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2,567,560

HEAT TREATMENT OF COPPER-SILVER BINARY ALLOYS

Filed May 6, 1948

2 Sheets-Sheet 1

FIGURE 1

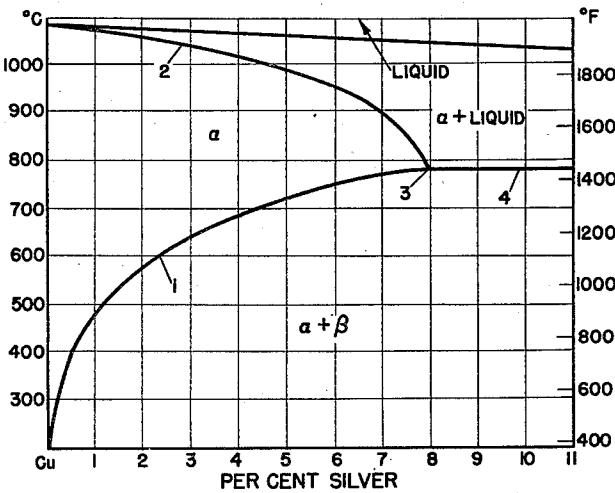
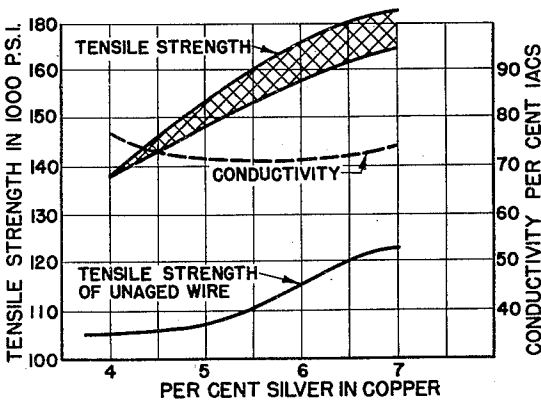


FIGURE 3



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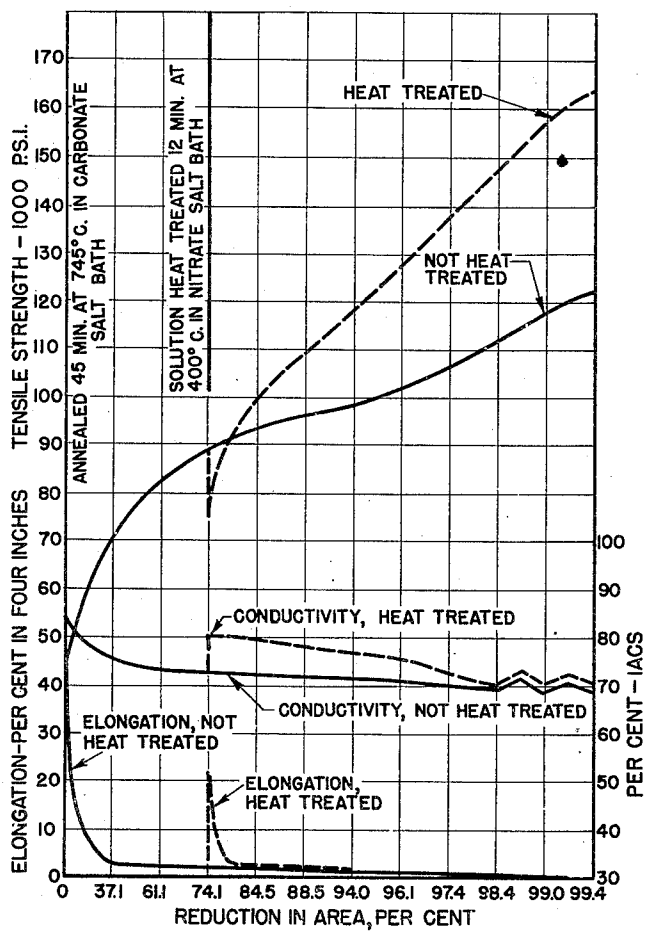
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2 Sheets-Sheet 2

FIGURE 2



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HEAT-TREATMENT OF COPPER-SILVER
BINARY ALLOYS

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mesne assignments, to Battelle Development
Corporation, Columbus, Ohio, a corporation of
Delaware

Application May 6, 1948, Serial No. 25,509

2 Claims. (Cl. 148—12.7)

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This invention relates to a method of processing binary alloys of copper and silver and to the product thereby produced. The present invention is particularly directed to the processing of the low-silver alloys wherein the silver does not exceed approximately 8%.

Binary alloys of copper and silver in which copper is the base metal have been known for some time, but exist primarily in the laboratory due to the fact that they are not characterized by sufficiently outstanding properties to offset the explicit expense of their production. These binary alloys, wherein the silver is present in amounts under 8%, do not compare favorably to the much cheaper metal copper. These alloys have a conductivity, when annealed, of about 90% of that of pure copper, only little higher tensile strength and a lower elongation. Consequently, very little work has been done with these alloys, particularly because preliminary processing attempts were discouraged by the discovery that, while hardness increased after an age-hardening heat treatment, the tensile strength went down.

The primary object of the present invention is to provide a method of processing silver-copper alloys containing less than about 8% of silver so as to produce a product having unusually high conductivity combined with excellent tensile strength.

Another object of this invention is to provide a method for aging and cold working a silver-copper binary alloy having a copper base wherein the aging time is reduced to less than one-half hour.

Other objects and advantages of the present invention will become apparent from the following detailed description thereof when read in conjunction with the accompanying drawings in which:

Figure 1 is a phase diagram of the copper-rich portion of the copper-silver system.

Figure 2 is a graph upon which curves are plotted to show the effect of aging and cold drawing upon the properties of a particular silver-copper wire, and

Figure 3 graphically illustrates the effect of variations of the silver content in the processed alloy.

It has been discovered, as described and claimed in the copending application, Serial No. 25,508, filed May 6, 1948, on "Copper-Silver Alloys," now abandoned, that binary alloys of copper and silver can be aged and then cold-worked to produce alloys having unusual and useful properties. The present invention lies in the discovery that preliminary cold working prior to aging the alloy increases the hardening and strengthening effect of subsequent cold working of the alloy over what can be otherwise attained

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without the preliminary cold working treatment. Furthermore, this preliminary cold working step lowers the aging temperature required and greatly diminishes the time necessary for the aging treatment.

The process comprising the present invention is applicable to alloys containing less than about 8% silver and which are composed of a single phase (alpha). These alloys fall within the area lying between lines 1 and 2 in Figure 1. Line 1 represents the limit of solid solubility at any given temperature of silver in copper, whereas line 2 is the solidus line, that is, the line below which the alloy is entirely in the solid form. The junction of lines 1 and 2 in Figure 1 is designated point 3 and is the maximum limit of solid solubility of silver in copper. Line 4 indicates the temperature at which the eutectic of this system solidifies, that is, about 779° C.

Since point 3 indicates the maximum solid solubility of silver in copper to be about 8%, silver in excess of this amount will produce a two phase alloy, to which the present invention is not applicable. It is very difficult to obtain complete solid solubility of over 7% silver in copper, so that it is preferred to restrict the silver content to 7% or slightly lower. The lower limit for silver is about 3%, because very little benefit is derived from the present process using alloys of lower silver content. The full effect of the aging step is not found in alloys containing as little as 3% silver, so that the lower preferred limit is about 5% silver.

As the alloy cools down after the copper and silver have been intermingled in the molten state, the copper-rich phase designated alpha in Figure 1 precipitates out first, leaving the alloy which solidifies last richer in silver. Consequently, the as-cast alloy contains both alpha and beta phase and must be solution annealed or solution heat treated to cause it to reform in the single alpha phase. It is essential that the alloy be first put into a single phase by solution heat treatment in order to age it. The step of solution heat treatment is well known to metallurgists and need not be described here in detail since it forms only an incidental part of the present invention. It has been found, nevertheless, that solution heat treatment at about 745° C. continued for two hours and followed by a water quench produces highly satisfactory results, if repeated often enough. About four of these "soaking" periods have proven to be sufficient to put the alloy substantially or entirely into the single alpha phase. Variations in time and temperature and manner of quench may be made in this procedure without in any way affecting the present invention. It is only critical that the

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alloy be substantially or entirely in the single copper-rich phase before it is cold worked.

In the present invention, the alloy is given a preliminary cold working treatment. The term "cold working," as employed in this application, includes any type of cold working, such as drawing, rolling, pounding, hammering, etc. There is no clearly definable minimum amount of cold work required in this preliminary treatment, because the advantages obtained from this step increase gradually up to about 75% reduction in area. Since the maximum benefit is derived from this step when reduction ranges from 75% to about 95%, this range is preferred.

The cold worked alloy is then aged by heating the alloy, usually in a molten salt bath or the like, until a marked drop in tensile strength is obtained. This phenomenon, as indicated above, is directly contrary to the usual age hardening treatment because normally other alloys that respond to the aging treatment increase in tensile strength upon aging. The aging effect is the combined product of time, temperature and composition, and the aging step itself, as it is practiced herein, is familiar to all metallurgists as being common practice in connection with a large number of alloys. In the present instance, it may be stated generally that temperatures between 350° C. and 500° C. produce excellent results with the binary copper-silver alloys to which this invention relates. The present aging treatment is remarkable, not only as respects the softening action above referred to, but as respects the short period of time required to effectively age this alloy. For example, an aging treatment of ten to fifteen minutes at about 400° C. produces very excellent results. This extremely short aging period is highly important from a commercial standpoint, because it greatly increases the rate of production.

After aging, the alloy is again cold worked until a tensile strength and hardness has been obtained sufficient for the purpose to which the alloy is to be put. The exact extent of this second cold working step will depend almost entirely upon the end use of the alloy, but normally sufficient cold working is employed to at least give the alloy a tensile strength greater than that which it had prior to the aging treatment. Actual practice has shown that maximum tensile strengths are obtained when the alloy is cold worked to about 97% reduction in area after the aging treatment. For example, an alloy of 6% to 7% silver, balance copper, aged 10 minutes to 15 minutes at 400° C. and cold worked before and after aging in this preferred manner will have a better combination of tensile strength and electrical conductivity than any other known alloy. Substantially the same result will be obtained with an aging time of 5 minutes at 425° C.

A graphic illustration of the effect of the treatment defined in the present application upon an alloy containing 6.5% silver and the balance copper is clearly shown in Fig. 2. The tensile strength is plotted against the per cent reduction in area on a logarithmic scale, and the alloy was tested in the form of a wire. The annealed alloy, having a tensile strength of 45,000 p. s. i., increases in tensile strength as it is cold worked up to the point of 74.1% reduction in area, at which point the alloy was aged. The aged alloy, represented by the dotted line, dropped in tensile strength rapidly from about 89,000 p. s. i. to 76,000 p. s. i. upon aging. However, it required less than 25% additional reduc-

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tion of area to raise the tensile strength of the heat-treated or aged alloy above that of the unheat-treated alloy represented by the solid line on Figure 2. Upon further cold working of the heat-treated or aged alloy, it is clearly apparent that this alloy was much more responsive to the cold working treatment than the alloy which was not cold worked prior to aging. At 97% additional reduction in area after aging the alloy attained a tensile strength of 165,000 p. s. i. and exceeded the tensile strength of the unaged alloy by 40,000 p. s. i.

Not only does the present process produce an alloy having greatly increased tensile strength, but the conductivity, as indicated in Figure 2, is also increased somewhat by the aging treatments. As above pointed out, the amount of increase in conductivity is dependent upon the length of the aging treatment. In Figure 2, the aging treatment was 12 minutes at 400° C. in a nitrate salt bath and was much too short for any substantial increase in conductivity to be obtained. This treatment is intended to give maximum strength with an electrical conductivity of at least 70% of that of pure copper.

In order to better enable those skilled in the art to more readily practice the present invention, the following examples are set forth:

Example 1

An alloy of 4% silver and 96% copper was cast and reduced to 0.135 inch diameter wire by cold rolling and drawing, and solution annealed at 750° C. and quenched. The wire was then drawn to 77% reduction of area. One part was aged 15 minutes at 400° C. One part was aged 1 hour at 400° C. Both were then drawn to 97% reduction of area. These wires had the properties shown below:

Aging Time, Minutes	Diameter, Inches	Tensile Strength, p. s. i.	Conductivity, percent IACS
15	.0106	135,000	77.0
60	.0106	137,000	79.9

Example 2

An alloy of 5% silver and 95% copper was treated in identical manner to that of Example 1. The wire produced had the following properties:

Aging Time, Minutes	Diameter, Inches	Tensile Strength, p. s. i.	Conductivity, percent IACS
15	.0106	148,000	73.1
60	.0106	134,000	80.9

Example 3

An alloy of 6% silver and 94% copper was treated identically to the foregoing examples and had the following properties:

Aging Time, Minutes	Diameter, Inches	Tensile Strength, p. s. i.	Conductivity, Per Cent IACS
15	.0106	160,000	74.2
60	.0106	126,000	82.2

Example 4

An alloy of 7% silver, 93% copper was treated as the foregoing examples down to the aging step. This wire was then aged at various times and

temperatures to obtain the maximum strength possible at each temperature after a reduction of area of 97% following aging. These times were found to be:

Aging Temperature, °C.	Aging Time, Maximum Strength	Maximum Tensile Strength, p. s. i.	Conductivity, Per Cent IACS
	Minutes		
375	20	162,000	70.0
400	7.5	167,000	68.0
425	3.0	169,000	69.0

In general, as indicated above, the time of heat treatment becomes shorter and more critical as the temperature increases, and the maximum strength is higher with higher temperatures. Also, it has been found that the ductility of the wire is poor at the point of maximum strength, but that nearly as high a strength is obtained with higher electrical conductivity and better ductility is reached after longer aging periods, such as 5 minutes at 425° C., 12 minutes at 400° C., 30 minutes at 375° C. (at 375° C. aging temperature, the ductility is definitely poorer than at higher temperatures).

Example 5

An alloy of 6% silver, 0.1% magnesium, balance copper, was solution heat treated and quenched from 750° C. in the form of wire of 0.144-inch diameter. This wire was then cold drawn 82% reduction of area and aged. Following the aging treatment, the wire was again drawn to 97% reduction of area. This wire had the properties noted below:

Aging Temperature, °C.	Aging Time, Minutes	Tensile Strength, p. s. i.	Conductivity, Per Cent IACS
400	10	164,000	70.1
400	15	160,000	72.7
400	30	158,000	74.0
425	3	161,000	67.5
425	5	167,000	67.5
425	10	163,000	69.0
425	15	158,000	71.4

Example 6

An alloy of 6.5% silver, 0.02% magnesium, balance copper was solution heat treated and quenched from 745° C. in the form of ¼ inch diameter rod. This was then drawn to 94% reduction of area, aged 12 minutes at 400° C., and then drawn to 97% reduction of area. The wire (.011 inch diameter) had the following properties:

Tensile Strength	Conductivity
162,000	72.6

A similar alloy without magnesium had practically identical properties after the same treatment.

Figure 3 graphically illustrates the tensile strength and electrical conductivity of the processed copper-silver alloys as the silver content is varied. The alloys were processed by drawing solution heat treated stock to 75 to 95% reduction in area, aging 12 to 15 minutes at about 400° C., and again drawing to about 97% additional reduction in area. The shaded area shows normal limits of variation in tensile strength. The ten-

sile strength of the unaged alloy is also shown for comparison purposes. Optimum properties appear to be reached at about 7% silver, although the tensile strength begins to level off at about 6% silver. Alloys containing 4% silver have lower tensile strengths, but have somewhat higher conductivity than alloys containing greater amounts of silver. Even the lowest tensile strength for 4% silver alloys (138,000 p. s. i.) is an improvement of more than 200% over pure copper. This increase in tensile strength is of supreme importance in producing light weight communication cable.

It is apparent from the above-detailed description that the present invention relates to the processing of copper-silver alloys containing from 3 to 8% silver, which comprises cold working the alloy prior to aging as well as after the aging step. By practicing the present invention in its preferred embodiment, a product may be produced having a tensile strength in excess of 160,000 p. s. i. and a conductivity greater than 70% of that of copper. The combination of these two properties provides a product so unusual that the relatively high cost of the binary silver-copper alloys is offset thereby.

What is claimed is:

1. A method of processing binary alloys of copper and silver which contain at least 3% and not more than 8% silver, which comprises solution heat treating and quenching the alloy, whereby substantially all of the alloy is in the copper-rich single phase, cold working the resulting alloy until a cross-sectional reduction in area of at least 75% and not more than 95% is obtained, aging the cold-worked alloy at temperatures ranging from 350° C. to 500° C. for a period of at least five minutes and less than thirty minutes, and cold working the aged alloy until an additional reduction in cross-sectional area of approximately 97% is produced.

2. A binary alloy of copper and silver which contains at least 3 per cent and not more than 8 per cent silver, in the treated state, produced by the process comprising solution heat-treating and quenching the alloy, whereby substantially all of the alloy is in the copper-rich single phase, cold-working the resulting alloy until a cross-sectional reduction in area of at least 75% and not more than 95% is obtained, aging the cold-worked alloy at temperatures ranging from 350° C. to 500° C. for a period of at least five minutes and less than thirty minutes, and cold-working the aged alloy until an additional reduction in cross-sectional area of approximately 97% is produced.

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