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(54) COPPER ALLOY WIRE ROD AND METHOD FOR PRODUCING COPPER ALLOY WIRE ROD

(57) It is an object of the present invention is to provide a copper alloy wire rod having excellent tensile strength even when the diameter of the wire rod is narrowed without impairing excellent conductivity, and a method for manufacturing the same.

A copper alloy wire rod having an alloy composition containing 1.5 to 6.0% by mass of Ag, 0 to 1.0% by mass of Mg, 0 to 1.0% by mass of Cr, and 0 to 1.0% by mass of Zr, with the balance being Cu and inevitable impurities, wherein, when a cross section parallel to a longitudinal direction of the copper alloy wire rod is observed, an area rate (A) of a precipitate precipitated coherently with Cu as a matrix phase in an observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (I):

$$(0.393 \times x - 0.589)\% \leq A \leq (3.88 \times x - 5.81)\% \qquad (I)$$

wherein x represents % by mass of Ag.

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Description

Technical Field

[0001] The present invention relates to a copper alloy wire rod which can be used for, for example, a tinsel wire and the like and has high tensile strength, and a method for manufacturing the copper alloy wire rod.

Background Art

[0002] For example, a coil and a diaphragm are mounted in a speaker. An electric current flows into the coil to cause the coil to vibrate, and the vibration of the coil causes the diaphragm to vibrate to produce sound. A tinsel wire is used for a wire rod which connects the coil and a substrate terminal to each other. Therefore, high vibration endurance which can endure vibration due to sound is required for the tinsel wire. The vibration endurance is generally improved by forming a wire rod into a fine structure according to a size effect. Meanwhile, when the diameter of the wire rod is narrowed, the tensile durability of the wire rod is decreased. This disadvantageously causes difficult handling of the wire rod while the wire rod is manufactured, so that disconnection and involution and the like occur to cause a decreased yield ratio of the wire rod.

[0003] Then, for example, a copper alloy which has a composition containing 8.0 to 20.0% by weight of Ag and 0.1 to 1.0% by weight of Cr, with the balance being Cu and inevitable impurities, and a constitution containing fine Cr precipitates dispersed in a basis material in which primary crystals and eutectic crystals are oriented in a fibrous form is proposed as an alloy material having improved tensile strength (Patent Literature 1).

[0004] However, in Patent Literature 1, the fine Cr precipitates are merely dispersed in the basis material in which the primary crystals and the eutectic crystals are oriented in a fibrous form, and the precipitation state of the fine Cr precipitates are not controlled in the constitution.

[0005] Therefore, the copper alloy of Patent Literature 1 has room for improvement in tensile strength when the diameter of a wire rod is narrowed. Furthermore, the copper alloy has room for improvement in increased handling properties while the wire rod is manufactured, and improvement in an increased yield ratio of the wire rod provided by preventing disconnection and involution and the like.

Document List

Patent Literature

[0006] Patent Literature 1: Japanese Patent Application No. 05-90832

Summary of Invention

Technical Problem

[0007] In view of the above situation, it is an object of the present invention to provide a copper alloy wire rod having excellent tensile strength even when the diameter of the wire rod is narrowed without impairing excellent conductivity, and a method for manufacturing the same.

Solution to Problem

[0008]

[1] A copper alloy wire rod having an alloy composition containing 1.5 to 6.0% by mass of Ag, 0 to 1.0% by mass of Mg, 0 to 1.0% by mass of Cr, and 0 to 1.0% by mass of Zr, with the balance being Cu and inevitable impurities, wherein, when a cross section parallel to a longitudinal direction of the copper alloy wire rod is observed, an area rate (A) of a precipitate precipitated coherently with Cu as a matrix phase in an observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (I):

$$(0.393 \times x - 0.589)\% \leq A \leq (3.88 \times x - 5.81)\% \qquad (I)$$

wherein x represents % by mass of Ag.

[2] The copper alloy wire rod according to [1], wherein a total of a content of at least one component selected from the group consisting of Mg, Cr, and Zr is 0.01 to 3.0% by mass.
[3] The copper alloy wire rod according to [1] or [2], wherein the precipitate precipitated coherently with Cu as the matrix phase is present in a fibrous form along the longitudinal direction of the copper alloy wire rod.
[4] The copper alloy wire rod according to [3], wherein, when the cross section parallel to the longitudinal direction of the copper alloy wire rod is observed, an average width (W) of the precipitate precipitated coherently with Cu as the matrix phase in the observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (II):

$$(8.3 \times d)\ \mathrm{nm} \leq W \leq (24.9 \times d)\ \mathrm{nm} \quad \text{(II)}$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod.
[5] The copper alloy wire rod according to [3] or [4], wherein, when the cross section parallel to the longitudinal direction of the copper alloy wire rod is observed, an average length (L) of the precipitate precipitated coherently with Cu as the matrix phase in the observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (III):

$$(11.3/d)\ \mathrm{nm} \leq L \leq (33.8/d)\ \mathrm{nm} \quad \text{(III)}$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod.
[6] The copper alloy wire rod according to any one of [3] to [5], wherein, when the cross section parallel to the longitudinal direction of the copper alloy wire rod is observed, an average spacing (S) of the precipitate precipitated coherently with Cu as the matrix phase in the observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (IV):

$$(760 \times x\text{^-}2.25) \times d\ \mathrm{nm} \leq S \leq (2300 \times x\text{^-}2.25) \times d\ \mathrm{nm} \quad \text{(IV)}$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod; and x represents % by mass of Ag.
[7] The copper alloy wire rod according to any one of [1] to [6], wherein the precipitate is coherent with Cu as the matrix phase in the same crystal axis direction.
[8] A method for manufacturing the copper alloy wire rod according to any one of [1] to [7], comprising the steps of:

melting a raw material;
casting the melted raw material to obtain an ingot;
subjecting a copper alloy material obtained from the ingot to a first heat treatment;
subjecting the copper alloy material further to a second heat treatment; and
subjecting the copper alloy material subjected to the second heat treatment to final wire-drawing to obtain the copper alloy wire rod,
wherein:

the first heat treatment step is performed at a temperature of 700°C or higher;
the second heat treatment step is performed at a temperature of 350 to 600°C; and
a degree of processing loge(A0/A1)^2 of the final wire-drawing step is 2.5 or more, wherein A0 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately before the final wire-drawing, and A1 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately after the final wire-drawing.

[9] The method for manufacturing the copper alloy wire rod according to [8], wherein wire-drawing is performed between the step of obtaining the ingot and the first heat treatment step, and/or between the first heat treatment step and the second heat treatment step.

Effects of Invention

[0009] The area rate (A) of the precipitate precipitated coherently with Cu in the observation region of 240 nm × 360 nm in the cross section parallel to the longitudinal direction of the copper alloy wire rod having an alloy composition containing 1.5 to 6.0% by mass of Ag, 0 to 1.0% by mass of Mg, 0 to 1.0% by mass of Cr, and 0 to 1.0% by mass of Zr, with the balance being Cu and inevitable impurities is within the above range, whereby the aspect of the present invention can provide the copper alloy wire rod having excellent tensile strength even when the diameter of the wire rod is narrowed without impairing excellent conductivity.

[0010] Thus, the copper alloy wire rod having excellent tensile strength can be obtained even when the diameter of the wire rod is narrowed, whereby, high vibration endurance is obtained, and handling properties while the wire rod is manufactured are increased. The disconnection and involution and the like of the wire rod are prevented to provide an increased yield ratio of the wire rod.

[0011] The total of the content of at least one component selected from the group consisting of Mg, Cr, and Zr is 0.01 to 3.0% by mass, whereby the aspect of the present invention contributes to further increase in vibration endurance and further increase in tensile strength even when the diameter of the wire rod is narrowed.

[0012] The precipitate precipitated coherently with Cu as the matrix phase is present in a fibrous form along the longitudinal direction of the copper alloy wire rod, and the average width (W), average length (L), and/or average spacing (S) of the precipitate present in a fibrous form are within the above ranges, whereby the aspect of the present invention contributes to further increase in vibration endurance and further increase in tensile strength even when the diameter of the wire rod is narrowed.

Brief Description of Drawings

[0013]

[FIG. 1] An electron microscope photograph of a diffraction spot occurring when an electron beam is made incident to a crystal of Cu in a [010] direction.
[FIG. 2] An electron microscope photograph showing a dark field image of a copper alloy wire rod.
[FIG. 3] A graph showing the calculated results of the number of pixels of a white contrast portion per row for binarized contrast of the dark field image.

Description of Embodiments

[0014] Hereinafter, a copper alloy wire rod of the present invention will be described in detail. The copper alloy wire rod of the present invention is a copper alloy wire rod having an alloy composition containing 1.5 to 6.0% by mass of Ag, 0 to 1.0% by mass of Mg, 0 to 1.0% by mass of Cr, and 0 to 1.0% by mass of Zr, with the balance being Cu and inevitable impurities. When a cross section parallel to a longitudinal direction of the copper alloy wire rod is observed, an area rate (A) of a precipitate precipitated coherently with Cu as a matrix phase in an observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (I):

$$(0.393 \times x - 0.589)\% \leq A \leq (3.88 \times x - 5.81)\% \qquad (I)$$

wherein x represents % by mass of Ag.

[Alloy Composition of Copper Alloy Wire Rod]

[0015] The copper alloy wire rod of the present invention contains 1.5 to 6.0% by mass of Ag (silver). Therefore, Ag is an indispensable additive component. Ag is an element present in a state of forming a solid solution in Cu (copper) as a matrix phase, or in a state of being crystallized as second phase particles during casting of a copper alloy material or precipitated as second phase particles in a heat treatment after casting the copper alloy material (herein, hereinafter, these may be generically referred to as "precipitate"), and exhibiting an effect of strengthening solid solution or dispersion. The second phase means a crystal having a crystal structure different from that of Cu as a matrix phase (first phase).

[0016] When the content of Ag is less than 1.5% by mass, the effect of strengthening solid solution or dispersion is insufficient, so that sufficient tensile strength and vibration endurance are not obtained. Meanwhile, when the content of Ag is more than 6.0% by mass, sufficient conductivity is not obtained, and the cost of a raw material also increases. From the above, from the viewpoint of obtaining excellent tensile strength even when the diameter of the wire rod is narrowed without impairing the conductivity, the content of Ag is set to 1.5 to 6.0% by mass. The demands for the tensile strength and conductivity vary depending on the application of the copper alloy wire rod, but the balance between the tensile strength and the conductivity can be desirably set by adjusting the Ag content within a range of 1.5 to 6.0% by mass. From the viewpoint that the balance between the tensile strength and the conductivity can be obtained in a wide variety of applications, the Ag content is preferably 1.5 to 4.5% by mass.

[0017] The copper alloy wire rod of the present invention may further contain, in addition to Ag as an indispensable additive component, at least one element selected from the group consisting of Mg (magnesium), Cr (chromium), and Zr (zirconium) as an optional additive component.

[0018] Each of Mg, Cr, and Zr is an element which is mainly present in a state of a solid solution in Cu as a matrix phase or in a state of the second phase, and exhibits an effect of strengthening solid solution or dispersion as with the case of Ag. The elements are contained together with Ag, whereby, for example, the elements are present as a ternary or higher second phase such as a Cu-Ag-Zr-based phase, and can contribute to further solid solution or dispersion strengthening.

[0019] From the above, from the viewpoint of sufficiently exhibiting the effect of strengthening solid solution or dispersion, the total of the content of at least one component selected from the group consisting of Mg, Cr, and Zr is preferably 0.01% by mass or more, more preferably 0.05% by mass or more, and particularly preferably 0.10% by mass or more. Meanwhile, when the content of each of Mg, Cr, and Zr is more than 1.0% by mass, excellent conductivity may not be obtained in some applications, whereby the content of each of Mg, Cr, and Zr is preferably 1.0% by mass or less, more preferably 0.7% by mass or less, and particularly preferably 0.5% by mass or less. Therefore, from the viewpoint of obtaining excellent tensile strength even when the diameter of the wire rod is narrowed without impairing the conductivity, the total of the content of at least one component selected from the group consisting of Mg, Cr, and Zr is preferably 0.01 to 3.0% by mass, more preferably 0.05 to 2.1% by mass, and particularly preferably 0.10 to 1.5% by mass.

[0020] The balance other than the components described above is Cu and inevitable impurities. Cu is a matrix phase of the copper alloy wire rod of the present invention. Ag as the indispensable additive component is present in a state of forming a solid solution or in a state of being precipitated as a precipitate in Cu as the matrix phase. At least one component selected from the group consisting of Mg, Cr, and Zr as the optional additive component is present in a state of forming a solid solution or in a state of being precipitated as a precipitate in Cu as the matrix phase as necessary.

[0021] The inevitable impurities mean impurities contained at a content level which may be inevitably contained during the manufacturing step of the copper alloy wire rod of the present invention. The inevitable impurities may cause a decrease in conductivity depending on the content thereof. Therefore, it is preferable to suppress the content of the inevitable impurities, considering the decrease in the conductivity. Examples of the inevitable impurities include Ni, Sn, and Zn.

[Area Rate (A) of Precipitate Precipitated Coherently with Cu as Matrix Phase]

[0022] In the copper alloy wire rod of the present invention, when a cross section parallel to a longitudinal direction of the copper alloy wire rod is observed, an area rate (A) of a precipitate precipitated coherently with Cu as a matrix phase (hereinafter, referred to as "coherent precipitate" in some cases) in an observation region in a rectangular shape of 240 nm $\times$ 360 nm is within a range of the following expression (I):

$$(0.393 \times x - 0.589)\% \leq A \leq (3.88 \times x - 5.81)\% \qquad \text{(I)}$$

wherein x represents % by mass of Ag.

[0023] Therefore, in the copper alloy wire rod of the present invention, the range of the area rate (A) of the coherent precipitate is also changed depending on the change in the content of Ag. The area rate (A) of the coherent precipitate is within the above range, whereby the copper alloy wire rod having excellent tensile strength and vibration endurance can be obtained even when the diameter of the wire rod is narrowed without impairing excellent conductivity. The above expression (I) is derived from the experimental results in which the Ag content in the copper alloy wire rod is variously selected.

[0024] When the area rate (A) of the coherent precipitate is less than $(0.393 \times x - 0.589)\%$, the amount of precipitation of the coherent precipitate is small, so that the coherent precipitate does not hinder the deformation of the copper alloy wire rod. As a result, excellent tensile strength and vibration endurance are not obtained. Meanwhile, when the area rate (A) of the coherent precipitate is more than $(3.88 \times x - 5.81)\%$, sizes such as the length and width of the coherent precipitate increase, so that, after all, the coherent precipitate does not hinder the deformation of the copper alloy wire rod. As a result, excellent tensile strength and vibration endurance are not obtained.

[0025] Since the coherent precipitate is mainly made of Ag, the area rate (A) of the coherent precipitate is changed depending on the content of Ag. That is, it is considered that, when the content of Ag increases, the area rate (A) increases, and when the content of Ag decreases, the area rate (A) decreases. When the area rate (A) of the coherent precipitate increases, the coherent precipitate hinders the deformation of the copper alloy wire rod. As a result, tensile strength and vibration endurance are increased. Meanwhile, even when the area rate (A) of the coherent precipitate is excessive, the coherent precipitate does not hinder the deformation of the copper alloy wire rod. As a result, it was found that excellent tensile strength and vibration endurance are not obtained. Therefore, in the copper alloy wire rod of the present invention, not only the range of the content of Ag but also the range of the area rate (A) of the coherent precipitate were adjusted, whereby excellent tensile strength and vibration endurance were achieved without impairing the conductivity.

[Precipitated Coherently with Cu as Matrix Phase]

[0026] Herein, the above "precipitated coherently with Cu as a matrix phase" means that the precipitate is precipitated to have a specific crystallographic orientation with respect to the crystal of Cu as a matrix phase. Examples of a technique for determining whether the precipitate is precipitated to have a specific crystallographic orientation with respect to the crystal of Cu as a matrix phase, that is, whether the precipitate is the coherent precipitate include a reading method using a diffraction pattern.

[0027] When a sample is irradiated with an electron beam in a transmission electron microscope, the diffraction of the electron beam occurs. A diffraction wave occurring from the diffraction of the electron beam is strengthened and weakened by the type of the crystal, an interatomic spacing forming the crystal, and the like, so that a specific diffraction pattern is formed according to the crystal. For example, when the electron beam is made incident in a [010] direction with respect to the crystal of Cu, as shown in FIG. 1, diffraction spots occur at vertices of a square and middle points thereof.

[0028] Since Cu and Ag have the same face-centered cubic lattice structure (fcc structure), Cu and Ag have the same diffraction pattern, but the lattice constants are different, so that Cu and Ag have different spacings between the diffraction spots. As the lattice constant is larger, the spacing between the diffraction spots is narrower, whereby the diffraction spot of Ag appears in a narrower range than the diffraction spot of Cu appears. When an Ag precipitate is present in a Cu alloy, and the crystal of the Ag precipitate is aligned in a specific direction, the diffraction spot of the Ag precipitate appears slightly inside the diffraction spot of Cu as a matrix phase. When the crystalline orientation of Cu and the crystalline orientation of Ag completely coincide with each other, that is, both the crystal of Cu and the crystal of Ag face a [100] direction, Cu and Ag have the same diffraction pattern, and the diffraction pattern of Ag appears slightly inside the diffraction pattern of Cu.

[0029] Meanwhile, when the crystalline orientation of Cu and the crystalline orientation of Ag do not completely coincide with each other although Cu and Ag are aligned in a specific direction, for example, when the crystal of Cu faces the [100] direction with respect to the direction of an observation axis [100], but the crystal of Ag faces the [110] direction, the diffraction pattern corresponding to the [100] direction of Cu and the diffraction pattern corresponding to the [110] direction of Ag appear.

[0030] From the above, when the diffraction pattern of Cu and the diffraction pattern of Ag are the same, and the diffraction pattern of Ag appears slightly inside the diffraction pattern of Cu, or when the diffraction pattern of Cu showing that the crystal of Cu corresponds to a predetermined direction and the diffraction pattern of Ag showing that the crystal of Ag corresponds to a predetermined direction appear, Ag is determined to be "precipitated coherently with Cu as a matrix phase," that is, the Ag precipitate is determined to be coherent with Cu as a matrix phase.

[0031] However, when Cu and Ag are not aligned at all, that is, when the crystallographic orientation of Cu and the crystallographic orientation of Ag do not coincide with each other at all, Ag is arranged in various crystal directions with respect to Cu, so that the diffraction pattern of Ag is formed at random with respect to the diffraction pattern of Cu. In this case, it is determined that the Ag precipitate is not coherent with Cu as a matrix phase.

[Average Width (W) of Precipitate Precipitated Coherently with Cu as Matrix Phase]

[0032] When the precipitate precipitated coherently with Cu as a matrix phase is present in a fibrous form along the longitudinal direction of the copper alloy wire rod, that is, when the precipitate is a fibrous substance extending generally in parallel with the longitudinal direction of the copper alloy wire rod, the precipitate is more effective. When the cross section parallel to the longitudinal direction of the copper alloy wire rod of the present invention is observed, an average width (W) of the fibrous coherent precipitate precipitated coherently with Cu as a matrix phase and extending in the longitudinal direction of the copper alloy wire rod, in the observation region in a rectangular shape of 240 nm × 360 nm is not particularly limited. From the viewpoint of further improving the hindering effect of the coherent precipitate with respect to the deformation of the copper alloy wire rod, it is preferable that the average width (W) be within a range of the following expression (II):

$$(8.3 \times \mathrm{d})\ \mathrm{nm} \le \mathrm{W} \le (24.9 \times \mathrm{d})\ \mathrm{nm} \quad \text{(II)}$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod. It is particularly preferable that the average width (W) be within a range of $(9.0 \times d)$ nm $\leq W \leq (24.0 \times d)$ nm. Therefore, in a preferable aspect of the copper alloy wire rod of the present invention, a preferable range of the average width (W) of the coherent precipitate is also changed depending on the change in the wire diameter. The above expression (II) is specified based on the wire diameter and the average width of the coherent precipitate in Examples of the present application to be described later.

[0033] When the average width (W) of the coherent precipitate is less than $(8.3 \times d)$ nm, the coherent precipitate is thinner than the wire diameter, so that the hindering effect of the coherent precipitate with respect to the deformation of the copper alloy wire rod may be limited. Meanwhile, when the average width (W) is more than $(24.9 \times d)$ nm, the size of the average width (W) with respect to the wire diameter increases, so that, after all, the hindering effect of the coherent precipitation with respect to the deformation of the copper alloy wire rod may be limited.

[Average length (L) of Precipitate Precipitated Coherently with Cu as Matrix Phase]

[0034] When the cross section parallel to the longitudinal direction of the copper alloy wire rod of the present invention is observed, an average length (L) of the fibrous coherent precipitate precipitated coherently with Cu as a matrix phase and extending in the longitudinal direction of the copper alloy wire rod, in the observation region in a rectangular shape of 240 nm × 360 nm is not particularly limited. From the viewpoint of further improving the hindering effect of the coherent precipitate with respect to the deformation of the copper alloy wire rod, it is preferable that the average length (L) be a range of the following expression (III):

$$(11.3/d)\ \text{nm} \leq L \leq (33.8/d)\ \text{nm} \qquad \text{(III)}$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod. It is particularly preferable that the average length (L) be within a range of $(14.0/d)$ nm $\leq L \leq (30.0/d)$ nm. Therefore, in a preferable aspect of the copper alloy wire rod of the present invention, a preferable range of the average length (L) of the coherent precipitate is also changed depending on the change in the wire diameter. The above expression (III) is specified based on the wire diameter and the average length of the coherent precipitate in Examples of the present application to be described later.

[0035] When the average length (L) of the coherent precipitate is less than $(11.3/d)$ nm, the coherent precipitate is shorter than the wire diameter, so that the hindering effect of the coherent precipitate with respect to the deformation of the copper alloy wire rod may be limited. Meanwhile, when the average length (L) is more than $(33.8/d)$ nm, the size of the average length (L) with respect to the wire diameter increases, so that, after all, the hindering effect of the coherent precipitation with respect to the deformation of the copper alloy wire rod may be limited.

[Average Spacing (S) of Precipitate Precipitated Coherently with Cu as Matrix Phase]

[0036] When the cross section parallel to the longitudinal direction of the copper alloy wire rod of the present invention is observed, an average spacing (S) of the coherent precipitate precipitated coherently with Cu as a matrix phase in the observation region in a rectangular shape of 240 nm × 360 nm is not particularly limited. It is preferable that the average spacing (S) be within a range of the following expression (IV):

$$(760 \times x\text{^-}2.25) \times d\ \text{nm} \leq S \leq (2300 \times x\text{^-}2.25) \times d\ \text{nm} \qquad \text{(IV)}$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod; and x represents % by mass of Ag. Therefore, in a preferable aspect of the copper alloy wire rod of the present invention, a preferable range of the average spacing (S) of the coherent precipitate is also changed depending on the changes in the wire diameter and Ag content. The above expression (IV) is derived from the experimental results in which the Ag content in the copper alloy wire rod is variously selected.

[0037] When the average spacing (S) of the coherent precipitate is less than $(760 \times x\text{^-}2.25) \times d$ nm, the spacing of the coherent precipitate is narrower than the wire diameter and the Ag content, so that the hindering effect of the coherent precipitate with respect to the deformation of the copper alloy wire rod may be limited. Meanwhile, when the average spacing (S) of the coherent precipitate is more than $(2300 \times x\text{^-}2.25) \times d$ nm, the spacing of the coherent precipitate is wider than the wire diameter and the Ag content, so that, after all, the hindering effect of the coherent precipitate with respect to the deformation of the copper alloy wire rod may be limited.

[Coherent Precipitate is Matched in the Same Crystal Axis Direction]

[0038] In the copper alloy wire rod of the present invention, it is preferable that the coherent precipitate be coherent with Cu as a matrix phase in the same crystal axis direction. "Matched in the same crystal axis direction" means that the crystal of Cu as a matrix phase and the crystal of the coherent precipitate mainly made of Ag are aligned in the same crystal axis direction. Such crystal arrangement causes distortion between the crystal of Cu as a matrix phase and the crystal of the coherent precipitate. This distortion hinders the deformation of the copper alloy wire rod, whereby higher tensile strength is conferred on the copper alloy wire rod.

[0039] The following method can determine whether the coherent precipitate is coherent with Cu as a matrix phase in the same crystal axis direction. First, a copper alloy wire rod as a sample is formed as a thin film by a Focused Ion Beam (FIB) method, and a predetermined observation region (for example, an observation region of a rectangle of 240 nm $\times$ 360 nm) is observed using a transmission electron microscope (TEM). A sample is cut out in parallel to the longitudinal direction. During TEM observation, the sample is observed in a state where the longitudinal direction is transversely set.

[0040] Thereafter, in order to confirm that the precipitate is coherently precipitated, as described above, a diffraction pattern is acquired. At this time, the diffraction pattern may be imaged according to any crystal zone axis incidence, for example, [110] crystal zone axis incidence providing a generally easily understandable pattern. The diffraction pattern due to the crystal of Cu as a matrix phase is observed at the highest luminance. Another diffraction pattern is also observed, and the precipitate is confirmed to be coherently precipitated by confirming a diffraction pattern in which the type of the diffraction pattern is the same as that of Cu, and a spot spacing is slightly narrow.

[0041] Thereafter, the angle of the sample is changed, and a diffraction pattern is acquired according to [100] or [111] crystal zone axis incidence with respect to Cu as a matrix phase. Similarly, it is confirmed whether a diffraction pattern in which the type of the diffraction pattern is the same as that of Cu, and a spot spacing is slightly narrow is present. When the same diffraction pattern as that of Cu can be confirmed according to crystal zone axis incidence at the two axes, the coherent precipitate is determined to be coherent with Cu as a matrix phase in the same crystal axis direction.

[Method for Manufacturing Copper Alloy Wire Rod of the Present Invention]

[0042] Thereafter, a method for manufacturing the copper alloy wire rod of the present invention will be described. The method for manufacturing the copper alloy wire rod of the present invention includes the steps of: (a) melting a raw material; (b) casting the melted raw material to obtain an ingot; (c) subjecting a copper alloy material obtained from the ingot to a first heat treatment; (d) subjecting the copper alloy material further to a second heat treatment after the first heat treatment step; and (e) subjecting the copper alloy material subjected to the second heat treatment to final wire-drawing to obtain the copper alloy wire rod, wherein a degree of processing loge(A0/A1)^2 of the final wire-drawing is 2.5 or more, wherein A0 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately before the final wire-drawing, and A1 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately after the final wire-drawing.

[0043] (a) The step of melting a raw material and (b) the step of casting the melted raw material to obtain an ingot can be carried out by known general methods. Each of raw materials used in step (a) is blended at a predetermined rate such that 1.5 to 6.0% by mass of Ag, 0 to 1.0% by mass of Mg, 0 to 1.0% by mass of Cr, and 0 to 1.0% by mass of Zr are set with the balance being Cu.

[0044] A heat treatment temperature in (c) the step of subjecting a copper alloy material to a first heat treatment is 700°C or higher. When the temperature of the first heat treatment step is lower than 700°C, it is difficult to fiberize a precipitate mainly made of Ag during the final wire-drawing, so that excellent tensile strength and vibration endurance may not be obtained. From the viewpoint of obtaining more excellent tensile strength, the lower limit of the temperature of the first heat treatment step is preferably 750°C, and particularly preferably 800°C. Meanwhile, the upper limit of the temperature of the first heat treatment step is not particularly limited, and it is preferably 900°C.

[0045] A heat treatment time of the first heat treatment step is not particularly limited, and from the viewpoint of largely dispersing the precipitate in the subsequent step to fiberize the precipitate, the heat treatment time is preferably 0.1 to 10 hours, and particularly preferably 0.5 to 5 hours.

[0046] After the first heat treatment step, the copper alloy material is cooled, and (d) the second heat treatment is further carried out. A heat treatment temperature of the second heat treatment step is 350 to 600°C. When the heat treatment temperature of the second heat treatment step is lower than 350°C or higher than 600°C, the precipitate mainly made of Ag is not sufficiently precipitated, so that excellent tensile strength and vibration endurance may not be obtained. The heat treatment time of the second heat treatment step is not particularly limited, and it is preferably 0.5 to 20 hours, and particularly preferably 1.0 to 15 hours.

[0047] After the second heat treatment step, the copper alloy material is cooled, and (e) the final wire-drawing is carried out. In the final wire-drawing, a degree of processing loge(A0/A1)^2 is 2.5 or more, wherein A0 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately before the final wire-drawing, and A1 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately after the final wire-drawing. When the degree of processing of the final wire-drawing is less than 2.5, the coherent precipitate cannot be sufficiently elongated and fiberized, so that excellent tensile strength and vibration endurance may not be obtained.

[0048] The degree of processing of the final wire-drawing may be 2.5 or more from the viewpoint of sufficiently elongating and fiberizing the coherent precipitate. A higher degree of processing provides excellent tensile strength. Therefore, the upper limit of the degree of processing of the final wire-drawing is not particularly limited.

[0049] As necessary, intermediate wire-drawing may be performed between (b) the step of obtaining an ingot and (c) the first heat treatment step and/ or between (c) the first heat treatment step and (d) the second heat treatment step. The degree of processing of the intermediate wire-drawing is not particularly limited, and from the viewpoint of increasing the degree of processing in the final wire-drawing, a degree of processing loge(B0/B1)^2 is preferably lower, wherein B0 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately before the intermediate wire-drawing, and B1 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately after the intermediate wire-drawing. In order to sufficiently precipitate the coherent precipitate and to sufficiently elongate and fiberize the coherent precipitate in the final wire-drawing, the degree of processing of the intermediate wire-drawing is preferably higher. From the above, the degree of processing is preferably 0 to 1.0 from the viewpoint of the balance between the two.

[0050] Particularly, the copper alloy wire rod of the present invention is subjected to (c) the first heat treatment step and (d) the second heat treatment step, whereby the copper alloy wire rod having excellent tensile strength can be manufactured even when the diameter of the wire rod is narrowed without impairing excellent conductivity.

Examples

[0051] Thereafter, Examples of the present invention will be described, but the present invention is not limited to these examples without departing from the spirit of the present invention.

Examples 1 to 40

[0052] Raw materials (oxygen-free copper, silver, magnesium, chromium, and zirconium) were introduced into a graphite crucible so as to provide alloy compositions of Table 1 below, and a furnace temperature in the crucible was heated to 1250°C or higher, to melt the raw materials. A resistance heating type heating furnace was used for melting. An atmosphere in the crucible was a nitrogen atmosphere so that oxygen was not mixed in melted copper. Furthermore, after the crucible was held at 1250°C or higher for 3 hours or more, an ingot having a diameter (ϕ) of about 10 mm was cast in a graphite mold while a cooling rate was set to 500 to 1000°C/s. After the casting was started, continuous casting was performed while the raw materials were appropriately introduced. When chromium was contained in the raw materials (Examples 23, 27, 28, 31, 33, and 34), the raw materials were melted while the temperature in the crucible was held at 1600°C or higher.

[0053] Thereafter, the ingot obtained as described above was subjected to a first heat treatment under conditions of temperatures and times shown in Table 1 below. A test material was subjected to intermediate wire-drawing such that the diameter (ϕ) of the test material was set to 8 mm after the first heat treatment step, and a second heat treatment was further carried out under conditions of temperatures and times shown in Table 1 below. The test material was subjected to final wire-drawing with a predetermined degree of processing such that the wire diameter of the test material was set to wire diameters shown in Table 1 below after the second heat treatment step, to obtain a copper alloy wire rod. The first heat treatment and the second heat treatment were performed in a batch furnace in a nitrogen atmosphere.

Comparative Examples 1 to 7

[0054] In each of Comparative Examples 1 and 4 to 7, a copper alloy wire rod was obtained in the same steps as those of the Examples under the manufacturing conditions shown in Table 1 below except that an ingot having a diameter (ϕ) of about 8 mm was cast, and the ingot was subjected to final wire-drawing such that the diameter (ϕ) of the ingot was set to 0.1 mm without performing intermediate wire-drawing. In Comparative Example 2, a copper alloy wire rod was obtained in the same steps as those of Comparative Examples 1 and 4 to 7 except that the first heat treatment and the second heat treatment were not carried out. In Comparative Example 3, a copper alloy wire rod was obtained in the same steps as those of Comparative Examples 1 and 4 to 7 except that the second heat treatment was not carried out. Therefore, in Comparative Example 3, an ingot was subjected to a first heat treatment such that the diameter (ϕ) of the ingot was set to 8 mm.

[Method for Observing Precipitate Precipitated Coherently with Cu as Matrix Phase]

[0055] The copper alloy wire rod in each of the Examples and the Comparative Examples was formed as a thin film by an FIB method, and an observation region of a rectangle having a cross section direction (short direction) length of 240 nm and a longitudinal direction length of 360 nm was observed using a transmission electron microscope (TEM). The copper alloy wire rod was cut out in parallel to the longitudinal direction. During TEM observation, the copper alloy wire rod was observed in a state where the longitudinal direction was transversely set. Thereafter, in order to confirm that the precipitate was coherently precipitated, a diffraction pattern was acquired. At this time, the diffraction pattern was imaged according to [110] crystal zone axis incidence providing a generally easily understandable pattern. The diffraction pattern due to the crystal of Cu as a matrix phase was observed at the highest luminance. Another diffraction pattern was also observed. By measuring the type of the diffraction pattern and a spot spacing, the precipitate having the diffraction pattern was identified to be Ag.

[0056] Thereafter, when an objective aperture is placed and observed such that only a diffraction wave of the diffraction pattern of the precipitate obtained above can be selected and observed, only a portion (that is, coherent precipitate) which produces the diffraction wave forming the diffraction pattern is brightly observed. This is referred to as dark field image, and this dark field image (shown in FIG. 2) was imaged for the copper alloy wire rod in each of the Examples and the Comparative Examples. The area rate, average width, average length, and average spacing of the precipitate (coherent precipitate) precipitated coherently with Cu as a matrix phase were obtained as follows from the dark field image obtained above.

[0057] First, contrast obtained in the dark field image was binarized. A p-tile method was used for binarizing. When the p-tile method is used, a threshold value is determined without the order of luminance being interchanged, whereby photographs obtained by shooting the same range in different observation environments can be substantially similarly binarized. However, as a premise, luminance is not changed in a local portion on an image in the environment. Then, the number of pixels of a portion of white contrast, that is, the precipitate coherently precipitated (coherent precipitate) was calculated with respect to the total number of pixels of the obtained photograph, and the area rate was calculated by dividing the number of pixels of the coherent precipitate by the total number of pixels.

[0058] The number of pixels of the coherent precipitate in the longitudinal direction was calculated with the cross section direction of the dark field image as row number, and as shown in FIG. 3, the number of pixels per row was graphed. Row numbers 0 to 275 observed in FIG. 3 correspond to a length of 240 nm in the cross section direction. A portion in which the number of pixels was 25 or more was taken as one peak, and the half-value width of each peak was defined as the width of the coherent precipitate. The width of the coherent precipitate was obtained from each peak. The average value of the widths was calculated, and taken as an average width. The maximum value of the peak was defined as the length of the coherent precipitate. The length of the coherent precipitate was obtained from the number of pixels of each peak with respect to the total number of pixels of the photograph. The average value of the lengths was calculated, and taken as an average length. A spacing between the maximum value of the peak and the maximum value of the adjacent peak was measured, and each spacing was defined as the spacing of the coherent precipitate. Each peak spacing was obtained. The average value of the peak spacings was calculated, and taken as an average spacing of the precipitate.

[0059] In each aspect of the coherent precipitate, the sample thickness of the thin film was calculated as a standard thickness of 0.15 μm. When the thickness of the copper alloy wire rod is different from the standard thickness, the thickness of the copper alloy wire rod is converted into the standard thickness, that is, (standard thickness/thickness of copper alloy wire rod) is multiplied by a dispersion density calculated based on the shot photograph, whereby a dispersion density can be calculated. In the Examples and the Comparative Examples, the sample thicknesses of all the copper alloy wire rods were set to about 0.15 μm by the FIB method.

[Method for Determining Coherent Precipitate to be Coherent with Cu as Matrix Phase in the Same Crystal Axis Direction]

[0060] As described above, according to procedures of a technique of acquiring a diffraction pattern according to [110] crystal zone axis incidence with respect to Cu as a matrix phase in order to confirm that the precipitate is coherently precipitated, and a technique of changing the angle of a sample and acquiring a diffraction pattern according to [110] or [111] crystal zone axis incidence with respect to Cu as a matrix phase in order to confirm that the coherent precipitate is coherent with Cu as a matrix phase in the same crystal axis direction, it is determined whether the coherent precipitate is coherent with Cu as a matrix phase in the same crystal axis direction. In Table 1, a case where the coherent precipitate is coherent with Cu as a matrix phase in the same crystal axis direction is mentioned as good, and a case where the coherent precipitate is not matched is mentioned as poor.

[Method for Measuring Tensile Strength]

[0061] A tensile test was performed using a precision universal tester (manufactured by Shimadzu Corporation) according to JIS Z2241, to obtain tensile strength (MPa). Three copper alloy wire rods according to each of the Examples and the Comparative Examples were subjected to the test, and the average value thereof (N = 3) was obtained and taken as tensile strength of each of the copper alloy wire rods.

[Method for Measuring Conductivity]

[0062] In a constant temperature bath held at 20°C (±0.5°C), resistivities were measured for three test pieces having a length of 300 mm using a four terminal method, and the average conductivity thereof was calculated. The distance between terminals was set to 200 mm.

Table 1

No.		Alloy composition						Manufacturing conditions					
		Ag	Mg	Cr	Zr	Mg+Cr+Zr	Cu and inevitable impurities	First heat treatment		Second heat treatment		Final wire-drawing	Wire diameter
								Temperature	Time	Temperature	Time	Degree of processing	
		% by mass	% by mass	% by mass	% by mass			°C	h	°C	h		mm
Examples	1	1,5	-	-	-	0,0	Balance	800	1	500	1	8,8	0,1
	2	2,0	-	-	-	0,0	Balance	800	1	500	1	8,8	0,1
	3	3,0	-	-	-	0,0	Balance	800	1	500	1	8,8	0,1
	4	4,0	-	-	-	0,0	Balance	800	1	500	1	8,8	0,1
	5	5,0	-	-	-	0,0	Balance	800	1	500	1	8,8	0,1
	6	6,0	-	-	-	0,0	Balance	800	1	500	1	8,8	0,1
	7	2,0	-	-	-	0,0	Balance	800	1	350	10	8,8	0,1
	8	2,0	-	-	-	0,0	Balance	850	1	400	10	8,8	0,1
	9	2,0	-	-	-	0,0	Balance	850	1	450	10	8,8	0,1
	10	2,0	-	-	-	0,0	Balance	800	2	500	10	8,8	0,1
	11	2,0	-	-	-	0,0	Balance	800	2	600	10	8,8	0,1
	12	3,0	-	-	-	0,0	Balance	800	1	350	5	8,8	0,1
	13	3,0	-	-	-	0,0	Balance	800	1	400	5	8,8	0,1

14	3,0	-	-	-	0,0	Balance	850	2	450	5	8,8	0,1
15	3,0	-	-	-	0,0	Balance	850	2	500	5	8,8	0,1
16	3,0	-	-	-	0,0	Balance	850	2	600	5	8,8	0,1
17	4,0	-	-	-	0,0	Balance	850	1	350	2	8,8	0,1
18	4,0	-	-	-	0,0	Balance	850	1	400	2	8,8	0,1
19	4,0	-	-	-	0,0	Balance	800	2	450	2	8,8	0,1
20	4,0	-	-	-	0,0	Balance	800	2	500	2	8,8	0,1
21	4,0	-	-	-	0,0	Balance	800	2	600	2	8,8	0,1
22	2,0	0,05	-	-	0,1	Balance	800	1	450	5	8,8	0,1
23	2,0	-	0,05	-	0,1	Balance	800	1	450	5	8,8	0,1
24	2,0	-	-	0,05	0,05	Balance	850	2	500	5	8,8	0,1
25	2,0	0,05	-	0,05	0,10	Balance	850	2	500	5	8,8	0,1
26	2,0	-	-	0,20	0,20	Balance	850	2	500	5	8,8	0,1
27	4,0	-	0,20	-	0,2	Balance	850	1	450	2	8,8	0,1
28	4,0	-	0,40	-	0,4	Balance	850	1	450	2	8,8	0,1
29	4,0	0,05	-	-	0,1	Balance	800	2	600	2	8,8	0,1
30	4,0	0,20	-	-	0,2	Balance	800	2	600	2	8,8	0,1
31	4,0	-	0,10	0,10	0,20	Balance	800	2	600	2	8,8	0,1

	32	6,0	-	-	0,30	0,30	Balance	800	1	400	10	8,8	0,1
	33	6,0	0,10	0,10	0,10	0,30	Balance	800	1	400	10	8,8	0,1
	34	6,0	0,15	0,10	-	0,3	Balance	850	2	400	10	8,8	0,1
	35	2,0	-	-	-	0,0	Balance	700	2	500	1	2,2	2,6
	36	2,0	-	-	-	0,0	Balance	700	2	500	1	10,2	0,05
	37	4,0	-	-	-	0,0	Balance	800	2	500	1	4,2	1
	38	4,0	-	-	-	0,0	Balance	800	2	500	1	12,0	0,02
	39	6,0	-	-	-	0,0	Balance	850	2	500	1	5,2	0,6
	40	6,0	-	-	-	0,0	Balance	850	2	500	1	12,0	0,02
Comparative Examples	1	8,0	-	-	-	0,0	Balance	800	1	450	10	8,8	0,1
	2	4,0	-	-	-	0,0	Balance	-	-	-	-	8,8	0,1
	3	2,0	-	-	-	0,0	Balance	800	1	-	-	8,8	0,1
	4	2,0	-	-	-	0,0	Balance	800	1	300	2	8,8	0,1
	5	2,0	-	-	-	0,0	Balance	800	1	700	1	8,8	0,1
	6	3,0	-	-	-	0,0	Balance	800	1	300	5	8,8	0,1
	7	4,0	-	-	-	0,0	Balance	800	1	700	1	8,8	0,1

Table 1 (cont.)

No.		Evaluation of constitution												
		Aspect of precipitate precipitated coherently with Cu as matrix phase												
		Area rate	Lower limit calculated value	Upper limit calculated value	Average width	Lower limit calculated value	Upper limit calculated value	Average length	Lower limit calculated value	Upper limit calculated value	Average spacing	Lower limit calculated value	Upper limit calculated value	Coherent precipitate is coherent with Cu as matrix phase in the same crystal axis direction
		%			nm			nm			nm			-
Examples	1	0,01	0,00	0,01	1,0	0,8	2,5	156	113	338	43,2	30,5	92,4	Good
	2	1,0	0,2	2,0	1,7	0,8	2,5	180	113	338	30,3	16,0	48,4	Good
	3	2,5	0,6	5,8	1,8	0,8	2,5	203	113	338	15,6	6,4	19,4	Good
	4	5,1	1,0	9,7	1,7	0,8	2,5	228	113	338	5,3	3,4	10,2	Good
	5	7,3	1,4	13,6	2,1	0,8	2,5	258	113	338	3,8	2,0	6,2	Good
	6	9,7	1,8	17,5	2,0	0,8	2,5	280	113	338	2,5	1,3	4,1	Good
	7	0,2	0,2	2,0	0,8	0,8	2,5	141	113	338	38,4	16,0	48,4	Good
	8	0,4	0,2	2,0	0,9	0,8	2,5	157	113	338	34,6	16,0	48,4	Good
	9	1,4	0,2	2,0	0,8	0,8	2,5	194	113	338	23,8	16,0	48,4	Good
	10	0,7	0,2	2,0	1,2	0,8	2,5	222	113	338	32,1	16,0	48,4	Good
	11	0,2	0,2	2,0	2,3	0,8	2,5	253	113	338	45,3	16,0	48,4	Good
	12	0,6	0,6	5,8	1,0	0,8	2,5	157	113	338	19,3	6,4	19,4	Good
	13	1,2	0,6	5,8	1,1	0,8	2,5	177	113	338	17,5	6,4	19,4	Good

14	4,0	0,6	5,8	1,4	0,8	2,5	213	113	338	9,1	6,4	19,4	Good
15	3,1	0,6	5,8	1,7	0,8	2,5	234	113	338	14,2	6,4	19,4	Good
16	2,5	0,6	5,8	2,4	0,8	2,5	270	113	338	16,4	6,4	19,4	Good
17	1,0	1,0	9,7	0,9	0,8	2,5	171	113	338	5,1	3,4	10,2	Good
18	1,8	1,0	9,7	1,2	0,8	2,5	194	113	338	4,6	3,4	10,2	Good
19	5,3	1,0	9,7	1,5	0,8	2,5	232	113	338	4,2	3,4	10,2	Good
20	6,2	1,0	9,7	2,0	0,8	2,5	251	113	338	3,8	3,4	10,2	Good
21	3,8	1,0	9,7	2,1	0,8	2,5	280	113	338	5,6	3,4	10,2	Good
22	0,8	0,2	2,0	0,9	0,8	2,5	180	113	338	30,3	16,0	48,4	Good
23	0,9	0,2	2,0	1,0	0,8	2,5	188	113	338	28,4	16,0	48,4	Good
24	0,7	0,2	2,0	1,1	0,8	2,5	213	113	338	26,9	16,0	48,4	Good
25	0,8	0,2	2,0	1,0	0,8	2,5	220	113	338	30,5	16,0	48,4	Good
26	0,7	0,2	2,0	1,2	0,8	2,5	217	113	338	32,1	16,0	48,4	Good
27	5,5	1,0	9,7	1,0	0,8	2,5	234	113	338	5,5	3,4	10,2	Good
28	5,2	1,0	9,7	1,1	0,8	2,5	229	113	338	5,8	3,4	10,2	Good
29	3,6	1,0	9,7	1,4	0,8	2,5	284	113	338	7,0	3,4	10,2	Good
30	3,8	1,0	9,7	1,5	0,8	2,5	277	113	338	6,1	3,4	10,2	Good
31	3,8	1,0	9,7	1,5	0,8	2,5	279	113	338	5,1	3,4	10,2	Good

	32	3,4	1,8	17,5	1,9	0,8	2,5	258	113	338	2,3	1,3	4,1	Good
	33	3,8	1,8	17,5	1,9	0,8	2,5	266	113	338	3,4	1,3	4,1	Good
	34	4,2	1,8	17,5	2,0	0,8	2,5	284	113	338	3,6	1,3	4,1	Good
	35	0,8	0,2	2,0	39,0	21,6	64,7	8	4	13	780	415	1257	Poor
	36	0,6	0,2	2,0	0,7	0,4	1,2	360	226	676	12,5	8,0	24,2	Good
	37	5,8	1,0	9,7	18,0	8,3	24,9	20	11	34	53,3	33,6	101,6	Poor
	38	5,2	1,0	9,7	0,4	0,2	0,5	360	565	1690	1,2	0,7	2,0	Good
	39	13,6	1,8	17,5	9,0	5,0	14,9	42	19	56	12,1	8,1	24,5	Good
	40	8,4	1,8	17,5	0,4	0,2	0,5	360	565	1690	0,4	0,3	0,8	Good
Comparative Examples	1	10,2	2,6	25,2	2,6	0,8	2,5	352	113	338	1,6	0,7	2,1	Good
	2	0,0	1,0	9,7	-	0,8	2,5	-	113	338	-	3,4	10,2	Poor
	3	0,0	0,2	2,0	-	0,8	2,5	-	113	338	-	16,0	48,4	Poor
	4	0,0	0,2	2,0	-	0,8	2,5	-	113	338	-	16,0	48,4	Poor
	5	0,0	0,2	2,0	-	0,8	2,5	-	113	338	-	16,0	48,4	Poor
	6	0,0	0,6	5,8	-	0,8	2,5	-	113	338	-	6,4	19,4	Poor
	7	0,0	1,0	9,7	-	0,83	2,49	-	113	338	-	3,4	10,2	Poor

Table 1 (cont.)

No.		Evaluation of characteristics			
		Tensile strength	Conductivity	Strength ratio with material not subjected to first and second heat treatments, and having the same amount of Ag and the same degree of processing	Conductivity ratio with material not subjected to first and second heat treatments, and having the same amount of Ag and the same degree of processing
		MPa	%IACS	times	times
Examples	1	850	86	1,13	0,99
	2	1102	76	1,34	0,89
	3	1251	74	1,37	0,91
	4	1410	68	1,42	0,87
	5	1543	63	1,41	0,84
	6	1596	61	1,37	0,82
	7	1098	78	1,34	0,92
	8	1105	77	1,35	0,91
	9	1188	74	1,45	0,87
	10	1162	76	1,42	0,89
	11	1062	78	1,30	0,92
	12	1222	75	1,34	0,92
	13	1235	75	1,36	0,92
	14	1321	71	1,45	0,87
	15	1277	73	1,40	0,89
	16	1254	74	1,38	0,91
	17	1405	69	1,41	0,88
	18	1422	69	1,43	0,88
	19	1456	68	1,47	0,87
	20	1497	67	1,51	0,86
	21	1438	69	1,45	0,88
	22	1123	71	1,33	0,89
	23	1136	67	1,36	0,88
	24	1125	65	1,34	0,88

	25	1148	63	1,32	0,88
	26	1179	56	1,36	0,80
	27	1454	57	1,33	0,86
	28	1482	56	1,32	0,86
	29	1433	67	1,36	0,89
	30	1482	60	1,37	0,88
	31	1458	57	1,34	0,88
	32	1680	45	1,37	0,83
	33	1712	42	1,41	0,78
	34	1657	48	1,38	0,89
	35	520	89	1,06	0,99
	36	1188	75	1,44	0,91
	37	762	87	1,11	1,06
	38	1648	58	1,32	0,80
	39	988	81	1,11	1,06
	40	1833	52	1,21	0,85
Comparative Examples	1	1612	54	1,25	0,76
	2	993	78	1,00	1,00
	3	760	91	0,93	1,07
	4	782	90	0,95	1,06
	5	803	90	0,98	1,06
	6	852	88	0,94	1,08
	7	903	87	0,88	1,13

[0063] As shown in Table 1 above, in Examples 1 to 40 in which the first heat treatment step at 700°C or higher and the second heat treatment step at 350 to 600°C were performed, and the area rate of the coherent precipitate was $(0.393 \times x - 0.589)\% \leq A \leq (3.88 \times x - 5.81)\%$, wherein x represents % by mass of Ag, the copper alloy wire rod having excellent tensile strength could be obtained even when the diameter of the wire rod was narrowed to 0.02 mm to 2.6 mm without impairing excellent conductivity.

[0064] Meanwhile, in Comparative Example 1 in which 8.0% by mass of Ag was added, the conductivity remarkably decreased. In Comparative Example 2 in which the first heat treatment step and the second heat treatment step were not performed, the coherent precipitate was not obtained, thus failing to obtain good tensile strength as compared with Example 4 having the same manufacturing conditions as those of Comparative Example 2 and the same composition as that of Comparative Example 2 except that the first heat treatment step and the second heat treatment step were performed. In each of Comparative Example 3 in which the second heat treatment step was not performed, Comparative Examples 4 and 6 in which the temperature of the second heat treatment step was as low as 300°C, and Comparative Examples 5 and 7 in which the temperature of the second heat treatment step was as high as 700°C, the coherent precipitate was not obtained, thus failing to obtain good tensile strength.

Claims

1. A copper alloy wire rod having an alloy composition containing 1.5 to 6.0% by mass of Ag, 0 to 1.0% by mass of Mg, 0 to 1.0% by mass of Cr, and 0 to 1.0% by mass of Zr, with the balance being Cu and inevitable impurities, wherein, when a cross section parallel to a longitudinal direction of the copper alloy wire rod is observed, an area rate (A) of a precipitate precipitated coherently with Cu as a matrix phase in an observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (I):

$$(0.393 \times x - 0.589)\% \leq A \leq (3.88 \times x - 5.81)\% \qquad (I)$$

wherein x represents % by mass of Ag.

2. The copper alloy wire rod according to claim 1, wherein a total of a content of at least one component selected from the group consisting of Mg, Cr, and Zr is 0.01 to 3.0% by mass.

3. The copper alloy wire rod according to claim 1 or 2, wherein the precipitate precipitated coherently with Cu as the matrix phase is present in a fibrous form along the longitudinal direction of the copper alloy wire rod.

4. The copper alloy wire rod according to claim 3, wherein, when the cross section parallel to the longitudinal direction of the copper alloy wire rod is observed, an average width (W) of the precipitate precipitated coherently with Cu as the matrix phase in the observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (II):

$$(8.3 \times d)\ \mathrm{nm} \leq W \leq (24.9 \times d)\ \mathrm{nm} \qquad (II)$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod.

5. The copper alloy wire rod according to claim 3 or 4, wherein, when the cross section parallel to the longitudinal direction of the copper alloy wire rod is observed, an average length (L) of the precipitate precipitated coherently with Cu as the matrix phase in the observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (III):

$$(11.3/d)\ \mathrm{nm} \leq L \leq (33.8/d)\ \mathrm{nm} \qquad (III)$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod.

6. The copper alloy wire rod according to any one of claims 3 to 5, wherein, when the cross section parallel to the longitudinal direction of the copper alloy wire rod is observed, an average spacing (S) of the precipitate precipitated coherently with Cu as the matrix phase in the observation region in a rectangular shape of 240 nm × 360 nm is within a range of the following expression (IV):

$$(760 \times x\text{^}{-2.25}) \times d\ \mathrm{nm} \leq S \leq (2300 \times x\text{^}{-2.25}) \times d\ \mathrm{nm} \qquad (IV)$$

wherein d represents a wire diameter (mm) of the copper alloy wire rod; and x represents % by mass of Ag.

7. The copper alloy wire rod according to any one of claims 1 to 6, wherein the precipitate is coherent with Cu as the matrix phase in the same crystal axis direction.

8. A method for manufacturing the copper alloy wire rod according to any one of claims 1 to 7, comprising the steps of:

melting a raw material;
casting the melted raw material to obtain an ingot;
subjecting a copper alloy material obtained from the ingot to a first heat treatment;
subjecting the copper alloy material further to a second heat treatment; and
subjecting the copper alloy material subjected to the second heat treatment to final wire-drawing to obtain the copper alloy wire rod,
wherein
the first heat treatment step is performed at a temperature of 700°C or higher;
the second heat treatment step is performed at a temperature of 350 to 600°C; and
a degree of processing loge(A0/A1)^2 of the final wire-drawing step is 2.5 or more, wherein A0 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately before the final wire-drawing, and A1 is a cross-sectional area in a direction orthogonal to the longitudinal direction of the copper alloy material immediately after the final wire-drawing.

9. The method for manufacturing the copper alloy wire rod according to claim 8, wherein wire-drawing is performed between the step of obtaining the ingot and the first heat treatment step, and/or between the first heat treatment step and the second heat treatment step.

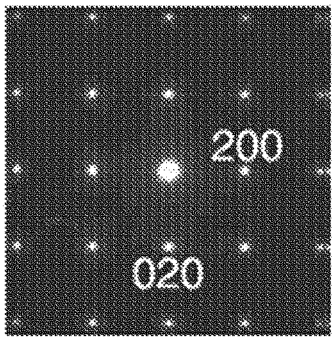

FIG.1

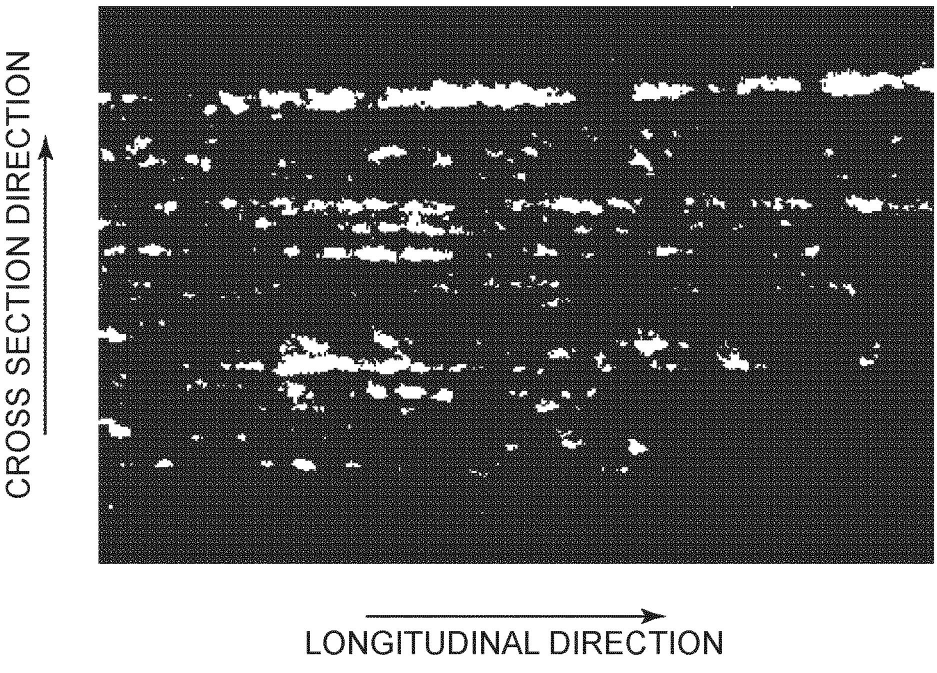

FIG.2

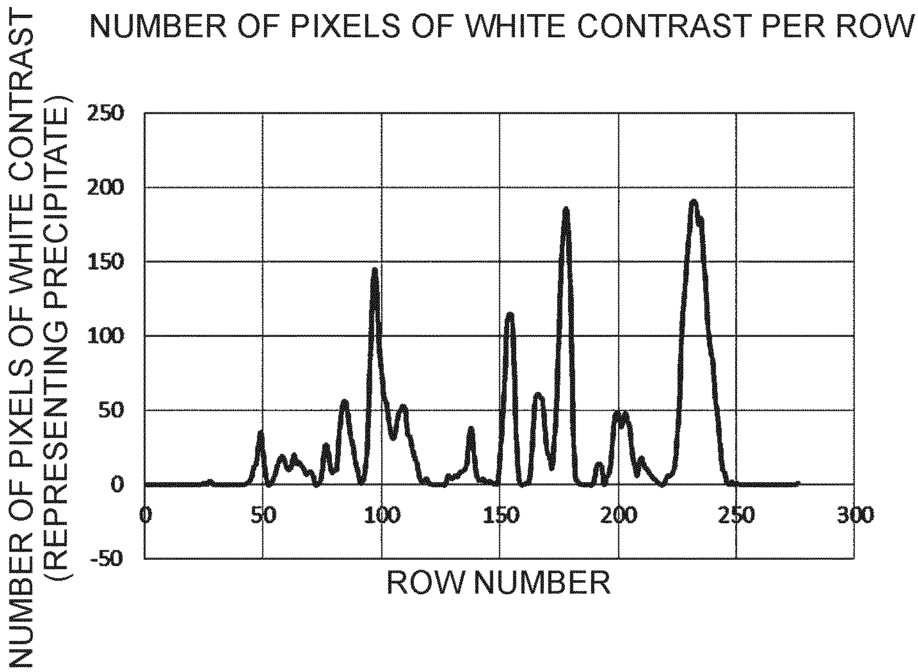
NUMBER OF PIXELS OF WHITE CONTRAST PER ROW
NUMBER OF PIXELS OF WHITE CONTRAST (REPRESENTING PRECIPITATE)
250
200
150
100
50
0
-50
0
50
100
150
200
250
300
ROW NUMBER

FIG.3

INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2019/005812

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. C22C9/00(2006.01)i, C22F1/08(2006.01)i, C22F1/00(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
Int.Cl. C22C9/00, C22F1/08, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 2011-246802 A (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 08 December 2011, paragraph [0058] & WO 2011/136284 A1 & CN 102869805 A & KR 10-2013-0093469 A	1, 3-9 2-7
Y	JP 2017-2337 A (FURUKAWA ELECTRIC CO., LTD.) 05 January 2017, paragraph [0010] (Family: none)	2-7
X	WO 2007/046378 A1 (INDEPENDENT ADMINISTRATIVE INSTITUTION NATIONAL INSTITUTE FOR MATERIALS SCIENCE) 26 April 2007, paragraphs [0014], [0029] (Family: none)	8-9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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“P” document published prior to the international filing date but later than the priority date claimed
“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
“&” document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 April 2019 (25.04.2019)	14 May 2019 (14.05.2019)

Name and mailing address of the ISA/	Authorized officer
Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/005812

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2015-21138 A (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 02 February 2015 (Family: none)	1-9
P, A	WO 2018/100919 A1 (FURUKAWA ELECTRIC CO., LTD.) 07 June 2018 & US 2018/0322979 A1 & CN 108463568 A & KR 10-2018-0116232 A	1-9

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