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3,097,093

COPPER BASE ALLOYS

Donald K. Fox, Pittsburgh, and William J. Reichenecker, Churchill Borough, Pa., assignors to Westinghouse Electric Corporation, East Pittsburgh, Pa., a corporation of Pennsylvania  
No Drawing. Filed May 31, 1961, Ser. No. 113,636  
10 Claims. (Cl. 75-156.5)

This invention relates to copper-base alloys, and more particularly to high strength yellow brasses having good ductility and improved resistance to stress corrosion.

This application is a continuation-in-part of application Serial No. 832,173, filed August 7, 1959, now abandoned, entitled "Copper-Base Alloys" by Donald K. Fox and William J. Reichenecker, and assigned to the assignee of the present application.

The high strength yellow brasses (or manganese bronzes as they are often designated) are casting alloys which possess high tensile and yield strength in the as-cast condition. They are used primarily in structural castings which must withstand considerable static and dynamic stresses in service.

The conventional yellow brasses of the type under consideration contain copper, aluminum, manganese, zinc and iron, and small but substantial percentages by weight of both tin and lead. This is of the order of .15% of tin and lead. It is generally considered that excess tin results in the formation of a brittle delta phase which adversely affects the strength and impact properties of the alloys, while excess lead, having limited solubility in the alloy, reduces the impact strength. For the reasons given, commercial specifications covering high strength yellow brasses restrict the amount of lead and tin which may be tolerated in the alloy to 0.2% maximum each, though as pointed out above the normal lead and tin content is substantial since commercial alloying constituents invariably contain a substantial quantity of lead and tin.

Another factor which limits the application of the high strength yellow brasses is the susceptibility of these alloys to stress corrosion. Ordinarily, the high strength yellow brasses are not employed where environmental conditions are conducive to stress corrosion cracking. Where such corrosive conditions exist, the aluminum bronzes, which are much less susceptible to stress corrosion cracking are employed. While the aluminum bronzes do have good corrosion resistance, the use of these alloys gives rise to problems resulting from the fact that they are also harder to machine and more difficult to cast than the high strength yellow brasses.

It is an object of this invention to provide high strength yellow brass alloys, and members composed thereof, containing predetermined amounts of copper, zinc, manganese, aluminum, and iron, in which good ductility is assured by restricting each of tin and lead to an amount below a critical weight of .01%.

It is a further object of this invention to provide high strength yellow brass alloys, and members prepared therefrom, containing predetermined amounts of copper, zinc, manganese, aluminum and iron, in which good corrosion resistance is obtained by the addition of a small but effective amount of boron or chromium or both.

Another object of this invention is to provide high strength yellow brass alloys, and members composed thereof, in which the alloy contains predetermined amounts of copper, zinc, manganese, aluminum and iron in which good ductility is assured by restricting the tin and lead in the alloy to amounts below 0.01% and in which high corrosion resistance is secured by the provisions of a small but effective amount of boron or chromium or both.

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Other objects of the invention will be obvious in part, and, in part, will appear hereinafter.

We have discovered improved high strength yellow brass alloys containing specified amounts of copper, zinc, aluminum, iron and manganese, in which good ductility is provided by limiting the weight percent of lead and tin to a maximum of .01% each, and, further, in which improved resistance to stress corrosion is provided by an addition of boron in the amount of the order of .003% to 0.5% or chromium in the amount of the order of 0.05% to 2% or both. A preferred range for boron in these alloys is from .05% to 0.3% while a preferred range for the chromium addition is from 0.05% to 0.5%. Alloys in which lead and tin are less than 0.01% and in which boron and/or chromium are present in the indicated proportions, are exceptionally outstanding. Either expedient may be employed alone to effect improvements in the alloys.

In its broadest aspects, the alloy of this invention comprises, by weight, from 52% to 68% copper, from 2.75% to 7.5% aluminum, from 2.5% to 5% manganese, from 1% to 4% iron, up to 0.2%, but preferably not exceeding .01% tin, up to 0.2%, but preferably not exceeding .01% lead, up to 0.5% boron, up to 2% chromium, and the balance zinc except for incidental impurities, the alloy having good ductility and also improved resistance to stress corrosion when boron or chromium is present.

One preferred composition range comprises, by weight, 55% to 59% copper, 2.75% to 3.75% aluminum, 2.8% to 3.5% manganese, 1% to 1.75% iron, up to .01% tin, up to .01% lead, and the balance zinc except for incidental impurities.

A specific alloy composition of this invention, having improved resistance to stress corrosion, comprises, by weight, from 55% to 59% copper, from 2.75% to 3.75% aluminum, from 2.8% to 3.5% manganese, from 1% to 1.75% iron, up to 0.2% lead, up to 0.2% tin, from .003% to 0.5% boron, and the balance zinc except for incidental impurities. Another specific alloy composition is similar to that described above except that from 0.02% to 2% chromium is substituted for the boron. In these last alloys, maintaining the lead and tin below 0.01% each, results in the optimum properties.

Typical of the high strength yellow brasses in commercial use at present are ASTM B147 (8B) and Alloy 36 which have the following compositions:

TABLE I

|                | ASTM B147<br>(8B), Percent | Alloy 36,<br>Percent |
|----------------|----------------------------|----------------------|
| Copper.....    | 60-68                      | 55-59                |
| Aluminum.....  | 3.0-7.5                    | 2.75-3.5             |
| Manganese..... | 2.5-5.0                    | 3.0-3.5              |
| Iron.....      | 2.0-4.0                    | 1.0-1.75             |
| Zinc.....      | Balance                    | Balance              |
| Tin.....       | 0.2 Max.                   | 0.2 Max.             |
| Lead.....      | 0.2 Max.                   | 0.2 Max.             |
| Other.....     |                            | 0.2 Max.             |

The mechanical properties of these alloys are set forth in the following Table II. The properties given are typical values for alloys in the composition range having about 0.05% to 0.2% each of tin and lead.

TABLE II

| Mechanical Properties (typical) | ASTM<br>B147 (8B) | Alloy 36 |
|---------------------------------|-------------------|----------|
| Tensile Strength.....           | 115,000           | 104,000  |
| Yield Strength.....             | 70,000            | 59,000   |
| Percent elongation.....         | 15                | 22       |
| BHN (3,000 kg.).....            |                   | 196      |

According to one aspect of the present invention, if the maximum weight percent of each of tin and lead are

restricted to less than .01%, an improvement in ductility of about 200% can be achieved in high strength yellow brass alloys falling generally within the composition range of ASTM B147 (8B) and Alloy 36. For example, in accordance with this invention, high purity alloys in the following composition ranges, in which all percentages are by weight, have been prepared and tested:

Example I

| Chemical Composition | Percentage |                |
|----------------------|------------|----------------|
|                      | Range      | Specific Alloy |
| Copper.....          | 55-59      | 57.91          |
| Aluminum.....        | 2.75-3.75  | 3.59           |
| Manganese.....       | 2.8-3.5    | 3.04           |
| Iron.....            | 1.0-1.75   | 1.61           |
| Zinc.....            | 33-37      | 33.77          |
| Tin.....             | .01 Max.   | Less than 0.01 |
| Lead.....            | .01 Max.   | Less than 0.01 |
| Other.....           | 1.0 Max.   | Less than 0.18 |

In preparing the above alloys, only raw materials of high purity are employed. The commercial grades of copper, zinc, etc. and the scrap of these materials which are ordinarily melted in foundry practice, contain quantities of lead and tin much in excess of the upper limit of 0.01% which can be permitted in these alloys, and consequently, the usual raw materials cannot be used. Thus, for example, the copper employed in making these alloys is the high purity type OFHC copper, and the master alloys used in making melts are laboratory grade.

The alloys set forth in Example I typically had the following mechanical properties:

TABLE III

Mechanical properties (typical):

|                                |         |
|--------------------------------|---------|
| Tensile strength (p.s.i.)..... | 106,000 |
| Yield strength.....            | 60,000  |
| Percent elongation.....        | 47      |
| BHN (3000 kg.).....            | 207     |

The ductility; i.e., percent elongation, of this alloy having substantially no tin and lead, is more than twice the typical value of ordinary Alloy 36 and three times that of ASTM B147 (8B), while strength and hardness levels are comparable with the same properties of the commercial alloys.

The amount of tin and lead in the alloy is highly critical. Alloys having essentially the composition of Alloy 36 were prepared wherein the constituents tin and lead were present in amounts of .03%. The typical mechanical properties of these alloys were:

TABLE IV

Mechanical properties (average):

|                         |         |
|-------------------------|---------|
| Tensile strength.....   | 104,000 |
| Yield strength.....     | 59,000  |
| Percent elongation..... | 23      |
| BHN (3000 kg.).....     | 197     |

It will be noted that the ductility (percent elongation) of these alloys is substantially the same as that of Alloy 36.

The mechanical properties which have been given above were obtained from individually cast test bars. The values obtained from such test bars are usually quite consistent but are not always consistent in practice with values obtained from test bars sectioned from large or complex castings of actual parts, which latter sometimes reveal severe reductions in ductility as the result of section size effects, gating and risering variations, and shrinkage porosity. In the case of Alloy 36, elongations as low as 4% have been obtained from sections of castings. This represents an 80% decrease in ductility below the minimum ductility ordinarily obtained in individually cast test bars, and such castings will be subject to brittle fracture. It is readily seen that if the low lead-tin alloys of this invention suffer a similar 80% reduction in ductility

in particular sections of a casting, the alloy would nevertheless retain ductility of the order of 8% to 10% and consequently, would be much less susceptible to brittle fracture. This is of particular importance in applications such as switchgear equipment where ductility, yield and impact strength are of primary importance rather than the ultimate strength.

In view of the high tensile and yield strength developed by the high strength yellow brasses (tensile strengths of the order of 100,000 p.s.i.) in the as-cast condition, these materials are often employed in structures which must withstand considerable static and dynamic stress. These alloys would find even wider application if their strength could be employed in corrosive environments by, in some way, improving their resistance to stress corrosion.

It has been found that the addition of from .003% to 0.5% boron or from 0.05% to 2% chromium, or both, to the high strength yellow brasses of the ASTM B147 (8B) and Alloy 36 type, markedly increases the time to failure of stress bars in a corrosive atmosphere when compared to similarly stressed bars of Alloy 36 and ASTM B147 (8B) not containing boron or chromium.

Boron and chromium containing alloys, having compositions otherwise quite similar to Alloy 36 of Table I, and identified as Alloy 36B and Alloy 36C, respectively, were prepared:

TABLE V

| Chemical Composition    | Alloy 36B |                | Alloy 36C |                |
|-------------------------|-----------|----------------|-----------|----------------|
|                         | Range     | Specific Alloy | Range     | Specific Alloy |
| Copper, percent.....    | 55-59     | 57.91          | 55-59     | 57.91          |
| Aluminum, percent.....  | 2.75-3.75 | 3.48           | 2.75-3.75 | 3.48           |
| Manganese, percent..... | 2.8-3.5   | 3.12           | 2.8-3.5   | 3.12           |
| Iron, percent.....      | 1.0-1.75  | 1.73           | 1.0-1.75  | 1.73           |
| Zinc, percent.....      | Balance   | 33.62          | Balance   | 33.53          |
| Lead, percent.....      | 0.2 max.  | 0.03           | 0.2 max.  | 0.03           |
| Tin, percent.....       | 0.2 max.  | 0.03           | 0.2 max.  | 0.03           |
| Boron, percent.....     | 0.003-0.5 | 0.011          | -----     | trace          |
| Chromium, percent.....  | -----     | trace          | 0.05-2    | 0.097          |
| Other, percent.....     | 0.1       | 0.1            | 0.1       | 0.1            |

In carrying out comparative corrosion resistance tests, standard tensile bars of Alloy 36 and Alloys 36B and 36C were loaded in an atmosphere of concentrated ammonia gas with water vapor to stress levels of 10,000 p.s.i., 15,000 p.s.i., and 20,000 p.s.i. in successive tests. In the 10,000 p.s.i. test, the Alloy 36 test bar failed in 28.45 hours whereas the Alloy 36B test bar failed in 129 hours and the Alloy 36C test bar failed in 83 hours. In the 15,000 p.s.i. test, the Alloy 36 test bar failed in 41 hours whereas the Alloy 36B test bar failed in 95.25 hours and the Alloy 36C test bar failed in 47 hours. At 20,000 p.s.i., the Alloy 36 test bar failed in 28.75 hours while the Alloy 36B test bar failed in 93 hours and the Alloy 36C test bar failed in 33 hours. These direct tension accelerated stress corrosion tests show an improved resistance to cracking is provided by both boron and chromium, with time for failure being at least doubled by the boron addition.

Additional boron and chromium containing alloys, generally similar to Alloy 36 in composition, and identified as Alloy 36D and Alloy 36E were prepared:

TABLE VI

| Chemical Composition:   | Alloy 36D | Alloy 36E |
|-------------------------|-----------|-----------|
| Copper, percent.....    | 57.91     | 55.03     |
| Aluminum, percent.....  | 3.48      | 3.30      |
| Manganese, percent..... | 3.12      | 3.51      |
| Iron, percent.....      | 1.73      | 1.34      |
| Zinc, percent.....      | 33.42     | 33.77     |
| Lead, percent.....      | 0.03      | 0.03      |
| Tin, percent.....       | 0.03      | 0.03      |
| Boron, percent.....     | 0.22      | trace     |
| Chromium, percent.....  | trace     | 1.98      |
| Other, percent.....     | 0.10      | 0.10      |

It will be noted that certain of the values given for the amounts of the various alloying constituents in Tables V and VI are identical. This is due to the fact that only one wet analysis was made for these elements, and that was performed on a basic alloy. In the case of the subsequent alloys with additives, a spectrographic analysis was made which indicated that the amount of the previously analyzed elements did not differ to any substantial degree from the basic alloy, and hence, the values are reported unchanged.

Test samples removed from castings of these compositions were loaded as simple beams in appropriate test jigs and exposed to an atmosphere of concentrated ammonia gas and water vapor. Stress levels of 15,000 p.s.i., 30,000 p.s.i., 40,000 p.s.i., and 50,000 p.s.i. were applied to the samples investigated. The results shown in Table VII again prove the superior resistance to stress corrosion cracking afforded by the boron and chromium additions, with the values given being an average of two samples at each stress level.

TABLE VII

| Stress Level, p.s.i. | Hours to Failure |           |           |
|----------------------|------------------|-----------|-----------|
|                      | Alloy 36         | Alloy 36D | Alloy 36E |
| 50,000.....          | 43               | 63        | 45        |
| 40,000.....          | 16               | 126       | 224       |
| 30,000.....          | 10               | 45        | 70        |
| 15,000.....          | 71               | 185       | 192       |

The somewhat erratic results obtained in the above tests are believed to be due to non-uniformities which occurred in the cast specimens tested. More important than any particular value in the above table is the general trend observable in the data, with the boron and chromium-containing alloys having greater corrosion resistance at each stress level.

It is important to note that standard tensile tests on Alloys 36B, 36C, 36D and 36E test bars show that the mechanical properties in the as-cast state are not adversely affected by the addition of boron and chromium. Typical properties of Alloys 36B, 36C, 36D, 36E and of Alloy 36 are set forth below for purposes of comparison:

TABLE VIII

| Mechanical Properties        | Alloy 36 (typical) | Alloy 36B (typical) | Alloy 36C (typical) | Alloy 36D (typical) | Alloy 36E (typical) |
|------------------------------|--------------------|---------------------|---------------------|---------------------|---------------------|
| Tensile strength, p.s.i..... | 104,000            | 104,000             | 103,000             | 103,300             | 107,050             |
| Yield Strength, p.s.i.....   | 59,000             | 58,000              | 59,000              | 60,000              | 58,550              |
| Percent Elongation.....      | 22                 | 22.5                | 22                  | 20                  | 23                  |
| BEHN (3,000 kg.)....         | 196                | 196                 | 195                 | 193                 | 207                 |

Boron has given the best results in practice. As has been shown above, chromium also produces an improvement in stress corrosion properties. However, the element chromium is somewhat less effective in this respect than is boron. Also both boron and chromium may be employed together, for example, 0.1% chromium and 0.01% boron.

In order to provide a high strength alloy having both good ductility and high resistance to corrosion in the broad range of high strength yellow brasses containing from 52% to 68% copper, the amount of tin and lead in the alloy must be held to .01% maximum each, and also, from .003% to 0.5% of boron or 0.05% to 2% of chromium must be added to the alloy. Samples of such alloys have been prepared and excellent results have been obtained.

Although the present invention has been described with particular reference to preferred embodiments, it will be apparent to those skilled in the art that variations and

modifications may be made without departing from the essential spirit and scope of the invention. It is intended to include all such variations and modifications.

We claim as our invention:

1. A high strength yellow brass having good ductility consisting essentially of, by weight, from 52% to 68% copper, from 2.5% to 5% manganese, from 2.75% to 7.5% aluminum, from 1% to 4% iron, up to .01% tin, up to .01% lead, from 0 to 0.5% boron, from 0 to 2% chromium, and the balance zinc except for incidental impurities, the boron and chromium, when present, imparting corrosion resistance to the alloy.

2. A high strength yellow brass consisting essentially of, by weight, from 55% to 59% copper, from 2.8% to 3.5% manganese, from 2.75% to 3.75% aluminum, from 1% to 1.75% iron, a maximum of .01% tin, a maximum of .01% lead, and the balance zinc except for incidental impurities, said alloy characterized in that it is highly ductile.

3. A high strength yellow brass consisting essentially of, by weight, from 52% to 68% copper, from 2.5% to 5% manganese, from 2.75% to 7.5% aluminum, from 1% to 4% iron, up to .01% tin, up to .01% lead, from .003% to 0.5% boron, and the balance zinc except for incidental impurities, the alloy exhibiting high ductility and good corrosion resistance.

4. A high strength yellow brass alloy consisting essentially of, by weight, from 55% to 59% copper, from 2.8% to 3.5% manganese, from 2.75% to 3.75% aluminum, from 1% to 1.75% iron, up to .01% lead, up to .01% tin, from .003% to 0.5% boron, and the balance zinc except for incidental impurities, said alloy characterized in that it is highly ductile and has good resistance to stress corrosion.

5. A high ductility, high strength yellow brass consisting essentially of, by weight, from 55% to 59% copper, from 2.8% to 3.5% manganese, from 2.75% to 3.75% aluminum, from 1% to 1.75% iron, a maximum of .01% tin, a maximum of .01% lead, about .01% boron, and the balance zinc except for incidental impurities, said alloy characterized in exhibiting good resistance to stress corrosion.

6. A high strength yellow brass consisting essentially of, by weight, from 55% to 59% copper, from 2.8% to 3.5% manganese, from 2.75% to 3.75% aluminum, from 1% to 1.75% iron, a maximum of 0.2% tin, a maximum of 0.2% lead, from .003% to .05% boron, and the balance zinc except for incidental impurities, said alloy characterized in that it is highly resistant to stress corrosion.

7. A high strength yellow brass alloy consisting essentially of, by weight, from 55% to 59% copper, from 2.8% to 3.5% manganese, from 2.75% to 3.75% aluminum, from 1% to 1.75% iron, a maximum of 0.2% tin, a maximum of 0.2% lead, about .01% boron, and the balance zinc except for incidental impurities, said alloy characterized in that it exhibits good resistance to stress corrosion.

8. A high strength yellow brass consisting essentially of, by weight, from 52% to 68% copper, from 2.5% to 5% manganese, from 2.75% to 7.5% aluminum, from 1% to 4% iron, up to .01% tin, up to .01% lead, from .05% to 2% chromium, and the balance zinc except for incidental impurities, the alloy exhibiting high ductility and good corrosion resistance.

9. A high strength yellow brass alloy consisting essentially of, by weight, from 55% to 59% copper, from 2.8% to 3.5% manganese, from 2.75% to 3.75% aluminum, from 1% to 1.75% iron, up to .01% lead, up to .01% tin, from .05% to 2% chromium, and the balance zinc except for incidental impurities, said alloy characterized in that it is highly ductile and has good resistance to stress corrosion.

10. A high strength yellow brass consisting essentially of, by weight, from 55% to 59% copper, from 2.8%

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to 3.5% manganese, from 2.75% to 3.75% aluminum, from 1% to 1.75% iron, a maximum of 0.2% tin, a maximum of 0.2% lead, from .05% to 2% chromium, and the balance zinc except for incidental impurities, said alloy characterized in that it is highly resistant to stress corrosion. 5

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