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3,366,477

COPPER BASE ALLOYS

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No Drawing. Continuation-in-part of application Ser. No. 584,935, Aug. 5, 1966. This application Apr. 17, 1967, Ser. No. 631,119

7 Claims. (Cl. 75—154)

ABSTRACT OF THE DISCLOSURE

The instant disclosure relates to those copper base alloys known as the aluminum-bronzes and teaches improved high strength beta containing aluminum-bronze alloys containing certain additives which provide greatly improved corrosion resistance.

This application is a continuation-in-part of copending application Ser. No. 584,935, filed Aug. 5, 1966, which in turn is a divisional of Ser. No. 458,740, filed May 25, 1965, now U.S. Patent 3,290,182, which in turn is a continuation-in-part of Ser. No. 328,184, filed Dec. 5, 1963, and Ser. No. 341,121, filed Jan. 29, 1964, now U.S. Patents 3,287,180 and 3,297,497, respectively.

The present invention relates to copper base alloys containing from 9.0 to 11.8% aluminum. These alloys are called aluminum-bronzes and find extensive utility in a wide variety of applications where high strength, resistance to abrasion and excellent corrosion resistance are required. For example, springs, screens, heat exchangers, wear plates, bearings, etc.

The aluminum-bronzes are generally characterized by exceptionally good corrosion resistance in most corrosion media, except hot water and steam. It is highly desirable to improve the stress corrosion in aluminum-bronzes in hot water and steam in order to provide wider application for these materials, particularly in the chemical processing and power generation industries. For example, for use in unfired pressure vessels.

The art has found that certain additions to alpha aluminum-bronzes improve the stress corrosion resistance in hot water and steam. The art does not teach additions to the beta aluminum-bronzes of the present invention which additions will successfully improve the stress corrosion resistance of these materials while retaining the rollability and other good mechanical properties of the beta aluminum-bronzes.

Accordingly, it is a principal object of the present invention to provide improved aluminum-bronze alloys.

It is a further object of the present invention to provide beta aluminum-bronze alloys which have good stress corrosion resistance, especially in hot water.

An additional object of the present invention is to provide alloys as aforesaid which have improved stress corrosion resistance while retaining the good mechanical properties of the beta aluminum-bronze alloys.

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 may be readily obtained.

The alloys of the present invention have the following composition from 9 to 11.8% aluminum; from 0.05 to 5.0% of at least one additional element which has a solid solubility in copper of less than 4.0% and which forms one or more intermetallic compounds with aluminum, with the total quantity of said additional elements being less than 10%; from 0.01 to 0.05% phosphorus, preferably also containing from 0.01 to 0.3% tin; balance essentially aluminum.

Throughout the present specification all percentages are percentages by weight.

In accordance with the present invention it has been found that the foregoing alloys significantly improve the stress corrosion resistance in hot water or steam of aluminum-bronzes without adversely affecting hot or cold rollability and also with a retention of the mechanical properties of the aluminum-bronzes. The foregoing advantages will be more apparent from a consideration of the examples which form a part of the present specification.

The present invention is applicable to copper base alloys containing from 9 to 11.8% aluminum. The aluminum content must critically be within the aforementioned range, preferably is within the more limited range 9.4 to 10.4% aluminum, and optimally is between 9.4 and 10.0% aluminum.

The alloys of the present invention preferably contain from 0.05 to 5.0% of at least one additional element which has a solid solubility in copper of less than 4.0% and which forms one or more intermetallic compounds with aluminum, with the total quantity of said additional elements being less than 10.0%. The additional element is preferably selected from the group consisting of the following preferred amounts: iron from 2.0 to 5.0%; chromium from 0.4 to 2.0%; titanium from 0.4 to 2.0%; zirconium from 0.05 to 0.2%; molybdenum from 0.4 to 2.0%; columbium from 0.4 to 2.0%; vanadium from 0.4 to 2.0%; and mixtures thereof. The preferred additional elements are iron, chromium and zirconium.

The additional element should be an intermetallic compound formed with aluminum. In addition, the additional element and/or intermetallic compounds formed should preferably form a dispersion in copper with limited solid solubility at temperatures up to 1800° F.

The alloys of the present invention contain from 0.01 to 0.05% phosphorus, and preferably 0.01 to 0.02%. Preferably, the alloys also contain from 0.01 to 0.3% tin, preferably 0.02 to 0.1%.

It is preferred to utilize alloys having from 5 to 95% beta phase, balance alpha phase, since these provide a good combination of physical properties. In general, gamma phase should be avoided as it deleteriously effects corrosion resistance.

The remainder or balance of the alloys 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. Exemplificative materials include zinc, lead, nickel, silicon, silver, magnesium, antimony, and bismuth.

The alloys of the present invention may be melted and cast in a suitable bar or ingot form using conventional practices to insure compositional and structural homogeneity. For example, cathode copper may be induction melted under a charcoal cover or suitable salt flux. High purity or commercial aluminum in the requisite quantity may then be added and the melt thoroughly stirred to insure adequate mixing. The additional elements may be added in the same manner, that is, high purity or commercial iron, chromium, titanium, zirconium, molybdenum, columbium, and/or vanadium may be added in the desired amount, preferably as copper or aluminum master alloys, 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 from entrained aluminum oxide.

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 requirements.

The alloy of the present invention is then hot worked at a temperature of from 1850 to 1000° F. 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 rolling 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 to 1000° F., with it being preferred to utilize a narrower temperature range of from 1650° F. to 1000° F.

In the process of the present invention, the as cast material 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 directly 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 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, it is preferred to commence the hot rolling at the more 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 lower temperature in the hot rolling temperature range, i.e. 100° F.

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 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 example, the alloy may be cooled slowly through this temperature range during the normal course of hot rolling or reheated to a temperature of from 1050 to 1100° F. upon completion of hot rolling and held there for at least two minutes and preferably longer.

Subsequent to the hot working step the alloy is cold worked at a temperature of below 500° 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 cold rolling is preferred and the present process will be described in more detail with reference to this preferred 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.

After the desired reduction has been effected in the cold rolling step, the alloy may be annealed at a temperature of from 1000° F. to 1400° F., preferably from 1000° 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 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.

In the preferred embodiment 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 a superior combination of strength and ductility 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 has a uniformly fine metallographic grain structure with a particle size less than 0.065 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, especially with regard to strength and ductility. For example, tensile strengths ranging from 12,000 to 160,000 p.s.i. and yield strengths from 60,000 to 80,000 p.s.i. (0.2 percent offset) may be developed in combination with elongations ranging from 12 to 9 percent. 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 considerably, e.g., to from 60,000 to 110,000 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 115,000 p.s.i. and higher may be achieved together with tensile strengths as high as 148,000 p.s.i.

The present invention will be more readily understandable from a consideration of the following illustrative examples.

EXAMPLE I

Alloys having the following compositions were prepared from a charge of cathode copper, aluminum-iron master alloy, commercial purity aluminum and the other alloying additions in elemental form in the form of 1¼" x 1¼" x 1¼" chill castings.

Table I

Alloy:

- A---Al 9.9%, Fe 3.1%, Sn 0.036%, Cu essentially balance.
- B---Al 9.8%, Fe 4.0%, Cd 0.023%, Cu essentially balance.
- C---Al 9.7%, Fe 4.2%, Pb 0.005%, Cu essentially balance.
- D---Al 9.9%, Fe 4.2%, Sn 0.019%, Pb 0.005%, Cu essentially balance.
- E---Al 9.7%, Fe 4.2%, Zn 0.84%, Cu essentially balance.

Each of the above alloys were hot rolled in the range of 1600° to 1300° F. Reductions of about 10 to 20% per pass were used in reducing the gage 1.75" to 0.01". Following hot rolling, the alloys were cold rolled from 0.1" to 0.030" with inter-anneals at 1150° F. All samples were cut to size (½" x 6") and the edges milled. These prepared samples were heated to 1550 to 1650° F. for 1 hour followed by a water quench and then tempered at 650° F. for 1 hour.

EXAMPLE II

The alloys of Example I after the treatments of Example I were subjected to stress corrosion tests in the following manner. The ½" x 6" samples were pre-stressed by bending around a ¾" diameter mandrel in the shape of the letter U, with the ends being tied together. This would produce a stress of over 60,000 p.s.i. The U-bent specimens were subjected to treatment in aerated steam at 250° F. Normally, the failure by stress corrosion cracking is exhibited at the apex of the sample as determined at a magnification of 20X. The following table shows the time to stress corrosion cracking of three samples of the foregoing alloys.

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Table II

Alloy:	Time to failure, days
A -----	21, 88, 90
B -----	40, 90, 22
C -----	68, 81, 90
D -----	74, 88, 142
E -----	40, 347, 354

EXAMPLE III

Alloys having the following compositions were prepared from a charge of cathode copper, aluminum-iron master alloy, commercial purity aluminum and elemental phosphorus and tin in the form of $1\frac{3}{4}$ " x $1\frac{3}{4}$ " x $1\frac{3}{4}$ " chill castings.

Table III

Alloy:	
F--Al 9.6%, Fe 3.0%, P 0.022%, Cu essentially balance.	
G--Al 9.9%, Fe 5.1%, P 0.019%, Cu essentially balance.	
H--Al 9.6%, Fe 5.2%, Sn 0.025%, P 0.009%, Cu essentially balance.	
I--Al 9.6%, Fe 5.1%, Sn 0.30%, P 0.021%, Cu essentially balance.	

Each of the above alloys were hot rolled in the range of 1600° to 1300° F. Reductions of about 10 to 20% per pass were used in reducing the gage from 1.75" to 0.1". Following hot rolling, the alloys were cold rolled from 0.1" to 0.030" with inter-anneals at 1150° F. All samples were cut to size ($\frac{1}{2}$ " x 6") and the edges milled. These prepared samples were heated to 1550 to 1650° F. for 1 hour followed by a water quench and then tempered at 650° F. for 1 hour.

EXAMPLE IV

The alloys of Example III after the treatments of Example III were subjected to stress corrosion tests in the following manner. The $\frac{1}{2}$ " x 6" samples were pre-stressed by bending around a $\frac{3}{4}$ " diameter mandrel in the shape of the letter U, with the ends being tied together. This would produce a stress of over 60,000 p.s.i. The U-bent specimens were subjected to treatment in aerated steam at 250° F. Normally, the failure by stress corrosion cracking is first exhibited at the apex of the sample as determined at a magnification of 20X. The following table shows the time to stress corrosion cracking of three samples of the foregoing alloys.

Table IV

Alloy:	Time to failure, days
F -----	135, 229, 420
G -----	135, 149, 310
H -----	249, 256, 500
I -----	229, 347, 354

A comparison of Tables II and IV shows that in general the stress corrosion life of comparative alloys A through E is from 20 to 90 days. Possibly the zinc containing alloy (alloy E) shows an improvement, but it is

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not consistent. On the other hand, the alloys of the present invention consistently show an increased life of over 130 days and generally substantially more. Increasing the life to over 130 days is a significant improvement, particularly in view of the very high stresses in Examples II and IV.

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 restrictive, 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.

15 What is claimed is:

1. An aluminum-bronze alloy containing a small but effective amount of phosphorus for improving the stress corrosion resistance of said alloy in hot water or steam, consisting essentially of: from 9.0 to 11.8% aluminum; from 0.05 to 5.0% of at least one additional element which has a solid solubility in copper of less than 4.0% and which forms at least one intermetallic compound with aluminum, with the total quantity of said additional elements being less than 10.0%; from 0.01 to 0.05% phosphorus; and the balance essentially copper.

2. An alloy according to claim 1 containing from 0.01 to 0.3% tin to further improve the stress corrosion resistance.

3. An alloy according to claim 2 wherein said aluminum content is from 9.4 to 10.4%.

4. An alloy according to claim 2 wherein said additional element is selected from the group consisting of iron, chromium, titanium, zirconium, molybdenum, columbium, vanadium and mixtures thereof.

5. An alloy according to claim 4 wherein said additional element is iron in an amount from 2.0 to 5.0%.

6. An alloy according to claim 2 wherein said phosphorus is present in an amount from 0.01 to 0.02%.

7. An alloy according to claim 2 wherein said tin is present in an amount from 0.02 to 0.1%.

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CHARLES N. LOVELL, *Primary Examiner*.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 35, "rane" should read -- range --; line 36, "100° F." should read -- 1000° F. --. Column 4, line 16, "12,000" should read -- 120,000 --.

Signed and sealed this 30th day of December 1969.

(SEAL)

Attest:

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Commissioner of Patents