

# United States Patent

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## [54] HIGH STRENGTH ALUMINUM BRONZE ALLOY

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[58] Field of Search .....148/11.5 R, 32, 32.5, 12.7;  
75/162

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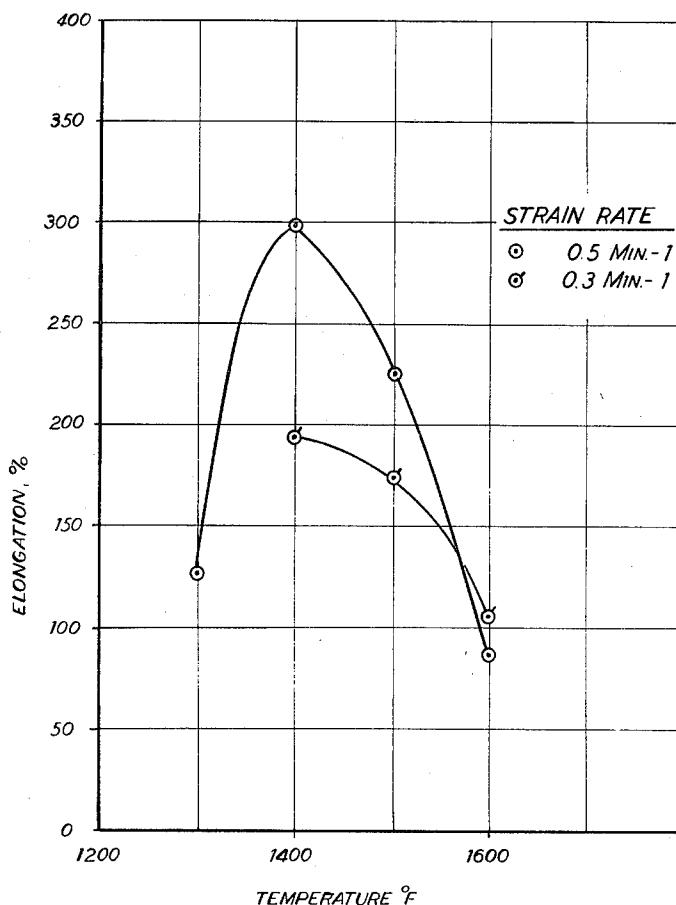
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### [57] ABSTRACT

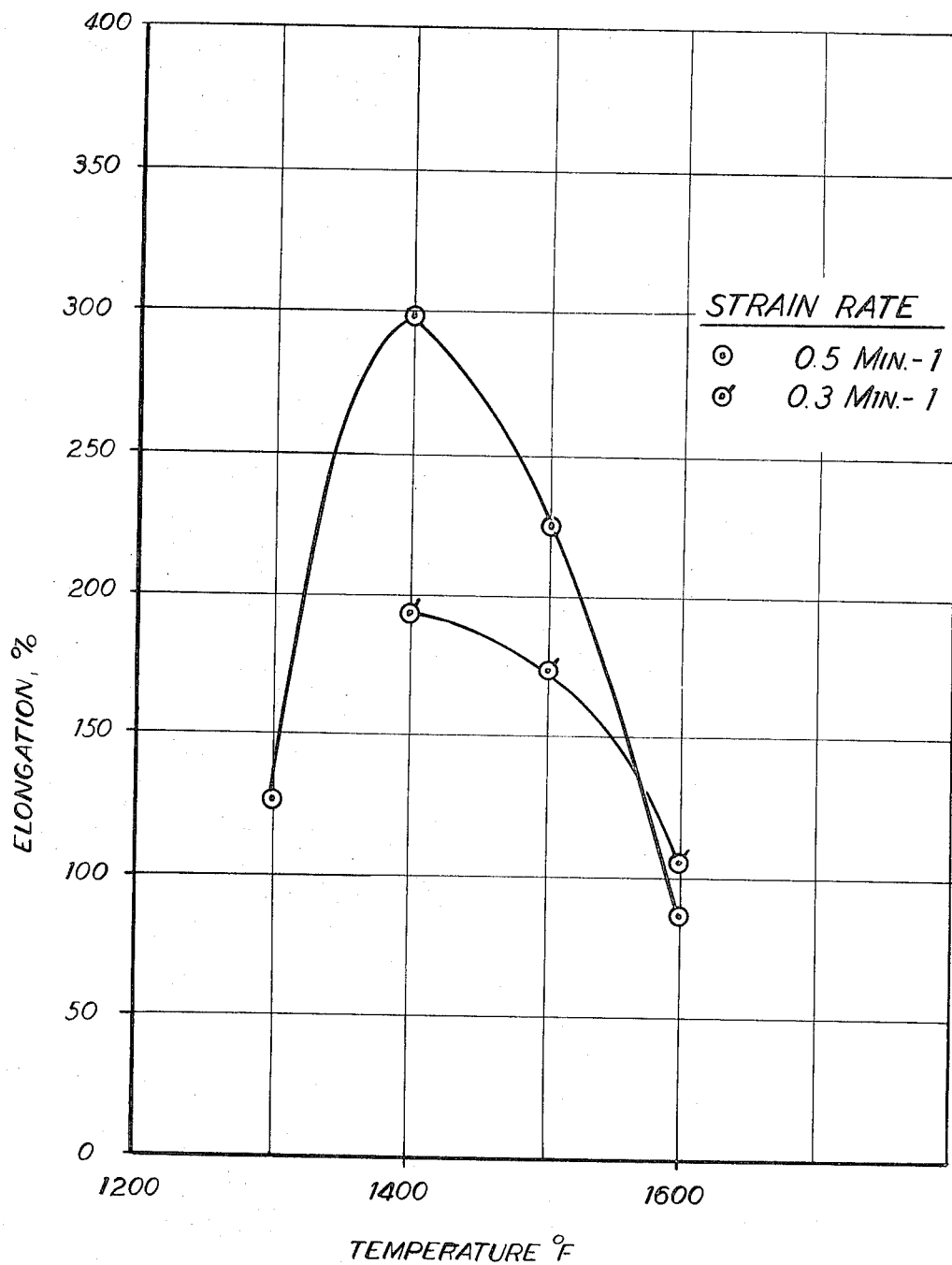
A high strength aluminum bronze alloy consisting essentially of 8.0 to 11.8 percent aluminum, 0.05 to 2.0 percent zirconium, 0.5 to 4.0 percent cobalt, 0.1 to 2.0 percent manganese, balance essentially copper, wherein the alloy has a metallographic structure containing 5 to 100 percent beta phase, remainder alpha phase, with a uniformly fine metallographic grain structure with a grain size of less than 0.065 mm., and a method of obtaining exceptional formability in these alloys.

19 Claims, 1 Drawing Figure



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## HIGH STRENGTH ALUMINUM BRONZE ALLOY

The present invention relates to improved aluminum bronze alloys. More particularly, the present invention resides in novel and inexpensive copper base alloys containing from 8.0 to 11.8 percent aluminum, 0.5 to 4.0 percent cobalt, 0.05 to 2.0 percent zirconium, 0.1 to 2.0 percent manganese, balance essentially copper. The foregoing alloy is prepared in such a manner as to be characterized by improved mechanical properties. For example, the novel alloys of the present invention contain surprisingly high tensile and yield strengths.

The combination of properties provides superior toughness and formability. In addition, the novel alloy of the present invention has reasonably good electrical conductivity plus good brazability, solderability, weldability, corrosion resistance, stress corrosion resistance, and fatigue strength.

The novel and inexpensively prepared alloys of the present invention readily attain high strength, as for example, a tensile strength ranging from 120,000 to 180,000 p.s.i. and yield strength ranging from 75,000 to 150,000 p.s.i. at 0.2 percent offset. In addition, electrical conductivity values ranging from about 10 to 16 percent IACS are attained. Properties of this type approximate those provided by the relatively expensive beryllium copper alloys. A lower cost alloy exhibiting properties similar to the aforementioned beryllium copper alloys would therefore find wide application in a variety of uses as a replacement for beryllium copper as for example, in the manufacture of electrical springs, contacts, and diaphragms.

Alloys exhibiting the foregoing properties would also tend to replace lower cost copper base alloys having a lower strength.

The present invention further relates to a method for obtaining exceptionally high formability of aluminum bronzes.

Typically, the aluminum bronze alloys are well-known for good formability at elevated temperatures, i.e., they may be readily hot rolled, forged, or extruded when in the all beta or predominantly all beta phase condition at elevated temperatures. Such alloys are extremely versatile and have a wide variety of uses, as aforementioned exemplified of which are: corrosion resistance parts, such as condenser tubes or valves; metal bellows and springs where strength and fatigue resistance are important; heat resistant parts in which resistance to corrosion at high temperatures is required, such as parts for internal combustion engines; wear resistance parts such as guides and ways, and metal and glass forming dies.

The method of the present invention provides for super plasticity of the zirconium, cobalt, and manganese containing aluminum bronze alloys at elevated temperatures. Aluminum bronze alloys exhibiting super plasticity would particularly find wide application in vacuum forming processes wherein high tensile properties are desired in the formed part. In addition, the process of the present invention is also readily applicable to the manufacture of articles of intricate shapes by forcing the aforementioned alloys into molds or dies while in the super plastic state and thereby taking advantage of the increased plasticity of the alloys.

Accordingly, it is a principal object of the present invention to provide a new and improved aluminum bronze alloy.

It is a further object of the present invention to provide an alloy as aforesaid which is characterized by improved mechanical properties and possessing a greatly improved combination of yield strength and tensile strength.

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

It is a still further object of the present invention to provide a method which is characterized by ductility or plasticity heretofore unattained in alloys of this type at elevated temperatures.

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

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 alloy of the present invention is a high strength aluminum bronze alloy consisting essentially of 9.0 to 11.8 percent aluminum, 0.5 to 4.0 percent cobalt, 0.05 to 2.0 percent zirconium, 0.1 to 2.0 percent manganese, balance essentially copper, said alloy characterized by high tensile and yield strengths as well as good electrical conductivity, brazability, solderability, weldability, corrosion resistance, stress corrosion resistance and fatigue strength.

The improved alloy of the present invention has a metallographic structure containing from 5 to 100 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. and generally less than 0.040 mm.

The alloying substituents, zirconium, and cobalt serve to inhibit the grain growth so that it is possible to obtain a fine grain size. This fine grain size is due to the formation of a fine dispersion of particles rich in these elements and the overall effect is to develop a high strength level in the present alloy.

The alloy of the present invention contains from 8.0 to 11.8 percent aluminum. 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 to 10.0 percent aluminum. In addition, the alloy of the present invention must critically contain from 0.05 to 2.0 percent zirconium, 0.5 to 4.0 percent cobalt, and 0.1 to 2.0 percent manganese.

The following discussion of preparing the alloy is directed to a preferred process which is generally in accordance with U.S. Pat. No. 3,287,180.

The alloy may be melted and cast in a suitable bar or ingot form using conventional practices to insure compositional and structural homogeneity.

It is only necessary that there be provided a homogeneous, sound and clean aluminum bronze alloy satisfying the foregoing compositional requirements.

The alloy may then be hot worked, e.g., hot rolling in the temperature range of 1,000° to 1,850° F.

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

Subsequent to hot rolling the alloy should contain the maximum amount of alpha phase possible, as governed by the phase equilibrium for the particular composition, and in addition a relatively large volume of the previously described dispersion. The maximum amount of alpha phase is assured by, either during or subsequent to hot rolling, holding the alloy the temperature range of 1,050° to 1,100° F. for at least 2 minutes. This may be done in a variety of ways either during the hot rolling or by thermal treatment subsequent thereto. For example, the alloy may be cooled slowly through this temperature range during the normal course of hot rolling and held there for at least 2 minutes and preferably longer.

Subsequent to the hot rolling step the alloy is cold worked at a temperature of below 500° F., and preferably from 0° to 200° F.

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 over 50 percent are attained within the broad compositional range (9.0 to 11.8 percent aluminum) toward the low aluminum end.

This ability permits the introduction of a whole new class of commercial products 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 been available commercially.

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 example, the alloy may be spray quenched, cooled in water or air cooled.

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 cold rolling steps dependent upon manufacturing economics. 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 1,000° to 1,400° F., preferably from 1,000° to 1,100° F. and optimally from 1,050° to 1,100° F. As the annealing temperature is increased the amount of beta phase increases and if subsequent cooling does not 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 elevated 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.

Preferably the cold rolling and annealing steps are repeated, preferably a plurality of times. 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 is this fine grained structure that results in the attainment of superior strengths in these alloys. If desired the alloy may be supplied in the as annealed condition also having a fine grain size. This form provides the maximum formability.

The alloy may be heat treated after cold rolling at 1,100° to 1,800° F. followed by rapid cooling. The temperature of heat treating varies inversely in relation to the aluminum content, 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 temperature is 1,500° to 1,650° 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 1,000° F., thereafter, the rate of cooling is not critical. The preferred mode of cooling is to cool in water, however, the alloy may be oil quenched or cooled in circulating air.

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 transformation which results in a significant increase in strength and results in an alloy having an excellent combination of strength and ductility. Thus, this combination of heat treatment and rapid cooling may be termed a "betatizing" procedure.

The dispersion present in the micro-structure of the present alloy acts to effectively inhibit grain growth during betatizing and thereby contributes to a finer final grain size.

Naturally impurities may also be present such as, for example, tin, zinc, lead, nickel, silicon, silver, phosphorus, magnesium, antimony, bismuth, and arsenic.

In the rapid cooling, it is necessary only that the alloy be cooled rapidly at least to below 1,000° F., i.e., to at least below the eutectoid transformation temperature, although the alloy may be rapidly cooled to a lower temperature if desired.

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 5 minutes at a temperature of from 500° to 900° 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.

Upon tempering, the present alloys develop higher strength levels. It is believed that this increased gain in strength is due

to precipitation hardening effects superimposed upon the normal tempering effects.

The aforementioned betatizing treatment, and the betatizing plus tempering treatments, results in strength levels of from about 120,000 to 180,000 p.s.i. tensile strength and about 75,000 to 150,000 p.s.i. in yield strength.

Another application of the alloy 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.

Another application is to form the annealed or temper rolled alloy into the desired shape. The formed part is then joined by such a treatment as brazing at 1,400° to 1,700° F., during which treatment the part is automatically converted to a high proportion of beta phase and if subsequently rapidly quenched very high strength levels are developed, i.e., betatizing. The presence of the dispersion in the present alloys has the same advantageous effects discussed above.

Another embodiment of the present invention is forming of the alloy into a desired shape in the temperature range of about 1,300° to 1,700° F. after the aforementioned hot rolling and cold rolling and annealing of the alloy at 1,000° to 1,400° F. The maximum time of annealing is not critical so long as grain growth does not become excessive, but is generally not longer than about 2 hours.

The aforementioned combination of cold working and annealing is to insure optimum refinement of the grain structure of the alloy prior to forming of the alloy into its desired shape. The grain size obtained is normally less than about 0.065 mm. and generally ranges from about 0.005 to 0.020 mm.

The aforementioned alloying substituents of cobalt and zirconium contribute to the development of the requisite fine grain size.

It is noted in this embodiment that, if desired, the alloy need not first be hot worked, prior to forming into the desired shape wherein the alloy is cold reduced or rolled, preferably at least 10% for a plurality of times, and annealed at about 1,000° to 1,400° F. for at least about 2 minutes. Generally, the cold reduction is from 40 to 90 percent and most preferably is at least 50%.

Naturally, the alloy after the aforementioned cold rolling steps of this embodiment need not be annealed prior to deforming at 1,300° to 1,700° F. since by heating to this temperature the alloy will recrystallize to the requisite fine grain structure.

In this embodiment it is also noted that prior to forming of the alloy into a desired shape the alloy need not have been subject to the aforementioned cold reducing and annealing steps, i.e., the alloy may be hot reduced preferably at least 20 percent for a plurality of times, while in the temperature range of about 1,000° to 1,400° F. in order to develop the requisite fine grain structure, and then formed into the desired shape at about 1,300° to 1,700° F. without intermediate cold reductions and anneals.

The surprising super plasticity found when the aforementioned alloys are processed in accordance with this embodiment appears to be associated with the combination of the relatively small grain size of the alloy and the proportions of the alpha and beta phases in the alloy at the forming temperature.

At the forming temperature the proportion of the beta phase in the alloy may range from nil up to 100 percent, depending upon the aluminum content in the alloy and the temperature, i.e., the aluminum content within the range of 8.0 to 11.8 percent. Optimally, however, the beta phase content ranges from about 40.0 to 70.0 percent which corresponds to an aluminum content of about 9.0 to 10.0 percent over the given temperature range.

The optimum beta content of about 40.0 to 70.0 percent allows a higher strain rate to be employed in the forming temperature range and is thus of practical importance as, for example, in providing for increased production of formed articles.

Superplasticity is felt to result in this instance from grain boundary sliding thereby allowing the grains to easily move past each other, without the occurrence of grain coarsening. With the presence of the beta structure in the alloy, optimally from about 40.0 to 70.0 percent, even greater plasticity results which is apparently due to the ease with which it can accommodate deformation of the less plastic alpha grains.

The strain rate of the present invention is defined as the cross head speed in inches per minute divided by the initial gage length of 2 inches, conforming to the test conditions employed with tensile specimens, which equals a numerical value.

In accordance with this embodiment, the deformation or forming is such as to provide for superplasticity and normally conforms to a strain rate of less than about 3.0 per minute and preferably about 0.5 per minute or less for applications where a particularly high elongation is desired. Generally, however, the strain rate of the present invention ranges from about 0.03 per minute to about 0.5 per minute for practical considerations.

Following the deformation step the formed article may be rapidly cooled at least to below 1,000° F. to insure retaining a high proportion of beta phase and then tempered, if desired, at a temperature range of from about 500° to 900° F., and preferably from 600° to 700° F., for at least 5 minutes, and preferably not longer than 4 hours in order to avoid coarsening of the structure, in order to develop a higher tensile strength and a particularly higher yield strength.

Naturally, if a slow cool, such as a normal air cool, is employed the formed article may be reheated to the temperature range of 1,100° to 1,800° F., and then rapidly cooled, as for example, quenching, and tempered as aforementioned.

It is to be noted, however, that relatively high tensile and yield strengths are attained wherein a normal or slow cool is employed, i.e., a yield strength of at least 40,000 p.s.i. and a tensile strength of at least 100,000 p.s.i.

Thus, this embodiment of the present invention is applicable to aluminum bronze having a fine grain size and containing the beta phase with the preferred beta phase content ranging from about 40.0 to 70.0 percent.

As will be apparent, the process of the present invention is exceptionally versatile and numerous other modifications 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 alloy possessing highly desirable, and in fact surprising mechanical properties heretofore unattainable in alloys of this type.

Further, the alloys of the present invention are less sensitive to the need for a high quench rate, than, for example, the alloys of U.S. Pat. No. 3,297,497, in order to retain the requisite amount of beta phase in the alloys upon cooling.

The alloy contains from 9.0 to 11.8 percent aluminum, 0.05 to 2.0 percent zirconium, 0.5 to 4.0 percent cobalt, 0.1 to 2.0 percent manganese, and as a preferred range, 9.4 to 10.4 percent aluminum, 0.08 to 0.15 percent zirconium, 0.8 to 1.5 percent cobalt, and 0.5 to 1.0 percent manganese, and the balance essentially copper. In addition the alloy has a metallographic structure containing from 5 to 100 percent beta phase, preferably 85 to 100 percent beta phase and the remainder alpha phase. In addition, the alloy contains a dispersion, as discussed above. The alloy has a uniformly fine metallographic grain structure with a particle size less than 0.060 mm., and generally less than 0.040 mm.

The alloys of the present invention possess properties which are unexpected and surprising in alloys of this type and which are not generally available. For example tensile strengths ranging from 120,000 to 150,000 p.s.i. and yield strengths from 75,000 to 100,000 p.s.i. (0.2 percent offset) may be developed. The electrical conductivities are good for alloys of this type, ranging from 10 to 16 percent IACS. In addition, modifications of the present invention improve the properties

still further. For example, tempering increases the yield strength and tensile strength considerably, e.g., to from 130,000 to 150,000 p.s.i. yield strength and 160,000 to 180,000 p.s.i. tensile strength.

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

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

#### EXAMPLE I

Alloys having the following compositions were prepared in the form of 1- $\frac{3}{4}$  inches  $\times$  1- $\frac{3}{4}$  inches  $\times$  4- $\frac{1}{2}$  inches chill castings.

| Alloy | Aluminum% | Cobalt% | Zirconium% | Manganese% | Copper%             |
|-------|-----------|---------|------------|------------|---------------------|
| A     | 9.7       | 0.8     | 0.2        | 0.44       | essentially balance |
| B     | 9.6       | 1.0     | 0.2        | 0.40       | essentially balance |
| C     | 10.0      | 1.0     | 0.2        | 0.31       | essentially balance |

The alloys were hot rolled in the temperature range of from 1,300° to 1,600° F. Reductions of about 5 to 10 percent per pass were used in reducing the gage from 2.5 inches to 0.35 inch, with the reductions being limited by the roll diameter.

#### EXAMPLE II

Following hot rolling, all of the alloys of Example I were annealed at 1,150° F. for 1 hour and subsequently air cooled for maximum cold rollability. The alloys were cold rolled from 0.35 inch to 0.030 inch gage reducing the thickness 40 percent between annealing at 1,150° F. A grain size of 0.010 mm. in diameter was developed in the alloys. The alloys were then betatized at 1,650° F. for 1 hour. As a result of this treatment the alloy exhibited:

| Alloy | *Yield Strength | Tensile Strength | Elongation |
|-------|-----------------|------------------|------------|
| A     | 88,000 psi      | 147,000 psi      | 3.0%       |
| B     | 90,000 psi      | 149,000 psi      | 2.0%       |
| C     | 81,000 psi      | 141,000 psi      | 2.0%       |

\*0.2% offset

#### EXAMPLE III

The alloys of Example II after betatizing were tempered at 650° F. for 1 hour and air cooled. As a result of this treatment the alloys exhibited:

| Alloy | *Yield Strength | Tensile Strength | Elongation |
|-------|-----------------|------------------|------------|
| A     | 139,000 psi     | 174,000 psi      | 0.5%       |
| B     | 140,000 psi     | 174,000 psi      | 1.0%       |
| C     | 147,000 psi     | 170,000 psi      | 0.5%       |

\*0.2% offset

#### EXAMPLE IV

The accompanying FIG. shows the elongation properties of a copper aluminum alloy containing 9.7 percent aluminum, 1.0 percent cobalt, 0.2 percent zirconium and 0.5 percent manganese, balance essentially copper, at a cross head speed of 1.0 in. per minute and 6 in. per minute at varying temperatures. This FIG. clearly shows the increase of plasticity of the alloy as the strain rate decreases. It is to be noted that due to limited cross head travel 370 percent elongation is the upper value of testing, and thus higher elongation values for the aforementioned alloy at a cross head speed of 1 in./min. is anticipated. The reported higher value resulted from elongation of the sample during removal from the furnace.

This invention may be embodied in other forms or carried out in other ways without departing from the spirit or essential characteristics thereof. The present embodiment is therefore to be considered as in all respects illustrative and not restric-

tive the scope of the invention being indicated by the appended claims, and all changes which come within the meaning and range of equivalency are intended to be embraced therein.

What is claimed is:

1. A method of obtaining exceptional formability in aluminum bronze alloys, which comprises:

A. providing an aluminum bronze alloy consisting essentially of 8.0 to 11.8 percent aluminum, 0.5 to 4.0 percent cobalt, 0.05 to 2.0 percent zirconium, 0.1 to 2.0 percent manganese, balance essentially copper,

B. cold reducing said alloy,

C. annealing said alloy at a temperature from 1,000° to 1,400° F. for at least 2 minutes.

D. superplastically deforming said alloy in the temperature range of 1,300° to 1,700° F.

2. The method of claim 1 wherein said deforming is at a strain rate of less than 3.0 per minute.

3. The method of claim 1 wherein said deforming is at a strain rate of 0.03 to 0.5 per minute.

4. The method of claim 2 wherein steps B and C are repeated at least once, and wherein the reduction of step B is at least 10%.

5. The method of claim 2 wherein said alloy contains from 9.0 to 10.0 percent aluminum.

6. The method of claim 4 wherein said strain rate is from 0.03 to 0.5 per minute.

7. The method of claim 6 wherein said beta content is from 40.0 to 90.0 percent.

8. The method of claim 6 wherein the temperature of deforming is from 1,400° to 1,600° F.

9. The method of claim 7 wherein said annealing is from 2 minutes to 2 hours.

10. The method of claim 9 wherein following step (D) said alloy is rapidly cooled and then reheated to the temperature

range of from 500° to 900° F. for at least 5 minutes.

11. The method of claim 10 wherein said reheating is not longer than 4 hours.

12. A method for obtaining exceptional formability in aluminum bronze alloys, which comprises:

A. providing an aluminum bronze alloy consisting essentially of 8.0 to 11.8 percent aluminum, 0.5 to 4.0 percent cobalt, 0.05 to 2.0 percent zirconium, 0.1 to 2.0 manganese, balance essentially copper,

B. hot working said alloy in the temperature range of from 1,000° to 1,400° F.,

C. superplastically deforming said alloy in the temperature range of 1,400° to 1,600° F.

13. The method of claim 12 wherein said deforming is at a strain rate of less than 3.0 per minute.

14. The method of claim 12 wherein said deforming is at a strain rate of 0.03 to 0.5 per minute and said reduction is at least 20 percent.

15. The method of claim 13 wherein the temperature of deforming is from 1,400° to 1,600° F.

16. A high strength aluminum bronze alloy consisting essentially of 9.0 to 11.8 percent aluminum, 0.5 to 4.0 percent cobalt, 0.05 to 2.0 percent zirconium, 0.5 to 2.0 manganese, balance essentially copper, said alloy having a metallographic structure containing from 5 to 100 percent beta phase and the remainder alpha phase and having a uniformly fine metallographic grain structure with a grain size less than 0.065 mm.

17. An alloy according to claim 16 containing from 85 to 100 percent beta phase.

18. An alloy according to claim 16 containing a discrete uniformly distributed dispersion rich in cobalt and zirconium.

19. An alloy according to claim 16 wherein the tensile strength of said alloy is from 120,000 to 180,000 p.s.i. and the yield strength is from 75,000 to 150,000 p.s.i.

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