United States Patent [19]

Shapiro et al.

[11] **3,880,678**

[45] **Apr. 29, 1975**

[54] **PROCESSING COPPER BASE ALLOY**

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[22] Filed: **Mar. 27, 1974**

[21] Appl. No.: **455,235**

[52] **U.S. Cl.** ..... **148/11.5 R**; 148/2; 148/13; 148/32

[51] **Int. Cl.** **C22f 1/08**

[58] **Field of Search** ..... 148/13, 11.5 R, 2, 32; 29/199

[56] **References Cited**

UNITED STATES PATENTS

1,706,198	3/1929	Wadsworth	148/11.5 R
3,778,236	12/1973	Goldman et al.	29/199

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[57] **ABSTRACT**

A method of improving the stress corrosion resistance of a stress corrosion susceptible copper base alloy. A formed part of said copper base alloy is subjected to a low temperature thermal treatment under specified conditions.

8 Claims, No Drawings

PROCESSING COPPER BASE ALLOY

BACKGROUND OF THE INVENTION

Certain manganese containing copper base alloys are highly useful as a substitute for the nickel-silvers in a variety of applications, for example, in flatware and hollow ware. This is particularly useful in view of the fact that the nickel-silvers present certain undesirable features. In the first place, these manganese containing copper alloys tend to be less expensive than conventionally used nickel-silvers, particularly in view of the high cost of nickel. Furthermore, in addition to the high cost of nickel, the nickel-silvers are difficult to fabricate with respect to hot rolling. The hot rolling temperature range is narrow and high. This is not only expensive processing, but necessitates the use of smaller ingots. Still further, articles of flatware, for example, are generally formed by rolling to shape and coining to provide the pattern. The finished article is then silver plated. A prime requirement for coinability is low hardness. A fine grain size is highly desirable to provide the bright finished, silver plated article. In the nickel-silvers, however, it is not possible to provide a low hardness with the desired fine grain size.

Still further, articles of hollow ware, for example, are frequently drawn or stretch formed. Such articles are often made from brass or other nonwhite alloys due to the limited drawability and formability of the low nickel-silvers. Hollow ware articles formed from materials of this type must be nickel plated prior to silver plating, with an attendant increase in cost.

Certain manganese containing copper alloys are admirably suited for use as a substitute for the nickel-silvers and overcome many of the disadvantages of the nickel-silvers as set forth in U.S. Pat. Nos. 3,778,236 and 3,778,237. It has been found, however, that parts manufactured from certain manganese containing copper alloys may be susceptible to stress corrosion cracking when exposed to the atmosphere or an accelerated stress corrosion cracking test environment. Stress corrosion cracking can be a serious problem in any formed part, such as flatware or hollow ware discussed above, and also in such formed parts as springs, lock parts, watch parts, towel racks and the like.

Accordingly, it is a principal object of the present invention to provide a process for improving the stress corrosion resistance of certain manganese containing copper alloys without substantial degradation of desirable mechanical properties.

It is a further and particular object of the present invention to provide a process for treating formed parts made from certain manganese containing copper alloys which improves the stress corrosion resistance thereof.

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

SUMMARY OF THE INVENTION

In accordance with the present invention it has been found that the foregoing objects and advantages may be readily achieved. The process of the present invention comprises providing a formed part of a manganese containing copper alloy and heat treating said formed part at a temperature of from 300° to 385°C for a period of time of from 15 minutes to 4 hours. It has been found that in accordance with the process of the present invention manganese containing copper base alloys

are rendered highly resistant to stress corrosion cracking in both accelerated tests and environmental exposure. It has further been found that the low temperature thermal treatment of the present invention provides an improved combination of strength and ductility properties.

Therefore, parts manufactured from manganese containing copper base alloys can be given the final low temperature thermal treatment of the present invention and achieve highly desirable properties.

DETAILED DESCRIPTION

The process of the present invention effectively improves the stress corrosion cracking properties of any manganese containing copper base alloy which contains from 5 to 20 percent manganese and 15 to 35 percent zinc. The preferred zinc content is from 20 to 31 percent and the preferred manganese content is from 8 to 16 percent.

The balance of the alloy is essentially copper. Naturally, one may employ desired additives in order to achieve particularly desirable results. Thus, for example, one may include nickel in an amount up to 5.0 percent. If nickel is present, the preferred nickel range is from 0.5 to 5 percent, and optimally from 3 to 5 percent. It is an advantage of the alloys processed herein that one may provide desirable properties without the presence of nickel and, hence, employ a nickel free alloy.

Naturally, the copper alloy substrate may contain small amounts of additional alloying elements to, for example, improve mechanical properties or corrosion resistance. In general, less than 0.5 percent each of the following materials may be added and preferably less than 0.3 percent each, in order to avoid undesirable second phases and avoid fabrication problems: aluminum, iron, tin, silicon, cobalt, magnesium and molybdenum. Phosphorus, arsenic and antimony may be added up to 0.3 percent. Lead may be added in quantities up to 3 percent in order to improve machinability. Small amounts of the foregoing alloying additions may readily be used, if desired, for example, 0.001 percent each.

Naturally, the alloys of the present invention may contain common impurities, generally up to 0.05 percent each, total 0.25 percent.

Throughout the instant specification all percentages are weight percentages.

As indicated hereinabove, the process of the present invention provides a low temperature thermal treatment on a formed part. The formed part of the copper alloys of the present invention may be obtained by any convenient method. Thus, for example, the forming of the required part may be performed from annealed or temper rolled strip.

Processing of the copper alloys involves casting utilizing a temperature below 1000°C. The alloys processed herein are cast from the molten state at a melt temperature no higher than 1000°C and generally at a melt temperature above 870°C. In the casting step it is preferred to submerge the manganese in order to prevent heavy loss of manganese by preferential oxidation. This may be accomplished by following the manganese addition by the addition of more copper. Following the cast step the material may be hot rolled at low temperatures using a starting hot rolling temperature of less than 850°C. The starting hot rolling temperature must

be less than 850°C and generally from 700° to 800°C. Further, it is important that hot rolling be terminated at a temperature not less than 400°C. After hot rolling the alloys are processed with cold rolling with or without intermediate or terminal anneals to the final desired gage. In the case of products having a final thickness in excess of 0.1 inch, it may be desirable to anneal the hot material for structural equilibration. The alloys may be subjected to a final anneal in order to render them in the optimum condition for high formability. The final annealing temperature is in the range of 400° to 800°C for at least 15 minutes and preferably 1 to 4 hours.

Thus, in accordance with the present invention, the alloy is formed into a desired shape following the foregoing processing. If desired, the alloy is formed into a desired shape utilizing the material in the cold rolled condition. Preferably, the formed part utilizes a starting material in the cold rolled and annealed condition since this material is the optimum condition for high formability.

The heat treating step of the present invention is performed on the formed part at a low temperature of from 300° to 385°C and preferably from 310° to 360°C, for from 15 minutes to 4 hours. It is preferred to utilize a time period of from 30 minutes to 2 hours.

In accordance with the present invention, there should be no subsequent forming or plastic deformation after the low temperature thermal treatment of the present invention. Subsequent deformation will obviate the advantageous effects of the process of the present invention unless the low temperature thermal treatment is performed again.

It has been found that the low temperature thermal treatment achieves a remarkable advantage. Without the process of the present invention, the manganese containing copper base alloys processed herein to the desired shape may be susceptible to stress corrosion cracking when exposed to the atmosphere or accelerated stress corrosion cracking test environment. These alloys have extremely poor stress corrosion resistance when compared to brasses. It is indeed surprising that the low temperature thermal treatment of the present invention attains so significant an improvement in this important property.

The process of the present invention is effective with any formed part from the foregoing copper alloys, or on a formed part which is to be subject to a plating operation. The specific advantages to be gained with respect to resistance to stress corrosion cracking may be readily appreciated in conjunction with the examples which form a part of the present specification. In particular, it should be noted that formed parts contain a variable amount of cold work, i.e., they are not uniformly cold worked from area to area within a formed part. It is especially significant that in accordance with the present invention one can obtain improvement in stress corrosion resistance over a range of cold work without a significant loss in properties and despite the variable amount of cold work on a given part.

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

EXAMPLE I

Alloys of the present invention were prepared using DC casting of 5-¼ inches × 29-¼ inches × 25 feet dimensions using a pouring temperature of 950°C. The alloys had the following composition: 12 percent manganese; 24.5 percent zinc; balance essentially copper.

The alloy thus prepared was processed in the following manner. The alloy was hot rolled starting at 775°C from 5.25 inches to 0.360 inch thickness in 11 passes. The alloy was then annealed and cold rolled and subsequently annealed and cold rolled a specified amount as indicated in Table I below. Some samples, as shown in the table, were given the treatment of the present invention, while others for comparison purposes were not. The different degrees of cold work simulate the variable deformation that is typical of a formed part. Tensile properties were determined as well as accelerated stress corrosion testing of U-bend samples in Mattson's solution of pH 7.2. The results are shown in Table I below.

TABLE I

EFFECT OF LOW TEMPERATURE THERMAL TREATMENT ON MECHANICAL PROPERTIES AND STRESS CORROSION RESISTANCE

Condition	0.2% Yield Strength ksi	Ultimate Tensile Strength ksi	Elongation % in 2"	Time to Failure in Mattson's pH 7.2, Hours
Annealed	20.0	55.0	40	2.9
Annealed + 330°C/1 Hour	20.5	56.0	41	>500 (no failure)
CR 20%	60.1	67.5	12	0.3
CR 20% + 330°C/1 Hour	45.6	64.0	22	~220
CR 40%	80.9	84.5	2	0.5
CR 40% + 330°C/1 Hour	65.7	78.0	12	>500 (no failure)
CR 60%	92.5	95.0	2	0.2
CR 60% + 330°C/1 Hour	73.9	83.8	9	>500 (no failure)

The foregoing data clearly shows a remarkable improvement in accordance with the process of the present invention. Irrespective of the degree of prior cold work, one goes from substantial stress corrosion susceptibility to virtual immunity to stress corrosion failure while retaining desirable mechanical properties.

EXAMPLE II

Alloys of the present invention were prepared using DC casting of 5-¼ inches × 29-¼ inches × 25 feet di-

mensions using a pouring temperature of 950°C. The alloys had the following composition: 5 percent nickel; 7 percent manganese; 29 percent zinc; balance essentially copper.

The alloy thus prepared was processed in the following manner. The alloy was hot rolled starting at 825°C from 5.25 inches to 0.400 inch thickness in 11 passes. The alloy was then processed as in Example I, with the results indicated in Table II below. Tensile properties were determined as well as accelerated stress corrosion testing of U-bend samples in Mattson's solution of pH 7.2 as in Example I. The results are shown in Table II below.

TABLE II

EFFECT OF LOW TEMPERATURE THERMAL TREATMENT ON MECHANICAL PROPERTIES AND STRESS CORROSION RESISTANCE

Condition	0.2% Yield Strength ksi	Ultimate Tensile Strength ksi	Elongation % in 2"	Time to Failure in Mattson's pH 7.2, Hours
Annealed	24.9	60.9	46	0.5
Annealed + 340°C/1 Hour	26.0	61.5	48	>500 (no failure)
CR 20%	57.0	65.9	16.5	0.08
CR 20% + 340°C/1 Hour	48.5	65.9	22	>500 (no failure)
CR 40%	85.5	89.8	4	0.1
CR 40% + 340°C/1 Hour	74.8	85.4	11.5	>500 (no failure)
CR 60%	96.2	102.4	2	0.3
Cr 60% + 340°C/1 Hour	87.6	97.0	6.5	>500 (no failure)

The foregoing results are similar to those obtained in Example I and show a remarkable improvement in accordance with the process of the present invention.

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.

What is claimed is:

1. A method of improving the stress corrosion resistance of a stress corrosion susceptible copper base alloy without substantial degradation of desirable mechanical properties, said copper base alloy consisting essentially of from 5 to 20 percent manganese, from 15 to 35 percent zinc, balance copper which comprises: providing said alloy in the wrought condition; finally forming said alloy into a desired shape; and heat treating said finally formed alloy at a temperature of from 300° to 385°C for from 15 minutes to 4 hours, with no further forming operations being performed after said heat treatment step.

2. A method according to claim 1 wherein said alloy is heat treated at a temperature of from 310° to 360°C for from 30 minutes to 2 hours.

3. A method according to claim 1 wherein said alloy is provided in the cold rolled condition.

4. A method according to claim 1 wherein said alloy is provided in the cold rolled and annealed condition.

5. A method according to claim 1 wherein said alloy contains from 0.5 to 5 percent nickel.

6. A method according to claim 1 wherein said alloy contains less than 0.5 percent each of a material selected from the group consisting of aluminum, iron, tin, silicon, cobalt, magnesium, molybdenum and mixtures thereof.

7. A method according to claim 1 wherein said alloy contains less than 0.3 percent each of a material selected from the group consisting of phosphorus, arsenic, antimony and mixtures thereof.

8. A method according to claim 1 wherein said copper alloy contains up to 3 percent lead.

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