United States Patent [19]

Shapiro et al.

[11] **3,841,921**

[45] **Oct. 15, 1974**

[54] **PROCESS FOR TREATING COPPER ALLOYS TO IMPROVE CREEP RESISTANCE**

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[22] Filed: **Mar. 2, 1973**

[21] Appl. No.: **337,310**

[52] **U.S. Cl.** ..... **148/11.5 R**, 75/154, 75/157, 75/162, 148/12.7, 148/160

[51] **Int. Cl.** **C21d 1/04**

[58] **Field of Search** ..... 148/11.5 R, 12.7, 160; 75/154, 157, 162, 156.6, 159

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[57] **ABSTRACT**

Improving the creep resistance and stress relaxation resistance of copper base alloys having a low stacking fault energy by cold working from about 10 to 90 percent; heating from about 25° to 360°C and cooling to room temperature.

19 Claims, No Drawings

PROCESS FOR TREATING COPPER ALLOYS TO IMPROVE CREEP RESISTANCE

BACKGROUND OF THE INVENTION

This invention relates to a process for improving the creep resistance and the stress relaxation resistance of copper base alloys having a low stacking fault energy. It is a desirable objective to be able to process copper base alloys in such a manner so as to provide suitable spring properties for use in electrical connectors and like components. The properties of the materials which are required for obtaining suitable performance in electrical contactors or connectors are diverse. Aside from stress corrosion and electrical conductivity requirements specifically applicable to most parts of this type, they also require that either good contact be maintained during service or that a given stress produce a given deflection. In most of these parts the load is cycled, and as a consequence on reloading the previously mentioned requirements must still be met.

It is known that materials can exhibit a time dependent strain under a stress that is below the yield strength as determined by engineering methods or if restrained may undergo a reduction stress. The former characteristic is called creep and the latter characteristic is referred to as stress relaxation. In spring loaded parts, it is thus a desirable feature of an alloy that it exhibit high creep resistance and high stress relaxation resistance under the highest desirable loads possible.

SUMMARY OF THE INVENTION

In accordance with this invention, a process has been developed for improving the creep resistance and stress relaxation resistance of copper base alloys having a low stacking fault energy. The alloys to which this invention is applicable contain as a first element a metal from the group consisting of about 2 to 12 percent aluminum, about 2 to 6 percent germanium, about 2 to 10 percent gallium, about 3 to 12 percent indium, about 1 to 5 percent silicon, about 4 to 12 percent tin, about 8 to 37 percent zinc and the balance essentially copper. The alloy may further include other additions such as, for example, a second element different from the first element and selected from the group consisting of about 0.001 to 10 percent aluminum, about 0.001 to 4 percent germanium, about 0.001 to 8 percent gallium, about 0.001 to 10 percent indium, about 0.001 to 4 percent silicon, about 0.001 to 10 percent tin, about 0.001 to 37 percent zinc, about 0.001 to 25 percent nickel, about 0.001 to 0.4 percent phosphorus, about 0.001 to 5 percent iron, about 0.001 to 5 percent cobalt, about 0.001 to 5 percent zirconium, about 0.001 to 10 percent manganese and mixtures thereof. Preferred ranges for these various elements are specified in the detailed description.

The alloys thus provided have a low stacking fault energy generally less than 30 ergs per square centimeter. In accordance with this invention, the alloys are cold worked from about 10 to 97 percent and then heated to a temperature of from about 200 ° to 360°C, followed by cooling to room temperature. The alloys as thus treated have improved resistance to creep and resistance to stress relaxation.

In accordance with another embodiment of this invention, intermediate cold working and annealing steps may be interposed before the aforenoted cold rolling and heating step.

Accordingly, it is an object of this invention to provide a process for improving the creep resistance and the stress relaxation resistance of copper base alloys having a low stacking fault energy.

It is a further object of this invention to provide a process as above including a low temperature thermal treatment which provides said improvements.

Other objects and advantages will become apparent to those skilled in the art from the ensuing detailed description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the process of this invention, an alloy consisting essentially of a first element selected from the group consisting of about 2 to 12 percent aluminum, about 2 to 6 percent germanium, about 2 to 10 percent gallium, about 3 to 12 percent indium, about 1 to 5 percent silicon, about 4 to 12 percent tin, about 8 to 37 percent zinc, and the balance essentially copper is provided. The alloy thus provided is cold worked from about 10 to 97 percent, and preferably from about 15 to 95 percent, and is then subjected to a low temperature thermal treatment which comprises heating the alloy to a temperature of from about 200° to 360°C, and preferably from about 220° to 350°C, followed by cooling to room temperature. The heat up and cool down rates for the low temperature thermal treatment are not a critical aspect of this invention, and conventional practices may be followed. Preferably, for the low temperature thermal treatment the alloy is held at temperature for at least one minute and most preferably for at least 15 minutes.

The alloy to which the process of this invention is applied may include further elements as additions. For example, the alloy may include at least one second element different from the first element, the second element being selected from the group consisting of about 0.001 to 10 percent aluminum, about 0.001 to 4 percent germanium, about 0.001 to 8 percent gallium, about 0.001 to 10 percent indium, about 0.001 to 4 percent silicon, about 0.001 to 10 percent tin, about 0.001 to 37 percent zinc, about 0.001 to 25 percent nickel, about 0.001 to 0.4 percent phosphorus, about 0.001 to 5 percent iron, about 0.001 to 5 percent cobalt, about 0.001 to 5 percent zirconium, about 0.001 to 10 percent manganese, and mixtures thereof.

With respect to the second element or elements, the use of aluminum, silicon, tin or zinc is effective to reduce the stacking fault energy of the alloy. Nickel, iron, cobalt, zirconium and manganese are effective to reduce the grain size of the alloy. The nickel and manganese are also effective as solid solution hardners without substantially affecting the stacking fault energy of the alloy. Phosphorous acts both as a deoxidant and as a grain refiner, either singly or in combination with other elements.

The first element is preferably selected from the group consisting of about 2 to 10 percent aluminum, about 3 to 5 percent germanium, about 3 to 8 percent gallium, about 4 to 10 percent indium, about 1.5 to 4 percent silicon, about 4 to 10 percent tin, and about 15 to 37 percent zinc.

The second element is preferably selected from the group consisting of about 0.01 to 4 percent aluminum,

about 0.01 to 3 percent germanium, about 0.01 to 7 percent gallium, about 0.01 to 9 percent indium, about 0.01 to 3.5 percent silicon, about 0.01 to 8 percent tin, about 0.01 to 35 percent zinc, about 0.01 to 20 percent nickel, about 0.01 to 0.35 percent phosphorus, about 0.01 to 3.5 percent iron, about 0.01 to 2 percent cobalt, about 0.01 to 3.5 percent zirconium, about 0.01 to 8.5 percent manganese.

The alloys treated in accordance with this invention preferably have a stacking fault energy of less than 30 ergs per square centimeter.

In accordance with another embodiment of this invention, one or more series of cold working and intermediate annealing steps may be employed prior to the cold working and low temperature thermal treatment set out above. In this embodiment, the alloys are provided as in accordance with the previous embodiment and are then cold worked from about 10 to 97 percent and preferably from about 15 to 95 percent, followed by intermediate annealing for at least one minute at a temperature of from about 300° to 750°C so as to recrystallize the alloys, and preferably from about 350° to 700°C. This intermediate series of cold working and annealing steps may be repeated as desired to obtain the desired gage and temper in the final material.

Following the intermediate annealing step, the alloy is processed as in the previous embodiment, namely, it is cold rolled from about 10 to 97 percent, and preferably from about 15 to 95 percent, and then heated to a temperature of from about 200° to 360°C, and preferably from about 220° to 350°C, followed by cooling to room temperature.

As the alloys are formed into desired articles following the low temperature thermal treatment of this invention, it may be necessary to repeat the low temperature thermal treatment following the forming operation in order to obtain the desired creep and stress relaxation properties. Strip which is to be extremely deformed to produce a final article may require either the final thermal treatment be provided before and after fabricating the article or just after fabrication.

The invention will now be illustrated by reference to specific examples.

EXAMPLE I

Table I below shows creep strain versus time for CDA Alloy 638 (2.5 percent aluminum, 1.9 percent silicon, 0.27 to 0.42 percent cobalt, balance copper) processed to a 0.003 millimeter grain size, cold rolled approximately 50 percent with and without a final low temperature thermal treatment in accordance with this invention.

For the creep tests the stress was 50 percent of the 0.2 percent yield stress and the temperature was 125°C. For the stress relaxation tests the stress was 90 percent of the 0.2 percent yield stress. The results of the test are tabulated in Table I.

TABLE I

Creep Stress, % Strain				Stress Relaxation Test % Relaxation		
Thermal Treatment	Stress, ksi	100 hr	1000 hr	Stress, ksi	24 hr	1000 hr
None	56	0.175	0.245	88.9	7.24	12.3
310°C for 1 hr	54.2	0.06	0.125	97.65	1.72	3.2

The data in Table I show that the low temperature thermal treatment of this invention improves the creep resistance and the stress relaxation resistance of the alloy. Low temperature thermal treatments from about 225° to about 350°C were shown to produce similar improvements in creep and stress relaxation resistance performance without significantly degrading tensile properties.

EXAMPLE II

Table II shows creep strain versus time and percent stress relaxation versus time for CDA Alloy 638 processed to a range of grain sizes, cold rolled 50 to 60 percent with and without a final low temperature thermal treatment in accordance with this invention. Test conditions were essentially the same as those of Example I.

TABLE II

Creep Tests, % Strain					Stress Relaxation Test % Relaxation		
Grain Size MM	Thermal Treatment °C	Stress, ksi	100 hr	1000 hr	Stress, ksi	24 hr	1000 hr
0.003	None	56	0.175	0.245	88.9	7.24	12.3
0.003	310	55.5	0.06	0.125	97.65	1.72	3.2
0.007	None	55.5	0.150	0.23	—	—	
0.007	310	53	0.038	0.080	95.4	1.04	2.3

The data tabulated above show that combinations of increasing the annealed grain size and the low temperature thermal treatment in accordance with this invention provide the greatest degree of improvement in the desired properties.

EXAMPLE III

Table III below shows that grain coarsening and the heat treatments in accordance with this invention do not adversely affect the conventional engineering strength of the alloy of the previous example.

TABLE III

Alloy	Grain Size	% CR	Treatment	UTS/0.2YS/% E
638	0.003 mm	50	None	125.9/111/5
638	0.003 mm	50	310°C	127/109/ND
638	0.007 mm	60	None	117/105/3
638	0.007 mm	60	310°C	117/106/3

EXAMPLE IV

A sample of cold rolled CDA Alloy 638 having a composition similar to that of Example I with a yield strength of about 81 to 95 ksi was fabricated into an electrical receptacle. In order to determine if the receptacle so formed performed acceptably, it was subjected to the following test: An oversize plug was first inserted into the receptacle and then removed. Then an undersize plug with a suitable weight hanging from it was inserted into the receptacle. The test requirements are that the weighted undersize plug must not fall out, i.e., a given contact pressure must be maintained between the receptacle and the prongs of the plug. A conventional cold rolled and formed CDA Alloy 638 part could not meet this test requirement. When the parts were given thermal treatments in accordance with this invention and submitted to the same test procedures the results obtained showed that the untreated material failed in multiple specimens; whereas, material treated from 280°C to 345°C passed in 18 out of 20 specimens.

The results indicated that low temperature thermal treatments in accordance with this invention increase the residual contact pressure after cycling with an oversize plug so that the undersize plug does not fall out. The results also indicate that optimum performance is dependent on the heat treatment temperature.

EXAMPLE V

Table IV below shows the effect of post-heat treatment deformation on the stress relaxation properties of the CDA Alloy 638 having a composition similar to Example I. Deformation was accomplished by prestraining by tension 2 ½ percent and by prestraining by cold rolling 10 percent. This simulates a forming step applied to a cold worked and heat treated strip in accordance with this invention.

TABLE IV

Alloy	Condition	% Relaxation* in 5 minutes
638, 0.003 mm	CR 30% + 310°C/1 hr	1.4
638, 0.003 mm	CR 30% + 310°C/1 hr + 2½% strain	1.8
638, 0.003 mm	CR 30% + 310°C/1 hr + 10% strain	2.7
638, 0.003 mm	CR 30% + 310°C/1 hr + 10% strain + 310°C/1 hr	1.5
638, 0.007 mm	CR 40% + 310°C/1 hr	1.6
638, 0.007 mm	CR 40% + 310°C/1 hr + 2½% strain	2.0
638, 0.007 mm	CR 40% + 310°C/1 hr + 10% strain	3.1
638, 0.007 mm	CR 40% + 310°C/1 hr + 10% strain + 310°C/1 hr	1.3

* 90,000 psi initial stress in each case.

The above data show that while deformation of strip given the low temperature thermal treatment in accordance with this invention reduces the previous effect of that heat treatment, the strip can be reheat treated after forming to recover the optimum creep and stress relaxation properties.

Therefore, this invention also includes the possibility of providing a forming operation for forming the thermally treated strip in accordance with this invention into a desired article, followed by a repetition of the low temperature thermal treatment in accordance with this invention.

EXAMPLE VI

Commercially produced CDA Alloy 510 was tested in two conditions (as cold rolled 54 percent and as cold rolled plus a low temperature thermal treatment in accordance with this invention at 220°C). The tests were carried out at 125°C and a stress equal to one-half the 0.2 percent offset yield stress at room temperature. The results are shown in Table V.

TABLE V

Condition	Test Stress, ksi	Creep Strain, % 100 hrs	Creep Strain, % 1000 hrs
untreated	51	0.080	0.155
treated	47	0.021	0.063

It is evident from the results tabulated above that the low temperature thermal treatment in accordance with this invention improves the creep properties of a wide variety of alloys such as Alloy 510 which is a tin bronze.

While the invention has been described with reference to a wide variety of alloys, it is particularly applicable to CDA Alloy 638 and CDA Alloy 668.

The above examples establish that the low temperature thermal treatment in accordance with this invention is effective to improve the creep resistance and stress relaxation resistance of a wide variety of copper base alloys having low stacking fault energy. The examples also illustrate that increasing or coarsening the grain size of the respective alloys is also effective for improving the aforenoted properties.

Therefore, it is possible in accordance with this invention to provide a step in the process for coarsening the grain size of the alloy to at least 0.006 mm, as, for example, by a process similar to that set out in U.S. application Ser. No. 309,345, now U.S. Pat. No. 3,788,902, filed Nov. 24, 1972, by the instant inventors. In accordance with that application, alloys having a composition similar to CDA Alloy 638 are subjected to grain coarsening by subjecting them to a cold reduction and anneal within specific ranges of reduction and

temperatures. For other alloys falling within the scope of the present application, the grain coarsening may be obtained by more conventional means.

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 process for improving the creep resistance and the stress relaxation resistance of copper base alloys having low stacking fault energy without significantly degrading tensile properties consisting essentially of:

a. providing a copper base alloy having a stacking fault energy of less than 30 ergs per square centimeter consisting essentially of a first element selected from the group consisting of about 2 to 12 percent aluminum, about 2 to 6 percent germanium, about 2 to 10 percent gallium, about 3 to 12 percent indium, about 1 to 5 percent silicon, about 4 to 12 percent tin, about 8 to 37 percent zinc, and the balance essentially copper;

b. cold working said alloy from about 10 to 97 percent;

c. forming said alloy into a desired final article;

d. heating said alloy without significantly degrading tensile properties to a temperature of from about 200° to 360°C for at least 1 minute; and

e. cooling said alloy to room temperature,

thereby improving the creep resistance and the stress relaxation resistance of said article.

2. A process according to claim **1** including the following step subsequent to said cold working step (b) but prior to said forming step (c): (f) heating said alloy without significantly degrading tensile properties to a temperature of from about 200° to 360°C for at least one minute.

3. A process as in claim **2** wherein said alloy includes at least one second element, different from said first element, said second element selected from the group consisting of about 0.001 to 10 percent aluminum, about 0.001 to 4 percent germanium, about 0.001 to 8 percent gallium, about 0.001 to 10 percent indium, about 0.001 to 4 percent silicon, about 0.001 to 10 percent tin, about 0.001 to 37 percent zinc, about 0.001 to 25 percent nickel, about 0.001 to 0.4 percent phosphorus, about 0.001 to 5 percent iron, about 0.001 to 5 percent cobalt, about 0.001 to 5 percent zirconium, about 0.001 to 10 percent manganese, and mixtures thereof.

4. A process as in claim **2** wherein said first element is selected from the group consisting of about 2 to 10 percent aluminum, about 3 to 5 percent germanium, about 3 to 8 percent gallium, about 4 to 10 percent indium, about 1.5 to 4 percent silicon, about 4 to **10** percent tin, and about 15 to 37 percent zinc.

5. A process as in claim **2** wherein said at least one second element is selected from the group consisting of about .01 to 4 percent aluminum, about 0.01 to 3 percent germanium, about 0.01 to 7 percent gallium, about 0.01 to 9 percent indium, about 0.01 to 3.5 percent silicon, about 0.01 to 8 percent tin, about 0.01 to 35 percent zinc, about 0.01 to 20 percent nickel, about 0.01 to 0.35 percent phosphorus, about 0.01 to 3.5 percent iron, about 0.01 to 2 percent cobalt, about 0.01 to 3.5 percent zirconium, about 0.01 to 8.5 percent manganese.

6. A process as in claim **2** wherein said alloy is cold worked from about 15 to 95 percent.

7. A process as in claim **2** wherein said heating steps are at a temperature of from about 220° to 350°C.

8. A process as in claim **7** wherein said heating steps are for at least 15 minutes.

9. A process as in claim **2** wherein prior to step (b) the grain size of said alloy is increased to at least 0.006 millimeters.

10. A process for improving the creep resistance and stress relaxation resistance of copper base alloys having a low stacking fault energy without significantly degrading tensile properties consisting essentially of:

a. providing a copper base alloy having a stacking fault energy of less than 30 ergs per square centimeter consisting essentially of a first element selected from the group consisting of about 2 to 12 percent aluminum, about 2 to 6 percent germanium, about 2 to 10 percent gallium, about 3 to 12 percent indium, about 1 to 5 percent silicon, about 4 to 12 percent tin, about 8 to 37 percent zinc, and the balance essentially copper;

b. cold working said alloy from about 10 to 97 percent;

c. annealing said alloy for at least one minute at a temperature of from about 300° to 750°C so as to recrystallize said alloy;

d. cold rolling said alloy from 10 to 97 percent;

e. forming said alloy into a desired final article;

f. heating said alloy without significantly degrading tensile properties to a temperature of from about 200° to 360°C for at least 1 minute; and

g. cooling said alloy to room temperature,

thereby improving the creep resistance and the stress relaxation resistance of said article.

11. A process according to claim **10** including the following step subsequent to said cold working step (d) but prior to said forming step (e): (h) heating said alloy without significantly degrading tensile properties to a temperature of from about 200° to 360°C for at least one minute.

12. A process as in claim **11** wherein said alloy includes at least one second element, different from said first element, said second element selected from the group consisting of about 0.001 to 10 percent aluminum, about 0.001 to 4 percent germanium, about 0.001 to 8 percent gallium, about 0.001 to 10 percent indium, about 0.001 to 4 percent silicon, about 0.001 to 10 percent tin, about 0.001 to 37 percent zinc, about 0.001 to 25 percent nickel, about 0.001 to 0.4 percent phosphorus, about 0.001 to 5 percent iron, about 0.001 to 5 percent cobalt, about 0.001 to 5 percent zirconium, about 0.001 to 10 percent manganese, and mixtures thereof.

13. A process as in claim **11** wherein said first element is selected from the group consisting of about 2 to 10 percent aluminum, about 3 to 5 percent germanium, about 3 to 8 percent gallium, about 4 to **10** percent indium, about 1.5 to 4 percent silicon, about 4 to 10 percent tin, and about 15 to 37 percent zinc.

14. A process as in claim **13** wherein said at least one second element is selected from the group consisting of

about 0.01 to 4 percent aluminum, about 0.01 to 3 percent germanium, about 0.01 to 7 percent gallium, about 0.01 to 9 percent indium, about 0.01 to 3.5 percent silicon, about 0.01 to 8 percent tin, about 0.01 to 35 percent zinc, about 0.01 to 20 percent nickel, about 0.01 to 0.35 percent phosphorus, about 0.01 to 3.5 percent iron, about 0.01 to 2 percent cobalt, about 0.01 to 3.5 percent zirconium, about 0.01 to 8.5 percent manganese.

15. A process as in claim **11** wherein said alloy is cold worked in said cold working steps from about 15 to 95 percent.

16. A process as in claim **15** wherein said alloy is heated in steps (f) and (h) to a temperature of from 220° to 350°C.

17. A process as in claim **16** wherein said alloy is heated in steps (f) and (h) for at least 15 minutes.

18. A process as in claim **11** wherein prior to step (d) the grain size of said alloy is increased to at least 0.006 millimeters.

19. A process as in claim **11** wherein steps (b) and (c) are repeated at least once.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,841,921 Dated October 15, 1974

Inventor(s) Eugene Shapiro and Jacob Crane

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

In the "ABSTRACT", lines 3 and 4, "from about 10 to 90 percent" should read ---from about 10 to 97 percent---;

In the "ABSTRACT", line 4, "from about 25° to 360°C" should read ---from about 200° to 360°C---.

In Column 6, line 28, "CDA Alloy 668" should read ---CDA Alloy 688---.

Signed and sealed this 21st day of January 1975.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334