

May 5, 1942.

F. R. HENSEL ET AL

2,281,691

PROCESS FOR HEAT TREATING COPPER ALLOYS

Filed March 8, 1934

3 Sheets-Sheet 1

Fig. 1.

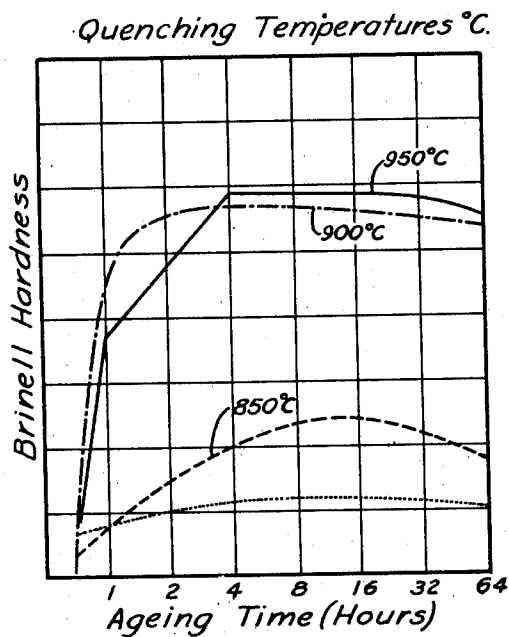
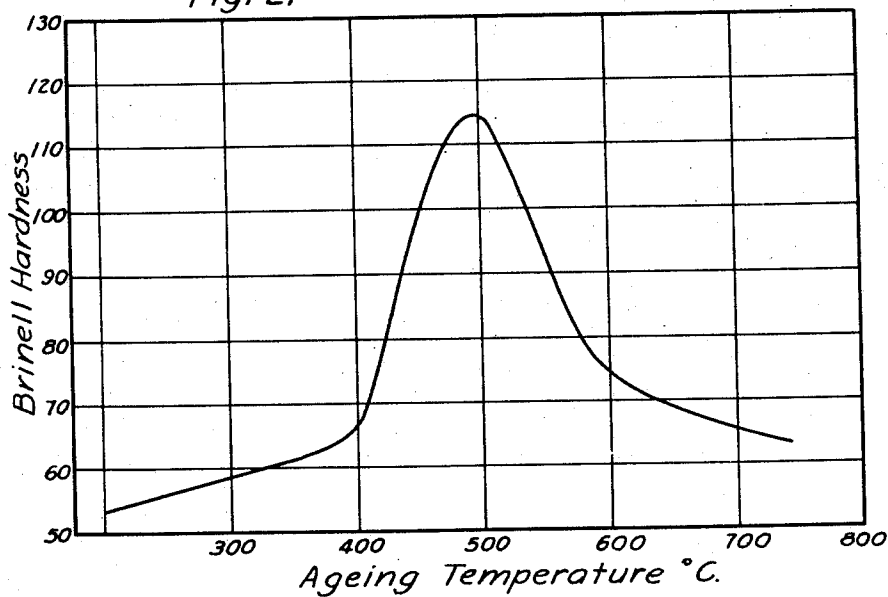


Fig. 2.



WITNESSES:

Fred. C. William
R. J. Fitzgerald

INVENTORS
Franz R. Hensel &
Earl I. Larsen
BY *Howard Flint*
ATTORNEY

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Fig. 3.

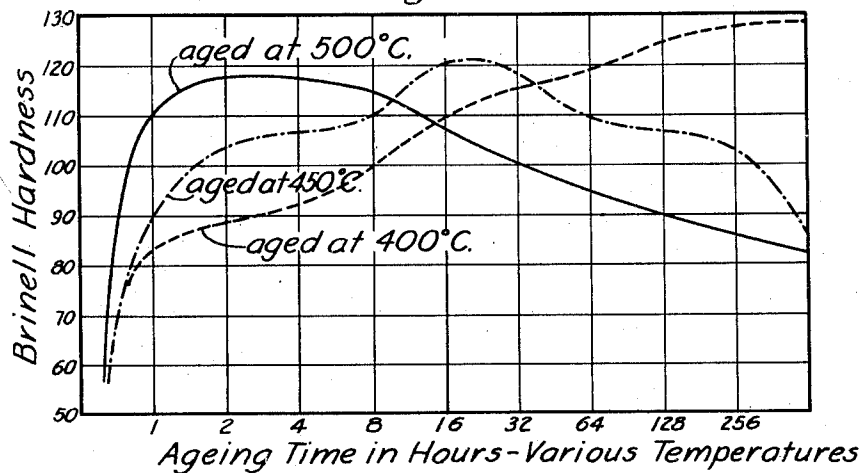
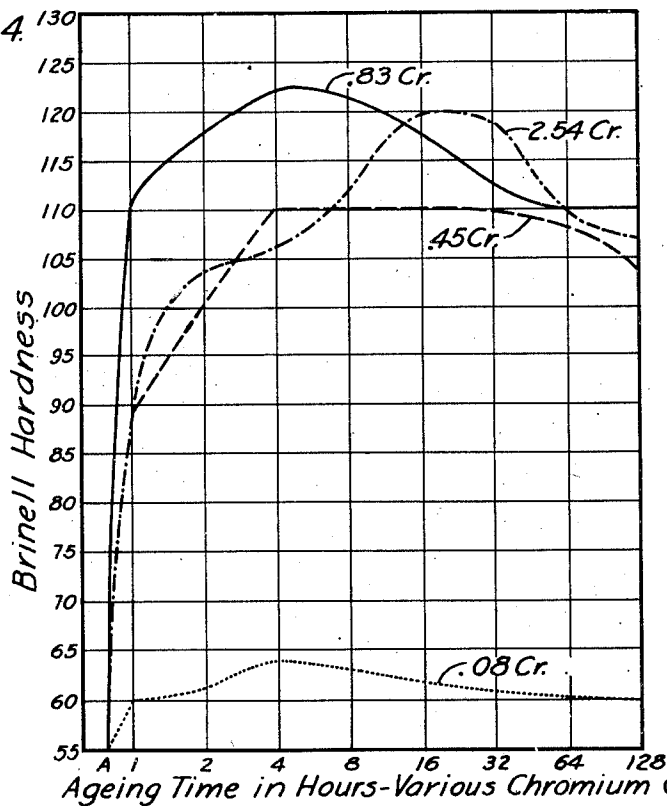


Fig. 4.



WITNESSES:

Fred. C. Milham

R. J. Fitzgerald

INVENTORS

Franz R. Hensel &

Earl I. Larsen

BY Howard Flint.

ATTORNEY

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3 Sheets-Sheet 3

Fig. 5.

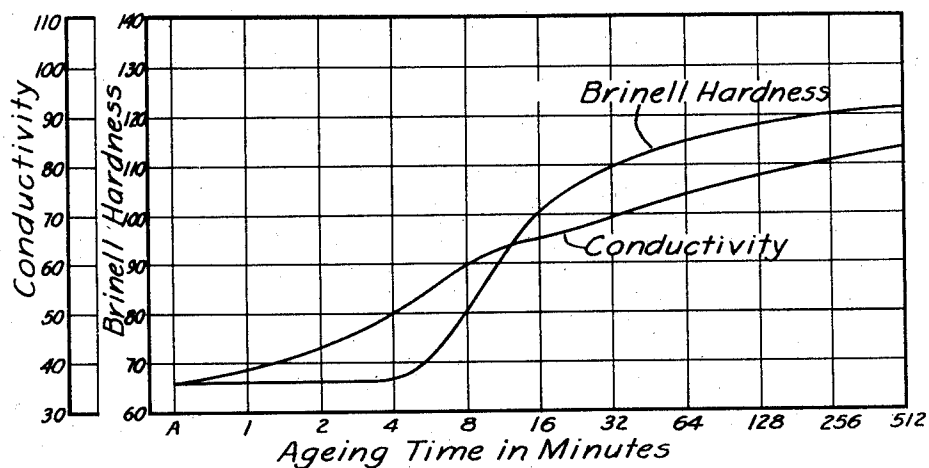
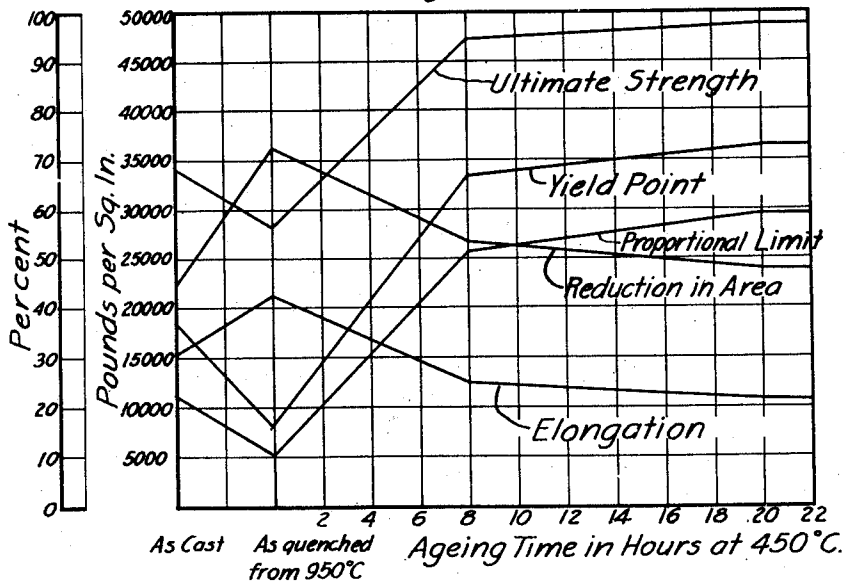


Fig. 6.



WITNESSES:

Fred C. Milham

R. J. Fitzgerald

INVENTORS

Franz R. Hensel &
Earl I. Larsen

BY

Howard Flint

ATTORNEY

UNITED STATES PATENT OFFICE

2,281,691

PROCESS FOR HEAT TREATING COPPER ALLOYS

Franz R. Hensel, Wilkinsburg, and Earl I. Larsen,
Turtle Creek, Pa., assignors to Westinghouse
Electric & Manufacturing Company, East Pitts-
burgh, Pa., a corporation of Pennsylvania

Application March 8, 1934, Serial No. 714,614

4 Claims. (Cl. 148—21.2)

This invention pertains to the art of treating copper for improvement in mechanical, thermal and electrical properties, and pertains to improvements in copper-base alloys.

In the past, copper has been hardened principally by deforming or cold-working the metal, but has readily lost such improved qualities when heated. Moreover many articles that have been shaped in some particular way, such as complicated castings, are not suitable for cold working. Increase in mechanical properties has been imparted also by adding certain metals to copper, but quite generally such compositions have been quite inferior to copper in ability to conduct electricity. Also there have been difficulties in controlling and duplicating resulting qualities.

An object of the present invention is to improve copper in mechanical properties while retaining high electrical conductivity and also high thermal conductivity. A further object is to improve copper articles that are not feasible to deform by cold working, such as complicated castings or forgings. Other objects will appear from further description and by reference to the accompanying drawings for illustrative data concerning preferred practices of this invention.

This invention is predicated on the discovery that copper containing even small proportions of chromium may be improved in both mechanical and electrical properties by certain heat-treatment comprising quenching. Preferably the copper composition is cooled quickly from temperatures above 850° C. and then reheated for a period of time at temperatures below 600° C.

Some reference to individual factors of the treatment will serve to illustrate, without limiting, variations in practice to which this invention is amenable.

Introduction of chromium into molten copper to form a solution is difficult. Chromium dissolves but slowly in copper, and the amount finally dissolved is small. The free chromium differs in density from copper and tends to segregate in the melt and to result in lack of homogeneity in the resulting solid product. Moreover, chromium, being lighter than copper, is difficult to keep submerged for the time required to dissolve. It tends to rise to the surface of the melt, and there form oxides that contaminate the product.

To overcome such difficulties of incorporating chromium in molten copper, preferred practice of this invention contemplates distributing the chromium in finely divided form. Preferably it is added as a powder with a soluble distributing

agent, such as a compacted mixture in the form of a cake, pellet or rod compacted from intermixed copper and chromium powders. For example the metals powdered to approximately 100 mesh size may be compressed to sufficient density to prevent floating on molten copper. A density of about 8.5 may be imparted to a mixture of copper and chromium powders by a pressure of about 60,000 pounds per square inch. Lower pressures and lower densities however are useful. Alternatively, pressure of the order of 4,000 pounds per square inch may be utilized to give form and coherence to the powdered mixture, followed by heating in reducing atmosphere to sinter the particles. A particularly effective method is to heat such a coherent cake in reducing atmosphere to approximately the melting point of copper, and then quickly strike a hard blow, as in a die under a punch press. It is desirable, through optional, to include some small amount of scavenging material in the cakes, such as appropriate forms of calcium, barium, magnesium phosphorus or silicon for example, or slag forming material such as B_2O_3 , borax or CaF_2 . To obtain high conductivity it is desirable that impurities, such as iron, be absent. As an alternative to compressing, sintering or cementing powders of chromium and copper, chromium powder may be enclosed in copper tubes, as for example of half inch diameter. The tubes then are swaged to suitable compactness for addition to the molten metal. Such articles are useful for addition to other alloys as hardening or scavenging means.

The amount of chromium added to molten copper affects the viscosity or pouring qualities of the melt. With a chromium content above 0.5 per cent the viscosity is considerably higher than of pure copper, but castings may be made in slower-cooling types of molds. Bottom-pouring constitutes preferred practice. Sand castings of complicated design may be made with 0.5 per cent chromium, and even up to about 1.5 per cent chromium, but above this latter amount the tendency is pronounced for the chromium to separate and even to segregate at the top of the casting unless rapidly cooled types of mold are used. An advantage of the present invention is that sound castings may be obtained of high mechanical and electrical and thermal properties without requiring more than very small amounts of chromium, as of the order of 0.5 per cent. Thus pouring qualities and homogeneity of a casting are maintained readily.

To age or develop and improve the mechanical and electrical properties, such a casting is heated to high temperatures somewhat below its melting point, quenched or cooled quickly, and then reheated to intermediate temperatures. Illustrative data are presented in the following description and accompanying drawings.

One of the important factors is the temperature to which the alloy is heated before quenching, though some latitude is possible. The effect of this quenching temperature is illustrated in Fig. 1, taking for example treatment of a sand-cast copper alloy containing about 0.45% chromium. The property of hardness as measured on the Brinell scale is illustrative of the changes brought about by this quenching control of the alloy. Practical ageing occurred after quenching from 900° C.; while quenching from 950° gave somewhat greater hardness, but tended to slow the final stage of subsequent reheating.

After quenching from suitable temperatures, the temperature of reheating is an important factor to develop mechanical and electrical properties. Fig. 2 illustrates that ageing of a quenched copper alloy of 2.54% chromium content occurred somewhat at 400° C., but reached a rather sharp maximum value on heating about two hours at about 500° C. Higher temperatures were rapidly deleterious. A preferred ageing temperature therefore is approximately 450° C. For other reasons also a temperature rather close to 450° is preferred, though the range 400° C.-550° C. may be regarded as accomplishing in a readily practical manner certain of the benefits of this invention.

The time of ageing correlates nicely to 450° C. as ageing temperature, as is illustrated in Fig. 3. Experience shows that after these alloys age to their optimum values they exhibit a tendency to deteriorate that is accelerated at the higher temperatures. Copper containing 2.54% chromium and quenched from 950° C. attained maximum hardness in 16 hours when aged at 450° C. The alloy if aged at 500° C. attained maximum hardness in only three hours, but became impaired with another hour of heating at that temperature. Ageing at 400° C. also is valuable, for it results in a somewhat higher hardness; and even months of continued heating at 400° fail to develop any decrease of hardness. However, maximum hardness was not developed at 400° C. until after 250 hours. But the observation evidences that this material aged at suitable temperature and time may be used safely at temperatures up to 400° C.

The effect of chromium content on the ageing characteristics is illustrated in Fig. 4, with curves based on quenching from 950° C. and ageing at 450° C. Even with as little as 0.08% chromium the copper increased definitely in hardness. Above about 0.45% chromium the initial increase was pronounced but in ultimate hardness, with ageing continued longer than sixteen hours, no advantage was gained from chromium above about 0.45%.

The influence of varying chromium contents on electrical conductivity is similar. With small amounts, such as 0.08% to 0.45% chromium, the conductivity improves during ageing, and is scarcely greater with greater amounts of chromium. Thus the conductivity with 0.45% chromium was about 40 per cent as quenched (pure copper 100 per cent), but on ageing at 450° C. the conductivity increased to about 87 per cent. This was substantially the same conductivity as at-

tained with a higher chromium content of 2.54% aged for the same length of time. Electrical conductivity is a property that is greatly influenced by small amounts of impurities, such as foreign elements or such as oxides taken up by the copper; hence the ability of this invention to utilize the smaller amounts of chromium minimizes the tendency to contamination that accompanies use of larger amounts of added metal. Indeed the deleterious conductivity effect of impurities in copper is such that even average "pure" copper sand castings seldom show conductivity values above 85 per cent. Their hardness is only about 35 to 40 Brinell. Under the present invention, sound, hard castings of copper-chromium have been made consistently under commercial conditions with an average conductivity of over 85 per cent, and under laboratory conditions with a conductivity of 94 per cent.

It is exceedingly important for many uses to achieve an increase simultaneously in both mechanical properties and in conductivity by quenching and subsequent ageing of copper alloys containing chromium according to the present invention. Fig. 5 illustrates the simultaneous increase of both hardness and conductivity of copper containing 0.8% chromium, during ageing after quenching from 950° C. Many age-hardening alloys exhibit considerable decrease in conductivity on ageing, but exceptionally noteworthy is the increase in conductivity of copper-chromium from the outset of ageing according to the present invention. It is noteworthy also that with copper-chromium thermal conductivity improves similarly to electrical conductivity in response to this invention.

This invention introduces marked improvement in copper with respect to tensile strength. This is illustrated in Fig. 6. With ageing preceded by quenching, sand castings showed considerable increase in ultimate strength, yield point and proportional limit, while desirable values of elongation and reduction of area were retained.

Improvement in impact strength also results from ageing copper-chromium after quenching, according to this invention. Thus a sand-cast alloy of copper containing 0.45 per cent chromium, quenched from 950° C. and aged at 450° C., exhibited an impact strength of 45-50 foot pounds even at temperatures as high as 400° C. Such impact strength is remarkable inasmuch as various other copper alloys or complex brasses have completely lost their impact strength at 300° C.

If desirable, the advantages of cold working may be used to supplement those of ageing according to this invention, where the form of the finished article permits cold working. Thus after quenching and ageing these copper-chromium alloys, cold-rolling to 15 percent reduction in thickness increased their hardness from 125 to 135 Brinell. The fully-aged article could withstand as severe cold working as 60 percent reduction in thickness without developing cracks.

Even when cold rolling is interposed between the quenching and ageing steps of this invention, the ageing step after 15 percent reduction of size brings about increase of hardness to 135 Brinell. As compared with other cold-worked copper alloys, which soften at about 250°-300° C., the high hardness of 135 Brinell after heating cold-worked copper-chromium alloys to 450° C. is remarkable.

Thus the present process is capable of utilizing small proportions of chromium below 0.5 per-

cent to obtain an unworked copper article that may be in massive and complicated forms and yet possess electrical conductivity of 85-93% together with hardness of over 110 Brinell, ultimate strength of 56,000 pounds per square inch, 25 percent elongation, and high resistance to creep. Particularly useful applications of this invention are in the manufacture of large castings, as commutator segments, or as collector rings for high-current generators. Other uses where the high strength and high conductivity of the product of this invention extends the field of uses are as tips for mechanically operated welding electrodes, or as welding wheels, or as current collecting nozzles on automatic arc welding heads. Further, an important use for this high strength alloy is as cylinder heads for internal combustion motors such as for automobile engines. These fields require a metal of high conductivity of electricity or of heat as the case may be, combined with high strength at somewhat elevated temperature. These alloys are suitable also for use at normal or low temperatures, as required for transmission wire. These copper-chromium alloys may be tinned or soldered without losing their strength after quenching and ageing according to this invention.

The present description of this invention comprising certain treatment of copper-chromium alloys is intended to be illustrative but not restrictive, inasmuch as modification is contemplated. For instance certain additions may be made to copper-chromium to obtain a ternary, or higher, alloy that exhibits high conductivity along with excellent mechanical properties. The addition of zirconium, for example, is particularly valuable. Thus alloys of copper containing as much as 1.5 percent chromium and 2.6 percent zirconium, after quenching from 950° C. exhibited Brinell hardness of 71 which on ageing at 450° C. was raised to 152 Brinell. At the same time electrical conductivity was raised from 27 percent to 65 percent. Decreasing the percentage of zirconium permits raising electrical conductivity of the age-hardened alloy to about 80 percent. Quenching may be from about 600°-950° C., with reheating to about 250°-600° C.

Zirconium moreover, accomplishes cleansing or scavenging of the alloy without such impairment of electrical conductivity as imposes caution in use of such scavengers as phosphorus, silicon or the alkali earth metals. The proportion of zirconium may range from extremely small amounts from traces to approximately 5 percent. Approximately 0.5 percent zirconium in the alloy is a suitable order of magnitude for many purposes; while the chromium may range from a few hundredths of a percent to about 5 percent. Particular requirements of hardness balanced against conductivity will impose infinite ways of adjusting the relative amounts of alloying metal. It may often be sufficient to obtain hardness of about 70 Brinell with high conductivity of about 80 relative to pure copper and thus utilize the high conductivity of sand cast copper with approximately double its hardness.

Other metals that we find are suitable additions for ageing copper-chromium alloys are cadmium, silver, cobalt, boron, uranium and thorium. Thus while boron is substantially insoluble in copper, it may be brought into solution in copper-chromium. Boron, boron carbide, calcium boride serve well the double purpose of scavenging flux and alloying element. An alloy of cadmium as high as 2 percent with about 1 percent chromium

and the balance copper, for example, when quenched from 950° C. exhibited hardness of 59 Brinell, but after ageing at 450° C. a hardness of 116 Brinell; while electrical conductivity of 50 percent after the quenching was raised to 90 percent by the ageing. Suitable ranges are about 0.1 to 5 percent cadmium with about 0.1 to 5 percent chromium in the copper, the relative amounts of cadmium and chromium being adjusted according to requirements of hardness or strength and conductivity. The heat treatment ranges are similar for various additions of the metals herein mentioned; namely quenching from 600-1000° C. and reheating from 250°-600° C.

Theories of the present invention impose no restriction, but applicants' present view is that the quenching temperature is such as assures solid solution in copper of the added metal to some degree that is high relatively to the ultimate solubility of the particular metal, or metals, in the particular solvent. This solution temperature therefore is variable over practicable ranges, but for the present copper solvent preferably is of the order of 950° C. This temperature is considered to affect not only the accomplishment of subsequent ageing or reheating but to some extent the rate of ageing. Quenching or rapid cooling appears to create a condition of supersaturation or metastability at normal temperatures. But on reheating suitably, the excess of dissolved metal is precipitated from solid solution so as to be distributed in extremely small particles with such relation to the matrix crystals as to harden and strengthen the entire solid. Time and temperature thus are to be adjusted to varied requirements, but for the present solvent of copper base 450° C. appears to be optimum for various purposes. During this reheating, the removal of solute from solution enhances electric conductivity and with the above-mentioned metals in copper enhances also thermal conductivity. In some cases, such removal appears to be facilitated, and also mechanical strengthening enhanced, by formation of a compound, as for example between copper and zirconium, which is of low solubility under the conditions of ageing and of use. The present invention, therefore, differs from annealing without quenching, in that it utilizes quenching as an element of control for avoidance of fortuitous results. Moreover, time and temperature of ageing are varied and controlled to avoid such agglomeration of the finely divided precipitate as would tend to diminish hardness. However some such decrease of hardness from maximum may be utilized to increase conductivity in cases where maximum hardness is not requisite.

An advantage of this invention is demonstrated in further treatment of these alloys to produce particularly high conductivity in selected portions of the finished article. For example, without being restrictive, a chromium alloy may be treated to yield a surface of especially high conductivity while the interior is made of high strength. Thus, the alloy while raised to a high temperature within the solution range, where solution and diffusion of the alloying metal are enhanced, such as about 950° C., may be exposed to oxidation, as in air, for a suitable period of time, such as 5 to 20 hours. Then occurs oxidation of the alloying metal at the surface selectively to the copper. The result is that subsequently on quenching and ageing, an article is produced with a high conductivity

though soft surface, but a hardened interior. For example, after heating copper-chromium for several hours at about 950° C. then quenching and ageing the article exhibited an interior of about 110 Brinell hardness, but a surface about 15 to 20 mils thick of which the hardness was only about 70 but thermal conductivity was about 15 to 20 percent greater than the core. The alloying elements mentioned herein are amenable to this preferential removal from alloyed condition in copper.

Although this invention has been described with references to what are regarded as present preferred practices and by illustrative examples, and principles, it is to be understood that this invention is susceptible of variation and extension and that the scope of the accompanying claims is to be interpreted broadly within the limitations of the prior art.

We claim as our invention:

1. In a process for heat treating an alloy consisting of from .08% to 2.54% chromium and the balance copper, the steps of heating the alloy to a temperature between 980° C. and the melting point of the alloy, quenching the alloy, and ageing the quenched alloy at a temperature of

440° C. to 460° C. to increase hardness and conductivity.

2. In a process for heat treating an alloy consisting of from .08% to 2.54% chromium and the balance copper, the steps of heating the alloy to a temperature between 980° C. and the melting point of the alloy, quenching the alloy, working the quenched alloy, and ageing the alloy at a temperature of 440° C. to 460° C. to increase hardness and conductivity.

3. In a process for heat treating an alloy consisting of from .08% to 2.54% chromium and the balance copper, the steps of heating the alloy to a temperature of 1000° C., quenching the alloy, and ageing the quenched alloy at a temperature of about 450° C. to increase hardness and conductivity.

4. In a process for heat treating an alloy consisting of from .08% to 2.54% chromium and the balance copper, the steps of heating the alloy to a temperature of 1000° C., quenching the alloy, cold working the quenched alloy, and heating the alloy to a temperature of about 450° C. to increase hardness and conductivity.

FRANZ R. HENSEL.
EARL I. LARSEN.