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(54) **A method for manufacturing an electrically conductive copper alloy material.**

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Description

The present invention relates to a method for manufacturing high electrically conductive, precipitation hardenable copper alloy wire material having both high electrical conductivity and mechanical strength.

Although copper is excellent conductivity, the electrical conductivity of a copper alloy is necessarily less than that of pure copper. Therefore, it is general practice to use pure copper in electric wires, cables and the like where the electrical conductivity is very important. However, when a twisted wire is manufactured from pure copper, it is defective in that it tends to overstretch or it is often accidentally broken during the twisting process when the wire diameter is small. Thus, it is proposed to use a copper alloy member with an additive for improving the mechanical strength. However, this is not suitable for electric wires or the like where the electrical conductivity is of prime importance. For example, it is possible to improve the mechanical strength of chrome-copper, zirconium-copper and so on by the precipitation hardening treatment. However, this results in a lower electrical conductivity, and this method is not suitable for mass production of, for example, electric wires since the solution treatment and the precipitation hardening treatment must then be performed.

GB-A-1 030 427 describes a copper alloy material comprising 0,01-0,15% Zr, the balance being high purity copper and having high electrical conductivity and mechanical strength at elevated temperatures as well as high thermal conductivity of 91.1 IACS or better, fine recrystallized grain size of less than 0,020 millimeters average diameter, and hardness after cold working of 95,6 Rockwell F or better. This copper alloy material is manufactured by solution annealing at about 805°C followed by quenching. This method permits producing an alloy material of the above small grain size.

Copper alloy compositions comprising chrome and/or zirconium are known from GB-A-1 353 430, GB-A-921 795, JP-A-52 3523, JP-A-52 3524 and US-A-3392 016. However, the methods disclosed in JP-A-52 3523 and JP-A-52 3524 don't mention the grain size but don't employ a solid solution treatment, whereas the methods known from GB-A-1353430, GB-A-921 795 and US-A-3392 016 do not teach a grain size control and the non-use of a solution treatment.

GB-A-1 194 888 discloses a high conductivity copper base alloy consisting of 0.1 to 2.5% chromium, 0.01 to 0.5% phosphorus, 0.001 to 0.25% boron, and the balance copper, apart from conventional impurities. This alloy is subjected to a treatment which involves heating for at least 30 minutes at 700 to 975°C, rolling in the aforesaid temperature range, cooling to below 300°C at a rate greater than 550°C per hour, and heating at a temperature of 350 to 550°C for at least one hour. It is to be observed that this document discloses all three of the usual process steps involved in precipitation hardening, i.e. holding for a prolonged period at elevated temperature so as to bring the alloying elements into solid solution, rapid cooling to retain them in solid solution, and finally holding for a significant period at a lower elevated temperature to effect precipitation hardening.

It is an object of the present invention to provide a method for manufacturing an electrically conductive precipitation hardenable copper alloy wire material which simplifies the above stated processing steps, while nevertheless achieving a high electrical conductivity, mechanical strength and suitability for mass production.

To solve this object the present invention provides a method for manufacturing an electrically conductive precipitation hardenable copper alloy wire material consisting of at least one alloying metal selected from chrome and zirconium, the balance copper, and optionally minor amounts of silicon, germanium, boron and magnesium which comprises the steps of making an ingot, hot-working so as to form the material into a suitable shape, and thereafter repeatedly cold-working and annealing, wherein the steps are performed without subjecting the material to solution treatment so as to obtain said copper alloy material having a grain size number of not less than 7 as defined by JISG 0551, a minimum electrical conductivity of about 88 (IACS %), and a minimum offset yield stress (0.2%) of about 22 kg/mm^2.

The most important point of the present invention is the manufacturing of a precipitation hardenable copper alloy material having high electrical conducitivity and mechanical strength by obtaining a grain size number of not less than 7, preferably 8-9 as defined by JIS G 0551 by repeatedly annealing and cold-working the copper alloy material without the solution treatment which has heretofore required a precipitation hardening treatment, The suitability for mass production obtained by eliminating the step of the solution treatment is also industrially advantageous.

The crystal grain size as defined by JIS G 0551 is calculated as follows.

$$n = 500(\frac{M}{100})^2(\frac{l_1 x l_2}{L_1 x\ L_2})$$

$$N = \frac{\log n}{0.301} + 1$$

Herein,

N: grain size number;

n: the number of grains counted within 25 mm square as magnified 100 times;
M: magnification of a microscope;
L_1 (or L_2): the total length of the whole segments in the direction of one of the lines crossing at right angles;
l_1 (or l_2): the total of the number of grains crossed by line L_1 (or L_2).

Relationships of grain size number with the number of grain and the average number of grain per unit are exemplified in the Table I below

TABLE I

N Grain size number	n The number of grains per 1 mm^2	Average cross-sectional area of grain	Average number of grains within 25 mm at 100 times magnification
5	256	0.00390	16
6	512	0.00195	32
7	1,024	0.00098	64
8	2,048	0.00049	128
9	4,096	0.000244	256
10	8,192	0.000122	512

A method for making an ingot of a starting copper alloy material before adjusting its grain size number to not less than 7 as defined by JIS G 0551 will first be described.

Making an ingot can be performed by general vacuum melting or atmospheric melting using a carbon melting pot.

In the latter ingot making method, oxygen, for example, is degassed in the form of CO_2 with the use of a carbon melting pot. When the cooling time after the melting of the alloy is shortened, the control of components which are liable to be oxidized can be easily carried out. In the easiest and most effective method, part of the desired copper base amounting about 10% in general of the total is thrown in after adding the additives for quenching the molten alloy. The base metal material preferably comprises a material containing little oxygen, such as a return material or oxygen free copper.

Quenching in this case means fast cooling from a temperature of 1,200-1,250°C at which the additives are added to a casting temperature of 1,100-1,150°C within a period of only 1-2 minutes. This method which adopts a carbon melting pot, is especially advantageous for a chrome-copper alloy, a zirconium-copper alloy, a chrome-zirconium-copper alloy and so on.

Chrome is preferably added in the form of a base alloy of chrome-copper alloy. This is because the addition of metallic chrome tends to cause segregation due to a difference in melting points and small solid solubility.

Zirconium may be added only for deoxidation or for inclusion in the alloy.

Zirconium to be included in the alloy is added separately from zirconium for deoxidation. That is, after sufficiently deoxidizing with zirconium, more zirconium to be included in the alloy may be added. The addition of Zr is in general preferably performed at a temperature higher than the melting point of the copper alloy. For adding both chrome and zirconium, after adding a chrome-copper base alloy, zirconium is added for deoxidation and more zirconium to be included in the alloy is added. This is because Zr is easily oxidized, and the addition of Zr is thus difficult before sufficiently deoxidizing the electrolytic copper. Special components such as silicon, germanium, magnesium, boron are added after the deoxidation by zirconium as needed. This is because addition of these elements after sufficient deoxidation results in a better yield. Boron is added simultaneously with chrome as a base metal. The ingot making method of the Cr-Zr-Cu alloy may be summarized as follows:

(1) Placing the electrolytic copper in an amount which is about 10% (by weight) less than the required amount.
(2) Raising the temperature to 1,080-1,150°C.
(3) Melting the copper.

(4) Adding the Cu-Cr base alloy, Cu-B base alloy and so on.
(5) Adding a flux and removing the slag (the flux is in general cryolite).
(6) Raising the temperature to 1,200-1,250°C.
(7) Adding Zr for deoxidation.
(8) Adding a flux and removing the slag.
(9) Adding Si, Ge, Mg, and so on.
(10) Adding Zr.
(11) Adding Cu (the rest of the Cu in (1) for quenching to a temperature of 1,100-1,150°C. Then, adding a flux and removing the slag during this process.
(12) Casting.

The features of the copper alloy melted by this method are found to be the same as those of a copper alloy obtained by a conventional vacuum melting method, and have the following advantages.

(1) It is possible to obtain products without an addition of an additive.
(2) Inclusion of impurities will be effectively prevented.
(3) Additives will be effectively alloyed with copper.
(4) Segregation of additives will be effectively prevented.

The atmospheric melting method which uses a carbon melting pot is advantageous in that it does not require special equipment as in the vacuum melting method and the manufacturing cost may be made less.

This atmospheric melting method may be advantageously applicable particularly to alloys such as 0.05-1.5% Cr-Cu, preferably 0.3-1.5% Cr-Cu, more preferably 0.3-0.9% Cr-Cu; 0.05-0.5% Zr-Cu, preferably 0.1-0.5% Zr-Cu, more preferably 0.1-0.4% Zr-Cu; 0.3-1% Cr, 0.1-0.5% Zr, and the balance of Cu; and Cu alloys containing further 0.005-0.1%, preferably 0.01-0.03% (all by weight) of silicon, germanium, boron or magnesium in addition to above ranges of Cr and Zr.

The present invention will now be described in more detail taking as an example a copper alloy consisting of 0.81% by weight of chrome, 0.30% by weight of zirconium, and the rest, copper.

In this example, the copper alloy material is repeatedly annealed and cold-worked after hot-working in order to obtain optimum results.

The alloy of the above composition was hot-worked at a temperature of 700-850°C by the atmospheric melting method using a carbon melting pot so as to obtain a wire of 7-10 mm in diameter. Then thus obtained wire was cold-worked after acid cleaning into a wire of 2 mm in diameter. After annealing it at a temperature of 500-650°C, it was further cold-worked into a wire of 0.26 mm in diameter. The characteristics of a copper alloy of cold working finish, a copper alloy of annealing finish at a temperature of 550°C, a copper alloy obtained by a conventional precipitation hardening treatment and pure copper are shown in Table II.

TABLE II

Characteristics	Alloy of present invention (annealing finish)	Alloy of present invention (cold working finish)	Pure copper	Alloy obtained by precipitation hardening treatment
Electrical conductivity (IACS %)	92	88	100	80
Thermal conductivity (W/m · K)	376.81	360.01	397.75	326.57
Resistance to acid (mg/cm^2)	10	10	75	10
Tensile strength (kg/mm^2)	45	50	20	60
Offset yield stress (kg/mm^2)	30	40	6	57
Repeated bending (number of times)	9	6	2	4
Pliability	Good	Good	Good	Bad
Plating readiness	Good	Good	Good	Good
Formability into wire	Good	Good	Bad	Good
Grain size number	10	9	8	5—6

The evaluation method was as follows:

Electrical conductivity (IACS: International Annealed Copper Standard %):

The specific resistance was measured at room temperature and was converted, taking 0.7241 (International Standard copper specific resistance) as 100.

Thermal conductivity (W/m · K):

The substance constant defining the which passes through a unit area during a certain period of time.

Resistance to acid (mg/cm^2):

The increase in oxidation when heated at 400°C for 30 Hrs.

Tensile strength:

A tensile force required to break (kg/mm^2).

Offset yield stress (kg/mm^2):

Stress when distorted 0.2%.

Repeated bending:

The number of bends until the substance is broken, when bends are repeated with a load of 250 gr, at 0.3 R through 90 degrees.

Pliability:

Presence or absence of flexibility when twisted in wire form.

Plating readiness:

Suitability for plating of Ag, Au, Ni, solder and so on.

Formability into wire:

Ease of forming into wire form (resistance to breakage: compared with pure Cu).

Grain size number:

According to JIS G 0551.

Thus, since the electrical conductivity changes depending on whether the alloy is of working or annealing finish, desired characteristics may be easily obtained. The grain forms are, in an alloy of rolling finish, relatively elongated and, in an alloy of annealing finish, relatively circular.

The procedure for using the alloy manufactured by the method of the present invention for electric wires and cables will now be described.

As was described earlier, pure copper is defective in that it tends to break or stretch too much during the manufacturing procedure. In contrast to this, these defects are not noted with the alloy manufactured by the method of the present invention. Therefore, this is especially preferable for use in a twisted form. Breakage and overstretching are related to the offset yield stress and formability into wire manufactured according to the present invention. Thus, the alloy manufactured by the method of the present invention is excellent in offset yield stress and formability into wire and is therefore especially suitable for use in electric wires and cables.

When twisted wires are manufactured from this wire material, no noticeable breakage or stretching are observed and the grain forms are equivalent as those before twisting process.

The characteristics of alloys with a grain size number of not less than 7 manufactured by repeated annealings and cold workings without requiring the solution treatment in accordance with the method of the present invention are shown in Table III. These alloys are an alloy (A) of 1% by weight of chrome and copper; an alloy (B) of 0.15% by weight of zirconium and copper an alloy (C) of 0.7% by weight of chrome, 0.3% by weight of zirconium and copper; an alloy (D) of 1% by weight of chrome, 0.03% by weight of silicon and copper; an alloy (E) of 0.15% by weight of zirconium, 0.03% by weight of silicon and copper; and an alloy (F) of 0.7% by weight of chrome, 0.15% by weight of zirconium, 0.03% by weight of silicon and copper.

When germanium, boron and magnesium were used in place of silicon in each alloy (D), (E) or (F), almost the same results were obtained.

Silicon, germanium, boron, magnesium and so on are effective for improving the mechanical strength and for suppressing the generation of coarse grains.

TABLE III

Characteristics	Cu-1% Cr (A)	Cu-0.15% Zr (B)	Cu-0.7% Cr-0.3% Zr (C)	Cu-1% Cr-0.03% Si (D)	Cu-0.15% Zr-0.03% Si (E)	Cu-0.7% Cr-0.15% Zr-0.03% Si (F)
Grain size number	8—9	8—9	9—10	9—10	9—10	10—11
Electrical conductivity (IACS %)	88—95	90—97	88—95	88—95	90—97	88—95
Thermal conductivity (W/m · K)	about 376.81	385.19	376.81	385.19	393.56	385.19
Resistance to acid (mg/cm^2)	18	18	15	12	12	10
Offset yield stress (kg/mm^2)	23—40	22—35	28—45	25—40	23—35	30—48
Repeated bending (number of times)	3—6	4—7	4—9	3—7	4—8	4—10
Pliability	Good	Good	Good	Good	Good	Good
Plating readiness	Good	Good	Good	Good	Good	Good
Formability into wire	Good	Good	Good	Good	Good	Good

In accordance with the present invention, improvements are realized in electrical conductivity, thermal conductivity, resistance to acid, offset yield stress, flex, resistance to fatigue and creep rupture, pliability, plating readiness and formability into wire. Thus, the present invention results in improvements in fields where pure copper has been conventionally used.

The electrically conductive copper alloy manufactured by the method of the present invention may be applied in wide range including cables for welders, elevator cables, jumpers for vehicles, crane cables, trolly hard copper twisted wires of cable rack wires for power stations and substations. lead wires and so on.

Claims

1. "A method for manufacturing an electrically conductive precipitation hardenable copper alloy wire material consisting of at least one alloying metal selected from chrome and zirconium, the balance copper, and optionally minor amounts of silicon, germanium, boron and magnesium which comprises the steps of making an ingot, hot-working so as to form the material into a suitable shape, and thereafter repeatedly cold-working and annealing, wherein the steps are performed without subjecting the material to solution treatment so as to obtain said copper alloy material having a grain size numer of not less than 7 as defined by JISG 0551, a minimum electrical conductivity of about 88 (IACS %), and a minimum offset yield stress (0.2%) of about 22 kg/mm^2."

Patentansprüche

1. Verfahren zur Herstellung eines elektrisch leitfähigen, aushärtbaren Kupferlegierungs-Drahtmaterials, bestehend aus mindestens einem Legierungs- bzw. Zusatzmetall aus der Gruppe Chrom und Zirkon, Rest Kupfer, und ggf. untergeordneten Mengen an Silizium, Germanium, Bor und Magnesium, umfassend die Schritte der Herstellung eines (Roh-)Blocks, einer Warmformgebung, um das Material in eine geeignete Form zu bringen, und des anschließenden wiederholten Warmformgebens und Anlassens oder Glühens, wobei diese Schritte durchgeführt werden, ohne das Material einer Lösungsbehandlung zu unterwerfen, und damit das Kupferlegierungsmaterial mit einer Korngrößenzahl von nicht weniger als 7, definiert nach JISG 0551, einer elektrischen Mindest-Leitfähigkeit von etwa 88 (IACS %) und einer Mindest-Versatzstreckspannung (0,2 %) von etwa 22 kg/mm^2 bereitzustellen.

Revendications

1. Procédé de fabrication d'un matériau pour fil en alliage de cuivre électriquement conducteur et apte au durcissement structural, qui consiste en au moins un métal d'alliage choisi entre le chrome et le zirconium, le reste étant du cuivre, et, facultativement, des quantités mineures de silicium, de germanium, de bore et de magnésium, le procédé comprenant les opérations consistant à préparer un lingot, le travailler à chaud de manière à mettre le matériau dans une configuration convenable, puis l'écrouir et le recuire de façon répétée, où on effectue ces opérations sans soumettre le matériau à un traitement de recuit de mise en solution, de sorte que ledit matériau d'alliage de cuivre obtenu possède un indice de dimension granulaire qui n'est pas inférieur à 7 selon la norme JIS G 0551, une conductivité électrique minimale d'environ 88 (% IACS), et une limite élastique déportée (0,2 %) minimale d'environ 22 kg/mm^2.