained structure. It of a superior combination of strength and ductility in these alloys. If desired the alloy may be supplied in the as an-<br>nealed condition also having a fine grain size. This form provides the maximum formability.<br>The process of the present invention is extremely versa-

tile and a great many variations will readily suggest them selves to those skilled in the art. For example, the alloy may be heat treated after cold rolling at  $1100^\circ$  F, to  $1800^\circ$ F. followed by rapid cooling. The temperature of heat treating varies inversely in relation to the aluminum con tent, i.e., the lower the aluminum content the higher the temperature of the heat treatment. For the composition containing the optimum amount of aluminum, the heat treatment temperaure is  $1500^\circ$  F. to  $1650^\circ$  F. The time at temperature is immaterial, it being necessary only to allow sufficient time to insure uniformity of temperature. After heat treatment the alloy is rapidly cooled below at least 1000° F.; thereafter, the rate of cooling is not critical. The preferred mode of cooling is to cool in water, how ever, the alloy may also be oil quenched or cooled in circulating air.<br>The heat treatment converts most of the alloy to the

beta phase. In the rapid cooling, the alloy retains a high proportion of beta phase and the beta phase undergoes a structural transformation known as a martensitic trans and results in an alloy having an excellent combination of strength and ductility. Thus, this combination of heat treatment and rapid cooling will be termed a "betatizing" procedure.<br>In the rapid cooling, it is necessary only that the alloy

This surprising and unexpected ability permits the in-<br>troduction of a whole new class of commercial products 55 though the alloy may be rapidly cooled to a lower tembe cooled rapidly at least to below 1000° F., i.e., to at least below the eutectoid transformation temperature, although the alloy may be rapidly cooled to a lower tem-

perature if desired.<br>Still greater improvements may be attained by a tempering procedure following betatizing. This results in still better strength, principally yield strength. It is accomplished by holding the alloy for at least 30 minutes at a temperature of from  $500^{\circ}$  F. to  $900^{\circ}$  F. and preferably from 600 to 750° F. Still further improvements in strength may be had by cold rolling either prior to or subsequent to tempering.<br>Another modification of the present invention is to

form the annealed alloy into component shapes taking advantage of its excellent formability. The alloy is then heat treated in the formed shape to high strength levels. This is particularly useful in, for example, bellows and diaphragms.<br>Another modification is to form the annealed or temper

to 1700 F., during which treatment the part is automat-<br>75 ically converted to a high proportion of beta phase and rolled alloy into the desired shape. The formed part is then joined by such a treatment as brazing at  $1400^\circ$  F. to  $1700^\circ$  F., during which treatment the part is automat-

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if subsequently rapidly quenched very high strength levels

Alternatively, subsequent to the brazing or heat treatment in the formed shape, further strength increases may be attained due to tempering. This may be accomplished by any subsequent treatment either by special thermal treatment or by additional joining, e.g., soldering, which is carried out in the tempering range.

As will be apparent, the process of the present inven tion is exceptionally versatile and numerous other modi fications will readily suggest themselves to one skilled in the art within the spirit of the present invention.

In accordance with the present invention it has been found that the simple and convenient process discussed above results in a new and improved aluminum bronze 5 alloy possessing highly desirable, and in fact surprising, physical properties heretofore unattainable in alloys of this type.

The alloy contains from 9.0 to 11.8 percent aluminum and the balance essentially copper. In addition, the alloy has a metallographic structure containing from 5 to 95 percent beta phase and the remainder alpha phase, preferably 85 to 95 percent beta phase. The alloy has a uniformly fine metallographic grain structure with a particle 25

size less than 0.065 mm.<br>The alloys of the present invention possess properties which are unexpected and surprising in alloys of this type, especially with regard to strength and ductility. For example, tensile strengths ranging from 110,000 to 120,000 p.s.i. and yield strengths from  $44,000$  to  $52,000$  p.s.i.  $(0.2)$ percent offset) may be developed in combination with elongations ranging from 9 to 12 percent. The electrical conductivities are good for alloys of this type, ranging from 14 to 16 percent I.A.C.S. In addition, modifications of the present invention improve the properties still further. For example, tempering increases the yield strength considerably, e.g., to from 80,000 to 95,000 p.s.i. at the expense, however, of ductility. In another modification consisting of cold rolling the alloy following an annealing operation, yield strength values as high as  $110,000$  p.s.i. and higher may be achieved together with tensile strengths as high as  $150,000$  p.s.i. 35 40

Still further, these properties are obtained with retention of the other desirable properties in alloys of this type, for example, good brazability, solderability, weldability, cor rosion resistance, stress corrosion resistance, and fatigue strength. 45

The present invention and improvements resulting there from will be more readily apparent from a consideration of the following illustrative examples.

#### Example I

Alloys containing 9.0, 10.0, 10.3, 10.5 and 11.1 percent aluminum and the balance essentially copper were made<br>from a charge of cathode copper and commercial purity 55 from a charge of cathode copper and commercial purity aluminum in the form of  $134''$  x  $134''$  x  $4½''$  chill cast-1ngS.

The alloys were hot rolled in the temperature range of from 1600 to 1300° F. Reductions of about 10 to 20 percent per pass were used in reducing the gage from 60 by the roll diameter, with reductions of as much as 30 percent per pass having been taken on alloys containing 10 percent or more aluminum having all beta structures at 1600 F. and therefore exhibiting maximum hot roll ability.

Following hot rolling, the alloys were betatized at 1100° F. for 30 minutes and subsequently air cooled for maximum cold rollability. In the low temperature, beta tized condition the 10 percent aluminum alloy, for example, exhibited a yield strength of 30,700 p.s.i., a tensile strength of 89,100 p.s.i. and 40.5 percent elongation.

Cold rolling of the 10 percent aluminum alloy 42 percent increased the properties of the 10 percent aluminum  $\overline{6}$  of 151,000 p.s.i. with a corresponding decrease in elongation to 2.5 percent. Cold rolling of the alloys containing 9.0 percent aluminum, 10.3 percent aluminum, 10.5 percent aluminum and 11.1 percent aluminum gave similar improvements, except the lower aluminum alloy had better ductility and slightly lower strength and the higher aluminum alloys had better strength and slightly lower ductility. All of the alloys had a uniformly fine metallo graphic grain structure with a grain size less than 0.065 mm. in diameter and contained a proportion of alpha to beta phase within the range of the present invention.

#### Example II

 $_{20}$  tained for each of the above alloys. The microstructures of the alloys, after the treatments of Example I, were further refined by cold rolling in three steps with intermediate annealing at 1100° F. after each cold roll. The gage was reduced from 0.100' to 0.050'. As a result of this cold rolling with inter anneals at 1100° F., grain sizes of about 0.020 mm. in diameter were ob

#### Example III

30 percent alumnum alloy exmolted a yield strength of  $53, -800$  p.s.i., a tensile strength of  $125,000$  p.s.i. and 8.5 per-Maximum tensile properties were developed in the al loys after the treatment of Example II by betatizing at suitably high temperatures to produce about 95 percent beta phase and 5 percent alpha phase. For the 10 percent aluminum alloy, maximum properties were obtained by betatizing at  $1525^\circ$  F. for 30 minutes followed by water quenching. As a result of this treatment, the 10 percent aluminum alloy exhibited a yield strength of 53, cent elongation. Further improvement in strength was accomplished by tempering at  $650^\circ$  F. for one hour. The yield strength of the 10 percent aluminum alloy was increased to  $98,600$  p.s.i., the tensile strength increased to  $127,000$  p.s.i. with a corresponding reduction in elongation to 1.5 percent. A full range of properties varying from those obtained by betatizing at  $1100^\circ$  F. to those obtained by betatizing at 1525° F. can be obtained by hot treatment alone.<br>Similar properties were otained in the other alloys by

achieving a comparable proportion of alpha and beta phase by suitable adjustment of the betatizing tempera ture.

### Example IV-Comparative

50 An alloy was cast in a manner after Example I contain ing 9.4 percent aluminum and the balance essentially copper. The alloy was hot worked by extrusion and then drawn into a final plate form. The resultant alloy had a tensile strength of  $75,000$  p.s.i., a yield strength of  $35,000$  p.s. i., and an elongation of 28 percent.

The maximum properties that were developed by beta-<br>tizing at 1600° F. and water quenching were only 109,000 p.s.i. tensile strength, 28,000 p.s.i. yield strength and 29 percent elongation owing to a comparatively coarse grained structure, none of the grains being under 0.065 mm. in diameter.

The response of this material to tempering increased the yield strength only a small amount to about 35,000 p.si.

#### Example V-Comparative

65 extremely difficult and at reduction of about 5 percent In a manner after Example I, an alloy containing 12.0. percent aluminum and the balance essentially copper was hot rolled, betatized and cold rolled. Cold rolling was the alloy fragmented beyond further use.

### Example VI-Comparative

70 An alloy containing 8 percent aluminum and the bal ance essentially copper was treated in a manner after<br>Example I. The properties attained were: 140,000 p.s.i. tensile strength; and 65,000 p.s.i. yield strength. Further heat treatment did not result in further improvement.

alloy to a yield strength of 114,000 p.s.i., a tensile strength 75 ried out in other ways without departing from the spirit This invention may be embodied in other forms or car-

or essential characteristics thereof. The present embodi ment is therefore to be considered as in all respects il Iustrative and not restrictive, the scope of the invention which come within the meaning and range of equiva- 5 lency are intended to be embraced therein.

What is claimed is:

1. The method of fabricating a high strength aluminum bronze alloy containing from 9.0 to 11.8 percent alumi num and the balance essentially copper, which comprises:  $_{10}$  hot working an alloy having the aforesaid composition at a temperature of from 1850° F. to 1000° F., and cold working said alloy at temperature of below 500° F.

2. The method of fabricating a high strength aluminum bronze alloy containing from 9.0 to 11.8 percent alumi-  $15$ num and the balance essentially copper, which comprises: hot rolling an alloy having the aforesaid composition at a temperature of from  $1850^\circ$  F. to  $1000^\circ$  F., and cold rolling said alloy at a temperature of below  $500^\circ$  F.

3. The method of fabricating a high strength aluminum 20 bronze alloy containing from 9.0 to 11.8 percent alumi hot rolling an alloy having the aforesaid composition at a temperature of from 1850° F. to 1000° F.; holding said alloy at a temperature of from  $1100^\circ$  F. to  $1050^\circ$  F. for at 25 least two minutes, and cold rolling said alloy at a temperature of below 500° F.

4. The method of claim 3 wherein said holding is dur ing hot rolling.

5. The method of claim 3 wherein said holding is a 30 thermal treatment subsequent to hot rolling.

6. The method of claim 3 wherein said hot rolling is at a temperature of from 1650° F. to 1000° F., with the hot rolling commencing at a higher temperature and gradual ly decreasing in temperature.

7. The method of claim 3 wherein said cold rolling is at a temperature of from  $0^{\circ}$  F. to  $200^{\circ}$  F.

8. The method of fabricating a high strength aluminum bronze alloy containing from 9.0 to 11.8 percent num bronze alloy containing from 9.0 to 11.8 percent aluminum and the balance essentially copper, which com- 40 prises: hot rolling an alloy having the aforesaid compo

sition at a temperature of from 1850° F. to 1000° F.; holding said alloy at a temperature of from  $1100^\circ$  F, to  $1050^\circ$ F. for at least two minutes; cold rolling said alloy at a temperature of below  $500^\circ$  F.; and annealing the alloy at a temperature of from 1000 F. to 1400 F.

9. The method of claim 8 wherein said cold rolling and annealing steps are repeated a plurality of times.<br>10. The method of claim 8 wherein said cold rolling

and annealing are repeated three times.

11. The method of claim 8 wherein said alloy is an nealed at a temperature of from  $1000^\circ$  F. to  $1100^\circ$  F.

12. The method of fabricating a high strength aluminum bronze alloy containing from 9.0 to 11.8 percent aluminum and the balance essentially copper, which comprises: hot rolling an alloy having the aforesaid composition at a temperature of from 1850° F. to 1000° F.; holding said alloy at a temperature of from  $1100^\circ$  F. to  $1050^\circ$ F. for at least two minutes; cold rolling said alloy at a temperature of below  $500^\circ$  F.; and heating the alloy to a temperature of from  $1100^\circ$  F. to  $1800^\circ$  F. followed by

rapidly cooling to a temperature of below at least 1000° F.<br>13. The method of claim 12 wherein said rapid cooling

is followed by holding said alloy at a temperature of from 500° F. to 900° F. for at least 30 minutes.

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