July 27, 1971 R. S BRAY 3,595,705

COPPER-BORON-SULFUR ALLOY AND METHOD OF TREATMENT

Filed June 13, 1969 4 Sheets-Sheet 1

FIG. 1

COPPER BORON SULFUR ALLOY

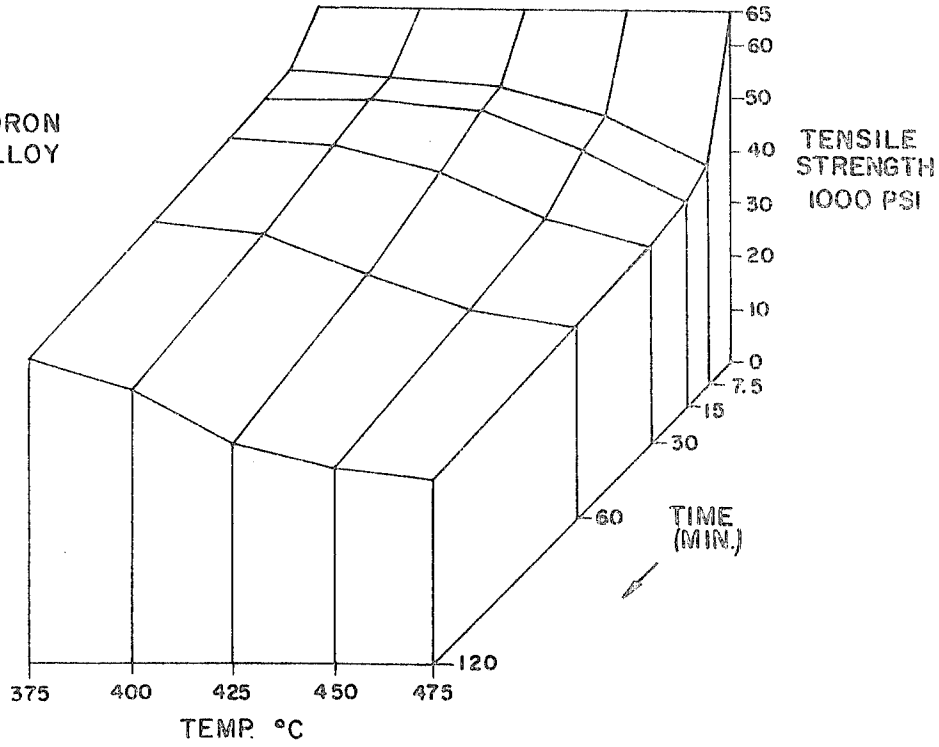
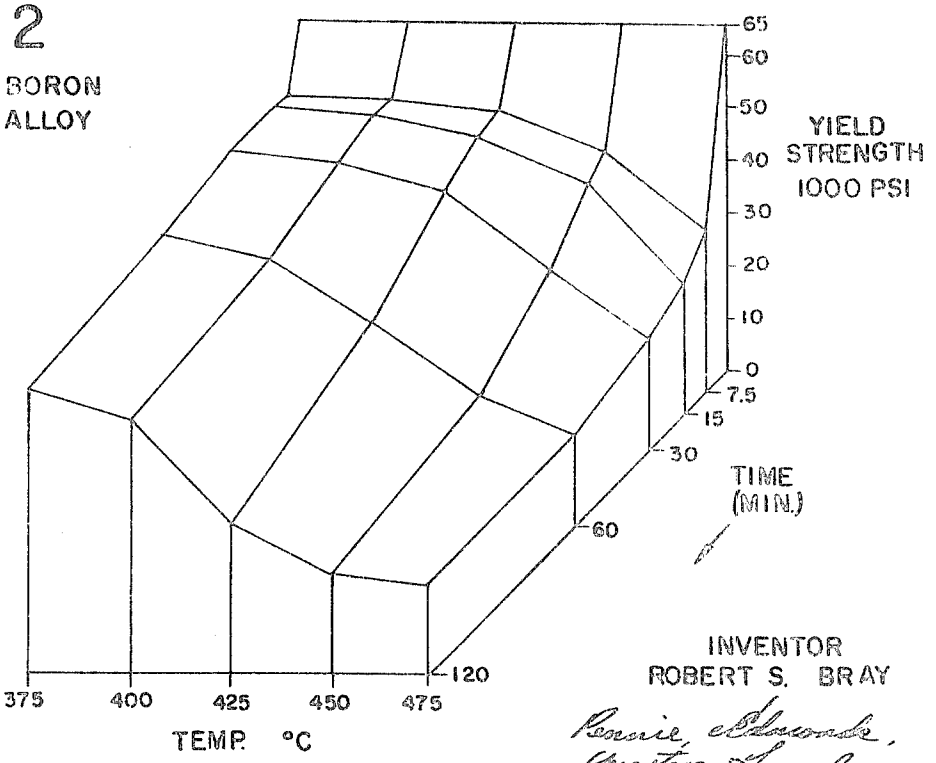


FIG. 2

COPPER BORON SULFUR ALLOY



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COPPER-BORON-SULFUR ALLOY AND METHOD OF TREATMENT

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FIG. 3
(PRIOR ART)
CADMIUM COPPER

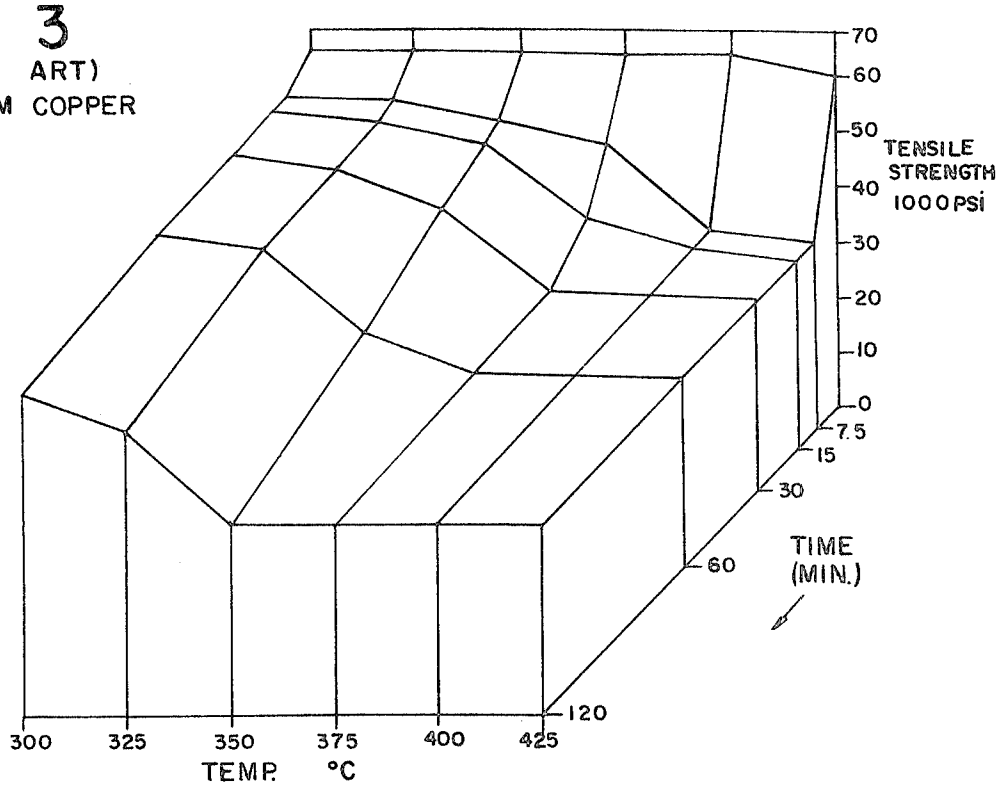
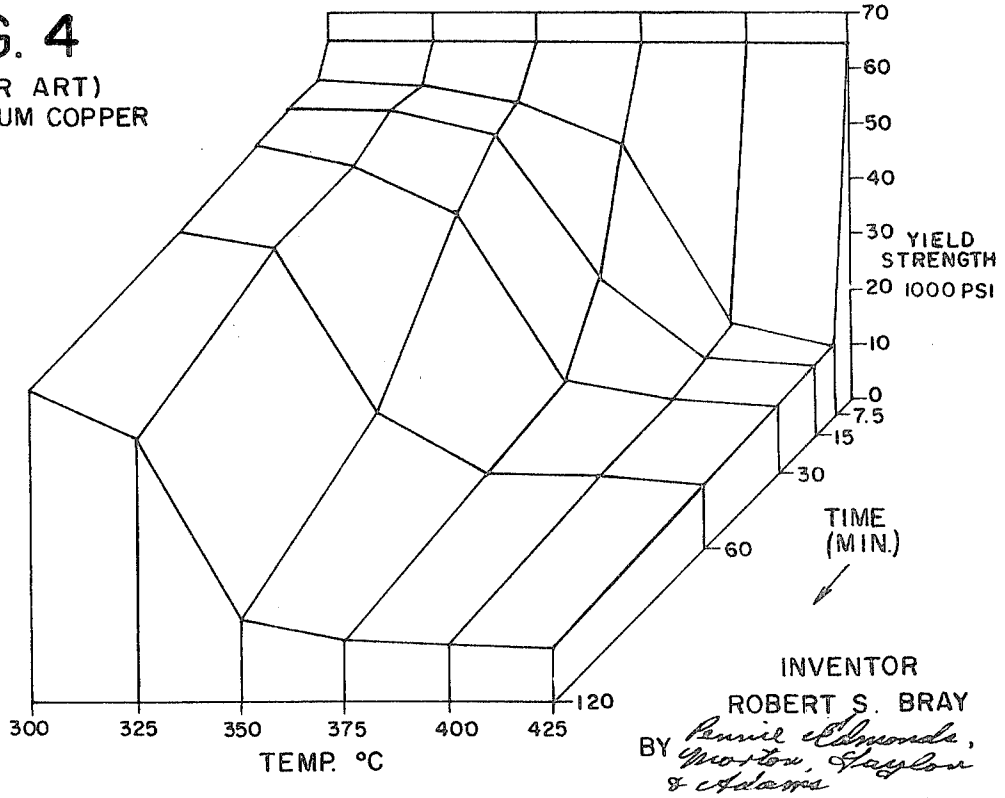


FIG. 4
(PRIOR ART)
CADMIUM COPPER



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FIG. 5
(PRIOR ART)
SILVER BEARING COPPER

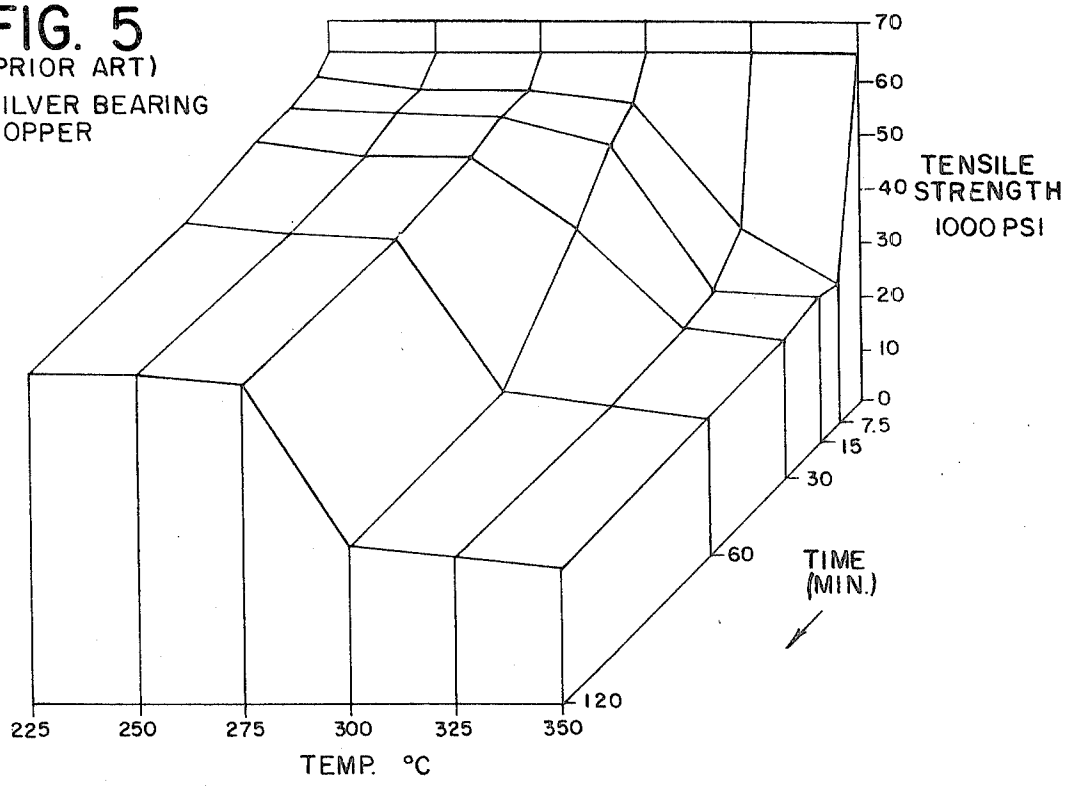
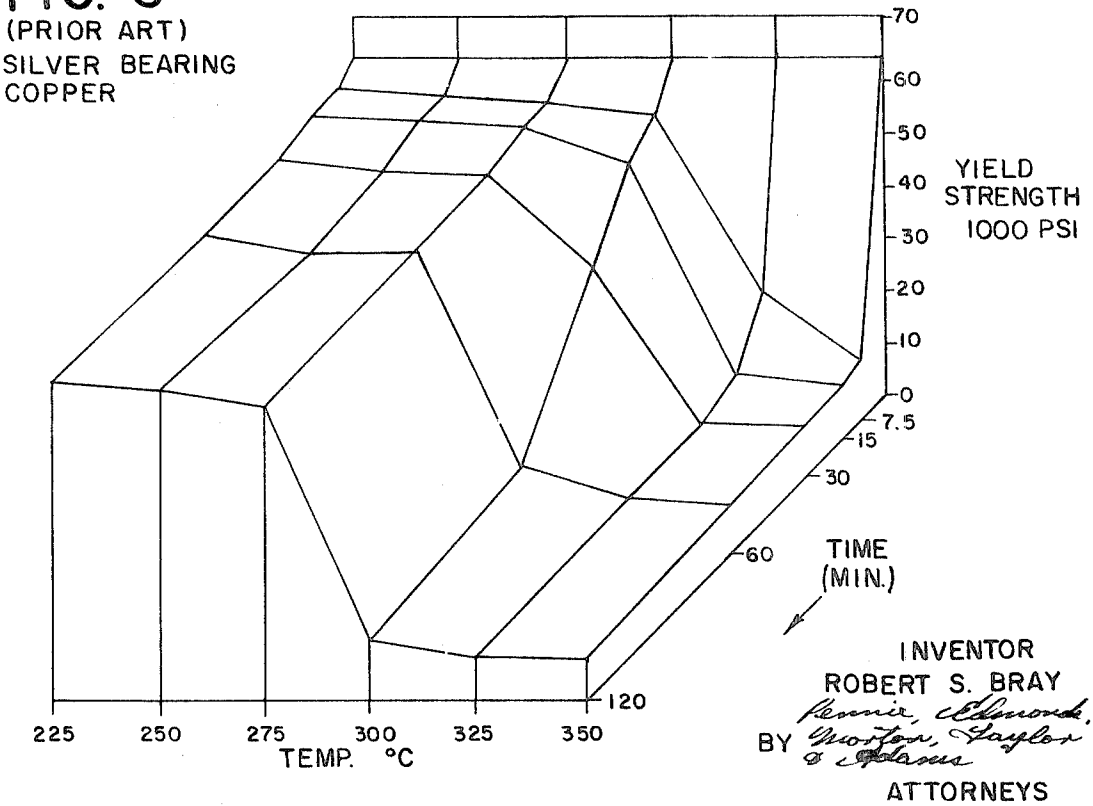


FIG. 6
(PRIOR ART)
SILVER BEARING COPPER



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COPPER-BORON-SULFUR ALLOY AND METHOD OF TREATMENT

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FIG. 7

TENSILE STRENGTH vs. ANNEALING TEMP.
for VARIOUS SOLUTION ANNEALED, QUENCHED
and 60% COLD WORKED ALLOYS.

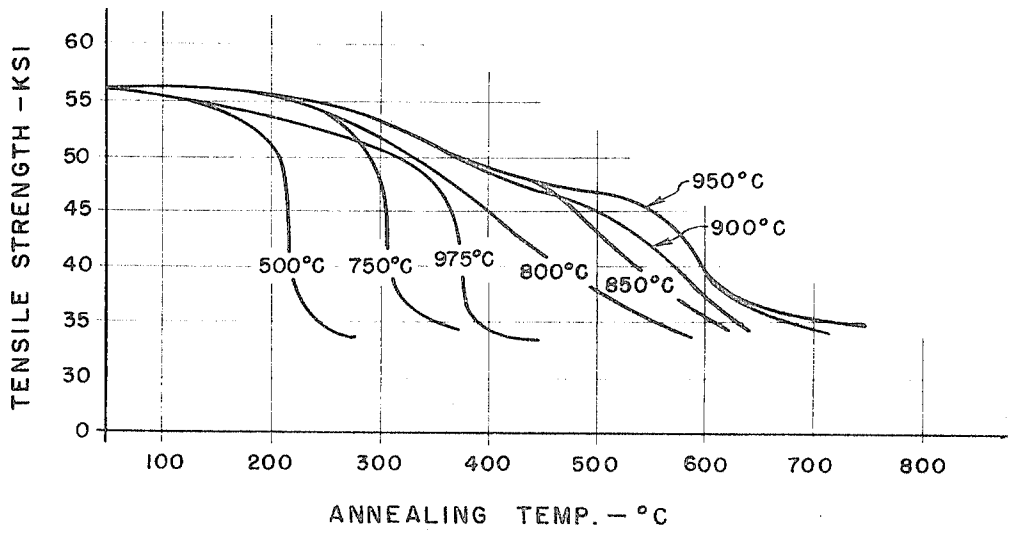
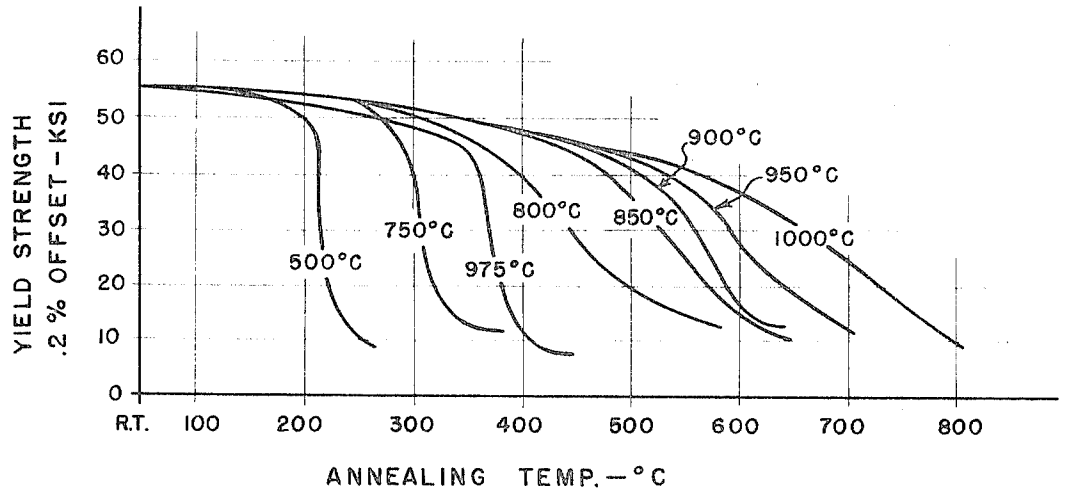


FIG. 8

YIELD STRENGTH .2% OFFSET vs. ANNEALING TEMP.
for VARIOUS SOLUTION ANNEALED, QUENCHED
and 60% COLD WORKED ALLOYS.



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3,595,705

COPPER-BORON-SULFUR ALLOY AND METHOD OF TREATMENT

Robert S. Bray, Cheshire, Conn., assignor to Anaconda American Brass Company

Continuation-in-part of abandoned application Ser. No. 613,460, Feb. 2, 1967. This application June 13, 1969, Ser. No. 832,977

Int. Cl. C22f 1/08

U.S. Cl. 148—11.5 6 Claims

ABSTRACT OF THE DISCLOSURE

A copper boron sulfur alloy containing minor amounts of boron and sulfur is provided by this invention. When this high conductivity alloy is solution annealed, rapidly cooled to room temperature and subsequently cold worked, it has a high softening temperature.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of my co-pending application Ser. No. 613,460, filed Feb. 2, 1967 now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to a copper boron sulfur alloy and to a method of treating the alloy to produce an alloy having a high softening temperature with high electrical conductivity. The alloy is further characterized by the property that after cold working it can be temper annealed to produce intermediate tempers.

Typical commercial copper will retain full hardness if heated to 175° C. but becomes fully soft if heated to 250° C. Attempts have heretofore been made to create copper alloys which will have higher softening temperatures; among these have been silver bearing coppers and cadmium coppers which will have softening temperatures near 300° C. or 400° C., respectively. Cadmium copper for instance, which after a high degree of rolling has a tensile strength of 68,000 p.s.i., will become soft at 400° C. after 10 minutes but the electrical conductivity of these alloys drop far below the high conductivity value of 100 percent IACS.

This invention is based on the discovery that the addition of minor amounts of boron and sulfur in a copper alloy gives an alloy which can be treated to improve the softening temperature to above 450° C. While retaining the high conductivity characteristics of copper. It is further characterized by the property that cold worked material can be temper annealed to intermediate tempers.

SUMMARY OF THE INVENTION

Broadly stated, the invention relates to a copper base alloy containing from .004 to .03 percent by weight boron and .002 to .01 percent by weight sulfur. The solution treated and cold worked alloy is further characterized by having a softening temperature above about 450° C. This material has an electrical conductivity of about 100 percent IACS.

The invention further relates to a method of imparting a high softening temperature to this alloy which involves solution annealing the alloy and rapidly cooling to room temperature and then cold rolling. The solution annealing

is preferably carried out between a temperature range of 900° C. and about 1040° C. and the material is rapidly quenched to room temperature in a period of less than 20 seconds.

This invention is further characterized by the property that the solution annealed and cold worked alloy can be temper annealed by heating the alloy to temperatures below its softening temperature.

By "softening temperature" used herein is meant the lowest annealing temperature which will cause a significant drop in hardness and tensile strength, as opposed to the gradual decrease with temperature and time, which results from changes due to metallurgical reactions such as recovery.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a three-dimensional chart showing the effect of temperature and time on the tensile strength of a boron sulfur copper alloy treated in accordance with the present invention.

FIG. 2 is a three-dimensional chart showing the effect of temperature and time on the yield strength of a boron sulfur copper alloy treated in accordance with the present invention. The solution annealing temperature for both FIGS. 1 and 2 was approximately 975° C.

FIG. 3 is a three-dimentional chart showing the effect of temperature and time on the tensile strength of a prior art cadmium copper alloy.

FIG. 4 is a three-dimensional chart showing the effect of temperature on the yield strength of prior art cadmium copper alloy.

FIG. 5 is a three-dimensional chart showing the effect of time and temperature on the tensile strength of a prior art silver bearing copper alloy.

FIG. 6 is a three-dimensional chart showing the effect of time and temperature on the yield strength of a prior art silver bearing copper alloy. All alloys described in FIGS. 1–6 were cold rolled in excess of 90%.

FIG. 7 is a graph showing the differing effects on the tensile strength of boron sulfur copper alloys when reheated or annealed to temperatures up to about 700° C. for alloys which have previously been solution annealed at various temperatures, quenched and cold worked. The effect of these variables on a copper alloy (CDA 109) initially treated at 975° C. but not having both boron and sulfur within the ranges of the invention is also shown, and

FIG. 8 is a graph showing the differing effects on the yield strength of boron sulfur copper alloys when reheated or annealed to temepratures up to about 700° C. for alloys which have previously been solution annealed at various temperatures, quenched and cold worked. The effect of these variables on a copper alloy (CDA 109) initially treated at 975° C. but not having both boron and sulfur within the ranges of the invention is also shown.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In one example, a boron copper sulfur alloy of the invention contained the following percentages by weight: .009 boron, .0026 sulfur and two impurities of less than .002 iron and .002 silicon. A .650 inch section of this alloy was solution annealed for one hour at 900° C. in an argon hydrogen atmosphere and immediately water quenched to water temperature. The section was then

cold rolled to .065 inch (90 percent cold reduction). Tensile specimens were machined from the strip and annealed in a salt bath at approximately 400° C., 450° C. and 500° C. for three, six and twelve minutes. The results of the measurements of tensile strength, yield strength and ductility are set out in Table I. It was observed that significant softening accurred only after six or more minutes at 500 C. It is also characteristic of this alloy that upon reheating the cold rolled copper below the softening temperature, the ductility (as measured by elongation in a tensile test) increases considerably without significantly reducing the yield strength.

TABLE I

Specimen	Tensile strength (K s.i.)	Yield strength 0.5% extension (K s.i.)	Percent elongation in 2"
As fabricated	62.0	61.5	7.5
Do	59.8	56.0	7
3 minutes, 400° C	54.0	51.3	6.5
Do	54.6	51.8	8
6 minutes, 400° C	53.8	50.6	6.5
Do	54.5	51.7	7
12 minutes, 400° C	54.7	51.9	7
Do	54.1	51.1	8
3 minutes, 450° C	48.5	44.4	10
6 minutes, 450° C	47.8	43.1	11
12 minutes, 450° C	47.0	42.0	11.5
3 minutes, 500° C	45.3	31.5	11.5
6 minutes, 500° C	38.1	22.5	26
12 minutes, 500° C	36.2	20.3	31

In a second example, a coil of 0.60 inch strip having a boron copper sulfur alloy composition of .009 percent by weight boron and .0021 percent by weight sulfur, plus normal impurities and the balance copper was annealed in a strand annealer in a cracked ammonia atmosphere for 7 minutes by passing the strand through a 15 foot hot zone at 925° C. at 2 feet per minute. The strand was quenched in water and cold rolled to .006 inch. Upon exposure to 450° C. for ½ hour, there was no appreciable softening of the alloy.

Data compiled from controlled tests of copper bearing alloy samples having boron and sulfur in the ranges of the invention shows that the range in which the alloy should be solution annealed to obtain the high softening temperature is above about 800° C. Solution annealing in the range of about 900° C. to 1040° C. for 10 minutes in preferred. Treatment at temperatures above 1000° C. does not increase the softening temperature appreciably. The following table shows the temperatures and times at which alloy specimens were heat treated and the softening characteristics of the alloy after reheating the alloy to various annealing temperatures. All the specimens tested included boron and sulfur in the ranges of the invention except the last listed alloy which was initially treated at 975° C.

TABLE II

Treatment temp. and time	Annealing temp., ° C.	.2% off Y.S., K s.i.	Tensile strength, K s.i.	Percent elongation
500° C., 1 hour	200	50.2	52.4	6.5
Do	225	16.8	38.2	30
Do	250	10.2	34.6	44
750° C., 10 minutes	250	52.8	54.1	4.5
Do	300	38.4	45.4	15.5
Do	325	18.1	37.5	35.0
Do	350	12.9	35.4	41.0
Do	400	12.1	34.9	44.0
Do	450	10.8	34.7	46.0
800° C., 10 minutes	None	56.4	56.8	3.5
Do	300	50.6	51.9	55
Do	400	39.7	45.3	15
Do	500	20.8	38.0	32
Do	550	14.9	35.5	41.5
Do	600	12.4	35.2	45
850° C., 10 minutes	None	54.3	55.5	4.0
Do	350	48.7	50.2	8.0
Do	450	44.5	47.9	10.5
Do	500	35.0	43.4	17.0
Do	550	25.0	39.7	25.5
Do	600	14.9	36.4	37.5
Do	650	10.2	34.1	43.0
900° C., 10 minutes	350	49.0	50.3	7.5
Do	500	42.5	46.7	11.0
Do	550	33.0	42.6	16.5
Do	600	14.6	35.8	35.5
Do	650	13.2	34.7	36.5
950° C., 10 minutes	350	49.5	50.9	5.5
Do	450	46.1	48.6	9.0
Do	550	40.0	45.7	13.5
Do	600	27.2	39.8	22.0
Do	650	16.1	37.4	33.0
Do	700	13.5	34.5	37.0
1,000° C., 10 minutes	350	48.4	49.9	6.0
Do	450	45.1	47.6	7.5
Do	550	41.3	45.8	10.0
Do	600	37.6	44.1	11.5
Do	650	31.6	42.1	17.0
Do	750	17.5	35.1	30.5
Do	800	10.3	32.8	37.0
CDA-109; prior art				
975° C., 10 minutes	250	51.1	52.6	3.5
Do	350	46.3	48.4	5.0
Do	375	27.9	40.6	18.8
Do	400	10.6	34.6	43.8
Do	450	7.7	33.7	49.5

All the above specimens tested were quenched from their solution annealing temperatures and were thereafter reheated for fifteen minutes to the various annealing temperatures to determine their softening characteristics. The data of Table II showing the marked increase in the softening temperatures of copper alloy in accordance with my invention is graphically presented in FIGS. 7 and 8. It will be noted that the alloy specimens of my invention which were solution annealed at 500° C. and 750° C. and the prior art copper alloy annealed at 975° C. have a low softening temperatures in that there is a rapid decline in their tensile and yield strengths when annealed at temperatures of about 400° C. and below. The other boron sulfur alloy specimens have softening temperatures above 450° C. when heat treated at 800° C., 850° C., 900° C., 950° C., and 1000° C. Quenching of the alloy in less than 20 seconds is preferred.

It has also been found that the copper boron sulfur alloys of the present invention will retain some of their strength even at very high temperatures if the alloy has been solution annealed in the range of 950° C.–1025° C. quenched and moderately cold worked. For example, an alloy in this condition will retain some of its strength when heated to about 815° C. for 1 to 5 minutes. A wire composed of an alloy in such condition which has a yield strength of 21.7K s.i. after 5 minutes at 805° C. Conventional coppers would show a yield strength of about 10K s.i. after such reheating.

While improved properties can be achieved with boron within a range of .004 to .03, it has been determined that the commercial range for boron will be from .007 to .015. For sulfur, the range is from .002 to .01 percent by weight and its commercial range will be from about .003 to .006 percent by weight.

In the metals mentioned above and in further examples made to determine the ranges given above, the conductivity values were all very close to 100 percent IACS and thus in all instances produced a high conductivity alloy.

In some comparison experiments it was found that essentially pure copper cold worked 75–95 percent, produced a softening temperature of about 250° C.; a silver bearing copper alloy worked to the same extent had a softening temperature of 300° C., and a cadmium copper similarly worked had a softening temperature of 400° C. while the copper boron sulfur alloy may be heated up to 600° C. for ½ hour without softening; a convincing demonstration of the advantages realized with this new alloy.

A further demonstration of the utility of this invention was made when several commercial lots representing over 30,000 pounds of metal were cast, rolled, annealed and finally rolled as described above. The boron content ranged from .007 to .015 percent and the sulfur content ranged from .0030 to .0059 percent. This commercial lot produced metal with the same desirable high softening

characteristics and had conductivities ranging from 100.7 to 101.4 percent IACS.

In a further comparison, a rolled cadmium copper having a tensile strength of 68,000 p.s.i. became soft in 10 minutes at 400° C. The commercially produced copper boron sulfur alloy of the invention which had a tensile strength of 65,000 p.s.i., as rolled, produced a tensile strength of 57,000 p.s.i. after 15 minutes at 400° C.; 47,000 p.s.i. after 15 minutes at 450° C.; and 54,000 p.s.i. after 1 hour at 400° C.; and 39,000 p.s.i. after 1 hour at 450° C. This property of a gradual falling off of the properties at a given temperature permits temper annealing. This gives a decided advantage in fabrication in that the metal can be reduced to its finished gauge in the cold rolling operation and the finished metal can then be commercially annealed to the desired intermediate temper. This permits sotcking a single supply of metal which can be annealed to satisfy a number of different commercial requirements.

As may be seen from FIGS. 1–6, the tensile and yield strengths of the alloy of the present invention charted in FIGS. 1 and 2 are respectively greater at every value for temperature and time than the tensile and yield strength of the cadmium copper alloy charted in FIGS. 3 and 4 and also greater than the tensile and yield strengths of the silver bearing copper alloy charted in FIGS. 5 and 6.

FIG. 1 illustrates what is meant by a gradual falling off of properties by three-dimensional depiction there of the present alloy's tensile strength slope as affected by temperature and time. The more acute slopes of the prior art alloys depicted in FIGS. 3–6 graphically demonstrate the improvement achieved with the present alloy.

I claim:

1. A method of imparting high softening temperatures to a copper alloy comprising providing in the alloy .004 to 0.3 percent by weight boron and .002 to .01 percent by weight sulfur, solution annealing the alloy at a temperature in the range of about 800° C. to about 1040° C. and maintaining it in that temperature range for a period of time, rapidly quenching the alloy from said annealing temperature to about room temperature and subsequently cold working the alloy.

2. A method according to claim 1 wherein the alloy is maintained in a nonoxidized atmosphere during heating and its maintenance in the temperature range.

3. A method according to claim 1 wherein the alloy is solution annealed at a temperautre from 900° C. to about 1040° C.

4. A method according to claim 1 wherein the rapid quenching time is less than 20 seconds.

5. A method according to claim 1 wherein the alloy is thereafter temper annealed by heating to a temperature less than its softening temperature.

6. An alloy having a conductivity of substantially 100% IACS containing .004 to .03 percent by weight of boron and .002 to .01 percent by weight of sulfur and the remainder copper, said alloy having been produced by the process of claim 1 and characterized by having a softening temperature above 450° C.

References Cited

UNITED STATES PATENTS

2,183,592	12/1939	Silliman	75—153
2,195,433	4/1940	Silliman	75—153
2,479,311	8/1949	Christensen et al.	75—153X
3,352,667	11/1967	Das et al.	75—153

FOREIGN PATENTS

668,602	8/1963	Canada	75—153

OTHER REFERENCES

German publication, Auslegeschrift 1, 129,038, May 1962, 75/153.

Anaconda Copper and Copper Alloys, Publication B–32, 10th ed. 1959, The American Brass Company.

CHARLES N. LOVELL, Primary Examiner

U.S. Cl. X.R.

75—153; 148—32