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Ence

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[54] HIGH-CONDUCTIVITY COPPER ALLOYS

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[63] Continuation-in-part of Ser. No. 729,502, May 16, 1968, abandoned, which is a continuation-in-part of Ser. No. 581,714, Sept. 26, 1966, abandoned.

[52] **U.S. Cl.** **148/32.5**, 75/153, 75/159

[51] **Int. Cl.** **C22c 9/06**

[58] **Field of Search** 75/153, 159; 148/32, 32.5, 148/13.2

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[57] **ABSTRACT**

New and improved copper base alloys combining high conductivity with good strength, with the composition consisting essentially of from 0.5 to 4.0 percent iron, from 0.2 to 2.5 percent cobalt, a material selected from the group consisting of phosphorus from 0.01 to 0.5 percent, boron from 0.001 to 0.25 percent and mixtures thereof, and the balance essentially copper, said alloy being characterized by the copper matrix having a fine, uniform dispersion of said iron, cobalt, phosphorus and boron precipitated throughout as complex intermetallic compounds.

10 Claims, No Drawings

HIGH-CONDUCTIVITY COPPER ALLOYS

This application is a continuation-in-part of U.S. Pat. application Ser. No. 729,502, filed May 16, 1968, for "High Conductivity Copper Alloys," by Elmars Ence, now abandoned, which in turn is a continuation-in-part of U.S. Pat. application Ser. No. 581,714, filed Sept. 26, 1966, for "High Conductivity Copper Alloys," by Elmars Ence, now abandoned.

It is, of course, highly desirable to obtain high-conductivity copper alloys having good strength characteristics. However, alloys of this type are either not readily available or quite expensive.

In copper base alloys a common method for obtaining good strength characteristics is by alloying. Alloying, however, normally lowers the conductivity, for example, solid solution hardening depends upon keeping alloying additions in solution. This is mutually incompatible with high conductivity.

There are other strengthening phenomena, such as precipitation hardening, dispersion hardening, order-disorder reactions, and martensite reactions. These also require the presence of alloying additions which in general are not completely removed from the copper matrix and, therefore, detract from the conductivity of the alloy.

Accordingly, it is a principal object of the present invention to obtain high-conductivity copper base alloys.

It is a further object of the present invention to obtain high-conductivity copper base alloys having good strength characteristics.

It is a still further object of the present invention to obtain alloys as aforesaid at a reasonable cost.

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

In accordance with the present invention it has now been found that the foregoing objects and advantages may be readily obtained. The novel alloys of the present invention consist essentially of from 0.5 to 4.0% iron, 0.2 to 2.5% cobalt and either phosphorus in an amount from 0.01 to 0.5% or boron in an amount from 0.001 to 0.25% or both phosphorus and boron in the foregoing amounts, and the balance essentially copper. In the preferred embodiment, the alloys contain iron, cobalt, phosphorus and boron. Optionally, cerium in an amount from 0.2 to 2.0% may be added in addition to the iron, cobalt, phosphorus and boron. The foregoing alloys are characterized by the copper matrix having a fine, uniform dispersion of said iron, cobalt, phosphorus and/or boron, and cerium if used, precipitated throughout as complex intermetallic compounds.

In accordance with the present invention it has been found the the foregoing alloy retains high conductivity while having improved strength characteristics. For example, the conductivity of the foregoing alloy is in excess of 75 percent IACS and generally in excess of 80 percent IACS while the yield strength at 0.2 percent offset is generally in excess of 50,000 p.s.i.

The foregoing improvements are attained in part due to the specific alloying additions and in part due to a method of treatment which precipitates secondary hardening phases of the alloying additions and disperses them throughout the copper matrix, resulting in improved strength while retaining high conductivity. These secondary hardening phases may be in either elemental form or intermetallic compound form or both. Generally, they will be found as complex intermetallic compounds containing alloying addition species and including copper, i.e., the intermetallic complexes will vary within a given alloy; however, each specific complex can contain all or some of the ingredient species and another intermetallic complex can also contain all or some of the ingredient species. For example, the iron and cobalt alloying additions in the foregoing amounts can be essentially precipitated from solid solution so that the copper matrix attains high conductivity but at the same time develops good strength through processing to disperse the hardening phases throughout the copper matrix. If these complex compounds did not form, each of the elements would be in solid solution to their solubility limits, which would result in prohibitively low conductivity for the alloy.

In accordance with the present invention the improved copper base alloys contain from 0.5 to 4% iron and preferably from 1.1 to 2.5% and from 0.2 to 2.5% cobalt and preferably from 0.3 to 1.5%. In addition, the present alloys contain either phosphorus or boron or both in the following amounts: phosphorus from 0.01 to 0.5% and preferably from 0.05 to 0.15%; and boron from 0.001 to 0.25% and preferably from 0.005 to 0.05%. In addition, cerium may be added in an amount from 0.2 to 2.0% and preferably from 0.3 to 1.0%. All percentages of ingredients are percentages by weight.

While excessive amounts of impurities are to be avoided, small amounts of impurities or other alloying additions may, of course, be tolerated provided that they do not greatly reduce the strength or conductivity characteristics. Also, naturally, alloying additions may be utilized in order to achieve a particular result.

In accordance with the present invention the melting and casting of the copper base alloys of the present invention are not particularly critical, although in the higher iron and cobalt ranges, higher melting and casting temperatures may be necessary. The alloys may be melted and cast in accordance with conventional techniques for copper base alloys, e.g., the alloys may be prepared using conventional induction melting techniques with the alloying additions preferably made in the form of copper master alloys. For example, in order to provide reasonable melting temperatures, it may be advisable to use a 5–10% cobalt master alloy, 5–10% iron master alloy, a 1% boron master alloy and a 10–15% phosphorus master alloy.

After casting the ingots are heated for hot rolling to a temperature of between 700° and 1,000° C. and preferably 850° to 975° C. A holding time at this temperature of at least 30 minutes is preferred. The ingots are then hot-rolled in the above temperature range to convenient gage, i.e., hot rolling should commence in this temperature range. This hot rolling could, if desired, be the final rolling step. The amount of reduction in the hot rolling step is not particularly critical. If desired, the ingots may be hot-rolled above 500° C. and preferably from 850° to 975° C., cooled at any desired cooling rate, and solution heat-treated as above, i.e., 700° to 1,000° C., preferably 850° to 975° C. for at least 30 minutes. In other words, the order of hot rolling and heat treating may be reversed.

After heat treating and hot rolling, or after hot rolling and heat treating, the strip must be rapidly cooled to below 300° C. at a rate of not less than 550° C. per hour and preferably at least 550° C. per minute. This is necessary to maintain alloying additions in solid solution so that they may be substantially precipitated in a proper dispersion to attain the desired strength and conductivity.

The alloy may, if desired, be cold-rolled after rapid cooling. The cold rolling step is optional and depends upon gage requirements. The cold reduction step may attain a reduction up to 96 percent in one or more passes. The temperature of the cold reduction is not particularly critical but is generally below 200° C.

Whether or not the material is to be cold-rolled, it must ultimately receive a thermal aging treatment which serves to precipitate constituents from solid solution and achieve the desired properties. This aging treatment may also serve as an interanneal or final anneal when cold rolling is used. This aging treatment should be at 250° to 575° C. for at least 1 hour and preferably less than 50 hours.

If desired, the strip may be interannealed once or more between cold rolling passes. Strip annealing techniques may be used, in which case the holding times are usually short, i.e., from 15 seconds to 5 minutes, and possibly as long as 1 hour, and the temperature is from 250° to 600° C. Batch annealing techniques may also be used, in which case temperatures of 250°–575° C. for up to 24 hours may be used. If interanneals are employed, the total time at temperature for all anneals should preferably be less than about 30 hours in order to achieve preferred properties. Cooling rates from this temperature range are not critical.

As stated hereinabove, some time during the processing an aging treatment must be employed. This may be after the final cold rolling pass, if the alloy is cold-rolled, or after the rapid cooling step if no cold reduction is utilized. The aging treatment may also precede a final cold reduction. This is a critical step of the present invention. The temperature of the critical anneal or aging treatment is from 250° to 575° C. and the holding times are at least 1 hour and generally less than 50 hours. The particular temperature and holding time chosen will depend upon the combination of strength and conductivity required. Normally, the aging treatment is conducted in a bell-type furnace which has a controlled atmosphere, however, this is not essential.

If desired, the following modification in the foregoing procedure may be employed. After the rapid cooling step the alloy may be cold rolled, for example, at a reduction between 30 and 70 percent, at a temperature of below 200° C. This may be followed by the critical aging step of the present invention, i.e., at 250° to 575° C. for at least 1 hour. The alloy may then be cold rolled below 200° C., with reduction depending on gage requirements, followed by strip or batch annealing, as indicated hereinabove. As many cycles of cold rolling and strip or batch annealing may be used to reach desired gage. Optionally, this may be followed by another critical anneal or aging treatment, if desired.

The resultant alloy attains the aforementioned desirable combination of strength and conductivity. The alloying additions are precipitated in a substantially fine, uniform dispersion throughout the copper matrix.

The present invention will be more readily apparent from a consideration of the following illustrative examples.

EXAMPLE I

An alloy of the present invention was prepared by conventional techniques used for preparation of alloys of this type including an induction furnace, a suitable crucible material, and protection of the molten metal from oxygen by an inert or reducing atmosphere.

OFHC-grade copper was melted down and the temperature of the melt raised to about 1,200° to 1,250° C. Iron and cobalt were added as a copper, 5 to 10% cobalt master alloy and copper, 5 to 10% iron master alloy. After the alloying additions had completely dissolved, phosphorus and boron were added to the melt in the form of a copper, 10 to 15% phosphorus master alloy and copper, 1% boron master alloy. The melt was then held at temperature for about 5 to 10 minutes during which time the melt was stirred and cast into cast iron molds. The composition of the resultant alloy was 1.5% cobalt, 2.5% iron, 0.03% phosphorus, 0.02% boron and the balance essentially copper.

EXAMPLE II

The ingot prepared in Example I was hot-rolled at 950° C. to 0.5 inch thickness and subsequently solution heat-treated for 1 hour at 925° C. followed by water quenching to room temperature in 5 seconds. The resultant alloy was cold rolled to 0.025 in. gage.

High strength and high electrical conductivity was developed by a final heat treatment of 24 hours at 500° C. The properties of this material is shown in Table I below identified as Alloy 1. Also shown in Table I below for comparison are properties of a copper, 0.9% chromium alloy identified as Alloy 2 in the table below.

TABLE I

	Alloy 1	Alloy 2
yield Strength —0.2% Offset	53,600 p.s.i.	45,000 p.s.i.
Ultimate Tensile Strength	67,800 p.s.i.	50,000 p.s.i.
Elongation	15%	%
Electrical Conductivity, % IACS	81	81

The microstructure of Alloy 1 was characterized as follows: the alloying additions were precipitated in a fine, uniform dispersion throughout the copper matrix.

EXAMPLE III

In a manner after Example I, an alloy, identified as Alloy 3, was prepared having the following composition: iron 2.5%, cobalt 1.5%, boron 0.15%, balance essentially copper. This alloy was then treated as in Example II, with the final heat treatment being for 4 hours. The properties were as follows: yield strength at 0.2% offset 55,000 p.s.i.; ultimate tensile strength 68,400 p.s.i.; elongation 15%; and conductivity 76.8% IACS.

EXAMPLE IV

After the treatment of Example III, Alloy 3 was cold-rolled 50% and heat-treated for 24 hours at 400° C. The properties were: yield strength at 0.2% offset 41,700 p.s.i.; ultimate tensile strength 60,7000 p.s.i.; elongation 17%; and conductivity 82.5% IACS.

EXAMPLE V

Alloy compositions identified as Alloys **4**, **5**, **6** and **7** were prepared by melting in an induction furnace under a charcoal cover. The copper was added as OFHC copper, the iron was added in the form of low-carbon 1010 steel, the cobalt as powder metal briquettes, the phosphorus as a Cu, 14% phosphorus master alloy, and the boron as a Cu, 1% boron master alloy. The melt was held at 1,300° C. for 15 minutes prior to casting into a cast iron mold. These alloys were hot rolled at 925° C., reducing the thickness from 1.25 in. down to 0.4 in. They were air-cooled to room temperature and then reheated for solution heat treating to 925° C. for 1 hour, followed by water quenching. They were then cold-rolled to a 94% reduction in thickness and finally given an aging-annealing treatment at 480° C. for 24 hours. The composition of Alloys **4**, **5**, **6** and **7** are shown in Table II and the properties obtained are shown in Table III.

TABLE II

Alloy	% Fe	% Co	% P	% B
4	1.5	0.4	0.06	0.010
5	1.5	0.7	0.06	0.008
6	1.2	0.4	0.06	0.007
7	1.2	0.7	0.06	0.015

TABLE III

Alloy	Yield Strength At 0.2% Offset P.S.I.	Ultimate Strength P.S.I.	Conductivity % IACS
4	50,800	**65,300**	75.5
5	45,100	**61,400**	**77.6**
6	**40,800**	**58,000**	**76.9**
7	47,900	**63,900**	77.7

EXAMPLE VI

Two alloys were prepared by conventional techniques used for the preparation of alloys of this type including an induction furnace, a suitable crucible material, and protection of the molten metal from oxygen by an inert or reducing atmosphere. OFHC-grade copper was melted down and the temperature of the melt raised to about 1,200° to 1,300° C. Iron and cobalt were added in elemental form. After the iron and cobalt had completely dissolved, phosphorus was added to the melt in the form of a copper, 15% phosphorus master al-

loy. The melt was then held at temperature for about 5 to 10 minutes during which time the melt was stirred and cast into cast iron molds. The compositions of the resultant alloys were as follows:

Alloy 8	Alloy 9
1.5% iron	1.5% iron
0.7% cobalt	0.7% cobalt
0.02% phosphorus	0.1% phosphorus
balance essentially copper	balance essentially copper

EXAMPLE VII

The alloys of Example VI were examined in the as-cast form by a microprobe analysis. The microprobe analysis of both alloys identified positively the evidence of a complex phosphide rich in iron and cobalt. This was established by the microprobe analysis according to which the phosphorus content of typical particles was found to be at least two orders of magnitude higher than in the matrix adjacent to these particles. This shows that in both alloys phosphorus selectively partitions to the iron-cobalt, despite the fact that the solubility of phosphorus in copper is greater than the amount in the alloys. This is so despite the fact that there is a fivefold difference in phosphorus content between Alloy 8 and Alloy 9. This is somewhat surprising in as much as Alloy 8 has so little phosphorus; but, the results can be attributed to (1) the melt was low in oxygen and (2) a reducing carbonaceous cover was used.

EXAMPLE VIII

The ingots prepared in Example VI were hot-rolled at 950° C. to 0.5 in. thickness and subsequently heat-treated for 1 hour at about 975° C. followed by water quenching to room temperature in 5 seconds. The alloys were aged at 450° C. for about 16 hours.

EXAMPLE IX

The alloys from Example VIII were both examined by electron microscopy. Both alloys showed the evidence of an aging phase. The crystallography of this aging phase as diffracted from Alloy 9 was clearly not elemental iron, elemental cobalt, elemental phosphorus or iron phosphides as the crystallography of this aging phase did not coincide with these known materials as cataloged in the ASTM card file entitled "Inorganic Index to the Powder Diffraction File." A comparison was made between substantially the same alloys without the phosphorus present. In these alloys without phosphorus, this aging phase was absent. The particulate was elemental iron, elemental cobalt and solid solutions thereof.

EXAMPLE X

A commercial lot of alloy was semicontinuously chill-cast to form a 10,000-pound ingot whose cross section was 5×28 in. The composition of this alloy was 2.5% iron, 1.5% cobalt, 0.1% phosphorus, balance essentially copper. A section of this ingot was removed to the laboratory, homogenized at 980° C. for 24 hours, hot-rolled at 950° C. to 0.5 in. thickness followed by water quenching to room temperature in 5 seconds. These materials were then examined by X-ray diffraction. The X-ray diffraction studies showed the presence of an unidentified phase which was not elemental iron, which was not elemental cobalt, which was not elemental phosphorus, and which was not one of the iron phosphides. The precise identification was precluded because it could not be cross-references in the foregoing ASTM card file.

From the foregoing data it is apparent that the alloys of the present invention are characterized by a copper matrix having a fine uniform dispersion of alloying additions precipitated throughout as intermetallic compounds. These compounds are believed to be complex ternary ro quaternary phosphides inasmuch as the foregoing ASTM card file is reasonably complete and accurate in terms of basic inorganic compounds. It is believed that the foregoing data substantiates this. Furthermore, the presence of complex compounds are indicated from phase diagram analysis.

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 high-conductivity, high-strength copper base alloy consisting essentially of from 0.5 to 4.0% iron, 0.2 to 2.5% cobalt, a material selected from the group consisting of phosphorus from 0.01 to 0.5%, boron from 0.001 to 0.25% and mixtures thereof, and the balance copper, said alloy characterized by the copper matrix having a fine, uniform dispersion of said iron, cobalt, phosphorus and boron precipitated throughout as complex intermetallic compounds.

2. An alloy according to claim **1** having a yield strength in excess of 40,000 p.s.i. and conductivity in excess of 75 percent IACS.

3. An alloy according to claim **1** wherein the iron is present in an amount of from 1.1 to 2.5 percent.

4. An alloy according to claim **1** wherein the cobalt is present in an amount from 0.3 to 1.5 percent.

5. An alloy according to claim **1** wherein phosphorus is present in an amount from 0.05 to 0.15 percent.

6. An alloy according to claim **1** wherein boron is present in an amount from 0.005 to 0.05 percent.

7. An alloy according to claim **1** containing from 0.2 to 2.0 percent cerium.

8. A high-conductivity, high-strength copper base alloy consisting essentially of from 1.1 to 2.5% iron, 0.3 to 1.5% cobalt, a material selected from the group consisting of phosphorus from 0.05 to 0.15%, boron from 0.005 to 0.05% and mixtures thereof, and the balance copper, said alloy characterized by the copper matrix having a fine, uniform dispersion of said iron, cobalt, phosphorus and boron precipitated throughout as complex intermetallic compounds.

9. An alloy according to claim **8** containing from 0.3 to 1.0 percent cerium.

10. An alloy according to claim **1** wherein said complex intermetallic compounds are complex ternary or quaternary phosphides.

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