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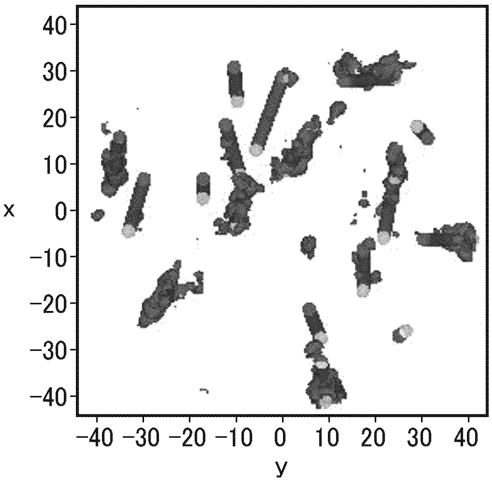
(54) CU-AG ALLOY WIRE

(57) Provided is a Cu-Ag alloy wire with high electric conductivity, controlled metallographic structure, and excellent bending fatigue resistance. The Cu-Ag alloy wire has a chemical composition comprising: 1.0 to 6.0 mass% of Ag; and a remainder of Cu and unavoidable impurities and has a matrix phase containing multiple Ag phases that are linearly distributed and connected approximately along the longitudinal direction of the Cu-Ag alloy wire, in which the Ag phases have an atomic concentration of Ag in the range of 0.5 to 50.0%. The Cu-Ag alloy wire also has a cross-section in which the number of the Ag phases with an average diameter of 0.5 to 20.0 nm is in the range of 10 to 400 per 10,000 nm^2 area measured perpendicular to the longitudinal direction of the Cu-Ag alloy wire.

FIG. 2



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Description

TECHNICAL FIELD

[0001] The present invention relates to a Cu-Ag alloy wire.

BACKGROUND ART

[0002] Currently, electric wires for use in electric or electronic device connection cables and so on are becoming smaller in diameter. In the field of electric wires, there is a trend toward using Cu alloy wires, such as Cu-Sn, Cu-Cr, and Cu-Ag wires, instead of pure Cu wires, which may be insufficient in strength. However, there is a trend in which the diameter of electric wires becomes smaller than usual, for example, as electric and electronic device products become more compact, as the space for installation of electric wires decreases, or as the number of signal wiring lines increases. Among copper alloy wires, Cu-Ag alloy wires have relatively high levels of tensile strength and electrical conductivity.

[0003] For example, Patent Document 1 discloses a method for producing a copper alloy having high strength and high electrical conductivity, which result from stretching a Cu-Ag eutectic phase into filaments. Unfortunately, the method disclosed in Patent Document 1 has a problem in that the distribution of precipitates, which will particularly contribute to the strength of the drawn alloy, may be so inadequately controlled as to provide insufficient strength properties. Patent Document 2 discloses a thin Cu-Ag alloy wire with a high strength resulting from a process including: performing heat treatment to develop a recrystallization texture in the course of the process; and then performing high-ratio drawing. Unfortunately, the technique disclosed in Patent Document 2 has a problem in that the product is not cost-competitive due to the low productivity of the process in which embrittlement of the material occurs during the heat treatment to make it difficult to reduce the thickness of the wire because appropriate drawing process conditions are not employed before the heat treatment. Patent Document 3 discloses a Cu-Ag alloy wire with high levels of tensile strength and electrical conductivity attributable to crystallized Ag particles, some of which are uniformly dispersed in the form of very fine particles. Patent Document 3 defines a certain distribution of crystallized Ag precipitates, but unfortunately, the wire disclosed in Patent Document 3 has a problem in that it does not always have high levels of tensile strength and electrical conductivity in a well-balanced manner even when the disclosed process is followed to obtain the desired structure.

PRIOR ART DOCUMENTS

Patent Documents

[0004]

Patent Document 1: Japanese Patent No. 3325639
Patent Document 2: Japanese Patent No. 5051647
Patent Document 3: Japanese Patent No. 5713230

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0005] Thus, the disclosures in Patent Documents 1 to 3 have a problem in that the metallographic structure control is insufficient and the studies are not enough to ensure the desired drawability for the reduction of the wire diameter to a level smaller than that of conventional Cu-Ag alloy wires or not enough to produce very thin wires (Cu-Ag alloy wires) with a good balance between high strength and high electrical conductivity. Moreover, they have a problem in that no study has been conducted to produce thinner Cu-Ag alloy wires that have improved resistance to fatigue breaking (improved bending fatigue resistance) under conditions of use where they are repeatedly bent. It is, therefore, an object of the present invention to provide a Cu-Ag alloy wire with high strength, high electrical conductivity, and high bending fatigue resistance.

Means for Solving the Problems

[0006] To achieve the object, the present invention has the following technical features.

(1) A Cu-Ag alloy wire having a chemical composition comprising: 1.0 to 6.0 mass% of Ag; and a remainder of Cu and unavoidable impurities, the Cu-Ag alloy wire having a matrix phase containing multiple Ag phases that are linearly distributed and connected approximately along the longitudinal direction of the Cu-Ag alloy wire, the Ag phases having

an atomic concentration of Ag in the range of 0.5 to 50.0%, the Cu-Ag alloy wire having a cross-section in which the number of the Ag phases with an average diameter of 0.5 to 20.0 nm is in the range of 10 to 400 per 10,000 nm^2 area measured perpendicular to the longitudinal direction of the Cu-Ag alloy wire.

(2) The Cu-Ag alloy wire according to aspect (1), wherein the average of shortest distances between adjacent ones of the Ag phases in the cross-section measured is in the range of 3 to 30 nm.

(3) The Cu-Ag alloy wire according to aspect (1) or (2), wherein the chemical composition of the Cu-Ag alloy wire further includes 0.05 to 0.30 mass% of at least one component selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr.

(4) The Cu-Ag alloy wire according to any one of aspects (1) to (3), wherein the Cu-Ag alloy wire is a round wire having a diameter of 0.01 mm to 0.08 mm.

(5) The Cu-Ag alloy wire according to any one of aspects (1) to (3), wherein the Cu-Ag alloy wire is a ribbon wire having an approximately rectangular cross-section, a width of 0.02 to 0.32 mm, and a thickness of 0.002 to 0.040 mm.

Effects of the Invention

[0007] The present invention provides a Cu-Ag alloy wire having high tensile strength, high electrical conductivity, and high bending fatigue resistance. This makes it possible to make electric and electronic devices more compact than ever, to make the space for installation of electric wires smaller than ever, or to increase the number of signal wiring lines to a level larger than ever, and will contribute to the production of high-value-added compact electric and electronic devices.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008]

FIG. 1 is a view of the iso-concentration surfaces of Ag phases with an atomic concentration of Ag of 2.0 at.%, which are data obtained by measuring, with a 3D atom probe field ion microscope (3DAP system), the Ag phases in a tip portion of an approximately conical sample prepared from a Cu-Ag alloy wire according to an embodiment of the present invention, in which the tip portion is a portion from a first position corresponding to the tip of the sample (0 nm position) to a second position 140 nm distant from the tip (140 nm position), and the data are the results of the measurement from the side of the tip portion;

FIG. 2 is a view of the iso-concentration surfaces of Ag phases with an atomic concentration of Ag of 3.5 at.%, which are data obtained similar to those shown in FIG. 1 by measuring a lower part of the tip portion of the sample, in which the lower part is a portion from a third position 80 nm distant from the first position (80 nm position) to the second position (140 nm position), and the data are the results of the measurement from the top face of the lower part;

FIG. 3 is a diagram showing the graphic results of calculating, from the results of the iso-concentration surfaces of Ag phases shown in FIG. 1, the number of the Ag phases and the direction in which each Ag phase extends;

FIG. 4 is a diagram showing the graphic results of calculating, from the results of the iso-concentration surfaces of Ag phases shown in FIG. 2, the distances between adjacent ones of Ag phases (and the average diameter of the Ag phases); and

FIG. 5 is a graph showing the results of atomic concentration analysis of the elements Cu, Ag, N, and O in one of the multiple Ag phases identified from FIG. 3 in the lower part of the tip portion (from the third position (80 nm position) to the second position (140 nm position)), in which the atomic concentration analysis is along the longitudinal direction of the Ag phase.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0009] Hereinafter, embodiments of the present invention will be described. It will be understood that the embodiments of the present invention will be described only by way of example and are not intended to limit the scope of claims.

[0010] A Cu-Ag alloy wire according to an embodiment of the present invention will be described. The Cu-Ag alloy wire according to an embodiment of the present invention has a chemical composition comprising: 1.0 to 6.0 mass% of Ag; and a remainder of Cu and unavoidable impurities. The Cu-Ag alloy wire has a matrix phase containing multiple Ag phases that are linearly distributed and connected approximately along the longitudinal direction of the Cu-Ag alloy wire and have an atomic concentration of Ag in the range of 0.5 to 50.0%. The Cu-Ag alloy wire has a cross-section in which the number of the Ag phases with an average diameter in the range of 0.5 to 20.0 nm is in the range of 10 to 400 per 10,000 nm^2 area measured perpendicular to the longitudinal direction of the Cu-Ag alloy wire.

Chemical Composition

[0011] The Cu-Ag alloy wire of the present invention contains 1.0 to 6.0 mass% of Ag. This means that Ag is an essential component. Ag forms a solid solution in the Cu matrix phase (first phase) or forms Ag phases (second phase), which are crystallized from liquid and precipitated from solid during the casting for the Cu-Ag alloy wire, to exert a solid-solution strengthening effect or a dispersion strengthening effect.

[0012] With an Ag content of less than 1.0 mass%, the wire may fail to have the desired metallographic structure due to insufficient precipitation of Ag phases and thus may have insufficient levels of tensile strength and bending fatigue resistance. An Ag content of more than 6.0 mass% will have no significant difference in the effect on tensile strength or bending fatigue resistance from an Ag content of at most 6.0 mass%, and the corresponding increase in Ag content will lead to an increase in cost. Thus, the Cu-Ag alloy wire of the present invention has an Ag content of 1.0 to 6.0 mass% so that it can maintain a certain electrical conductivity and can have high cost performance and high levels of tensile strength and bending fatigue resistance even when reduced in diameter to an ultrafine level. For a wide variety of applications where the balance between electrical conductivity and other properties are more important, the Cu-Ag alloy wire preferably has an Ag content of 1.0 to 4.5 mass%.

[0013] Moreover, the Cu-Ag alloy wire according to an embodiment of the present invention preferably further contains 0.05 to 0.30 mass% of at least one optional component selected from the group consisting of Sn, Mg, Zn, In, Ni, Co, Zr, and Cr. These optional element components can all mainly form a solid solution in the Cu matrix phase and can exert a solid-solution strengthening effect or a dispersion strengthening effect like Ag. Moreover, the Ag phase and at least one of these optional components in the wire can form a second phase comprising at least three elements, such as Cu-Ag-Zr (ternary or polynary system), which may more contribute to solid-solution strengthening or dispersion strengthening.

[0014] Hereinafter, the content of each of the components will be described.

Sn: 0.05 to 0.30 mass%

[0015] Sn (tin) at a content of 0.05 mass% or more will contribute to improving the strength of the copper alloy wire, and Sn at a content of 0.30 mass% or less will not significantly reduce the electrical conductivity. Thus, the Sn content may be 0.05 mass% or more and is preferably 0.07 mass% or more, more preferably 0.08 mass% or more, even more preferably 0.10 mass% or more. On the other hand, the Sn content may be 0.30 mass% or less and is preferably 0.18 mass% or less, more preferably 0.15 mass% or less, even more preferably 0.12 mass% or less.

Mg: 0.05 to 0.30 mass%

[0016] Mg (magnesium) at a content of 0.05 mass% or more will contribute to improving the strength of the copper alloy wire and will be effective in mitigating the brittleness of the copper alloy wire. Mg at a content of 0.30 mass% or less will not significantly reduce the electrical conductivity of the copper alloy wire or the casting manufacturability. Thus, the Mg content may be 0.05 mass% or more and is preferably 0.07 mass% or more, more preferably 0.08 mass% or more, even more preferably 0.10 mass% or more. On the other hand, the Mg content may be 0.30 mass% or less and is preferably 0.18 mass% or less, more preferably 0.15 mass% or less, even more preferably 0.12 mass% or less.

Zn: 0.05 to 0.30 mass%

[0017] Zn (zinc) at a content of 0.05 mass% or more will contribute to improving the strength of the copper alloy wire and will be effective in mitigating the brittleness of the copper alloy wire. Zn at a content of 0.30 mass% or less will not significantly reduce the electrical conductivity of the copper alloy wire. Thus, the Zn content may be 0.05 mass% or more and is preferably 0.07 mass% or more, more preferably 0.08 mass% or more, even more preferably 0.10 mass% or more. On the other hand, the Zn content may be 0.30 mass% or less and is preferably 0.25 mass% or less, more preferably 0.20 mass% or less, even more preferably 0.15 mass% or less.

In: 0.05 to 0.30 mass%

[0018] In (indium) at a content of 0.05 mass% or more will contribute to improving the strength of the copper alloy wire, and In at a content of 0.30 mass% or less will not significantly reduce the electrical conductivity. Thus, the In content is preferably 0.05 mass% or more, more preferably 0.07 mass% or more, even more preferably 0.08 mass% or more, furthermore preferably 0.10 mass% or more. On the other hand, the In content may be 0.30 mass% or less and is preferably 0.18 mass% or less, more preferably 0.15 mass% or less, even more preferably 0.12 mass% or less.

Ni: 0.05 to 0.30 mass%

[0019] Ni (nickel) at a content of 0.05 mass% or more will be effective in improving the strength of the copper alloy wire. Ni at a content of 0.30 mass% or less will not significantly reduce the electrical conductivity of the copper alloy wire. Thus, the Ni content may be 0.05 mass% or more and is preferably 0.07 mass% or more, more preferably 0.08 mass% or more, even more preferably 0.10 mass% or more. On the other hand, the Ni content may be 0.30 mass% or less and is preferably 0.25 mass% or less, more preferably 0.20 mass% or less, even more preferably 0.15 mass% or less.

Co: 0.05 to 0.30 mass%

[0020] Co (cobalt) at a content of 0.05 mass% or more will contribute to improving the strength of the copper alloy wire, and Co at a content of 0.30 mass% or less will not significantly reduce the electrical conductivity. Thus, the Co content may be 0.05 mass% or more and is preferably 0.07 mass% or more, more preferably 0.08 mass% or more, even more preferably 0.10 mass% or more. On the other hand, the Co content may be 0.30 mass% or less and is preferably 0.18 mass% or less, more preferably 0.15 mass% or less, even more preferably 0.12 mass% or less.

Zr: 0.05 to 0.30 mass%

[0021] Zr (zirconium) at a content of 0.05 mass% or more will contribute to improving the strength of the copper alloy wire and will be effective in mitigating the brittleness of the copper alloy wire. Zr at a content of 0.30 mass% or less will not significantly reduce the electrical conductivity of the copper alloy wire or the casting manufacturability. Thus, the Zr content may be 0.05 mass% or more and is preferably 0.07 mass% or more, more preferably 0.08 mass% or more, even more preferably 0.10 mass% or more. On the other hand, the Zr content may be 0.30 mass% or less and is preferably 0.20 mass% or less, more preferably 0.15 mass% or less, even more preferably 0.12 mass% or less.

Cr: 0.05 to 0.30 mass%

[0022] Cr (chromium) at a content of 0.05 mass% or more will contribute to improving the strength of the copper alloy wire, and Cr at a content of 0.30% or less will not significantly reduce the electrical conductivity. Thus, the Cr content may be 0.05 mass% or more and is preferably 0.07 mass% or more, more preferably 0.08 mass% or more, even more preferably 0.10 mass% or more. On the other hand, the Cr content may be 0.30 mass% or less and is preferably 0.18 mass% or less, more preferably 0.15 mass% or less, even more preferably 0.12 mass% or less.

Optional components: 0.05 to 1.0 mass% in total

[0023] The total content of the above optional components in the Cu-Ag alloy wire is preferably in the range of 0.05 to 1.0 mass%. The optional components at a content of less than 0.05 mass% will hardly reduce the electrical conductivity but will not contribute to increasing the tensile strength. The optional components at a content of more than 1.0 mass% may provide a higher tensile strength but may cause a significant reduction in the electrical conductivity, which may make it impossible to maintain highly conductive properties. Thus, the total content of the optional components is preferably in the range of 0.05 to 0.7 mass%. The total content of the optional components is more preferably in the range of 0.05 to 0.5 mass%.

Remainder: Cu and unavoidable impurities

[0024] The remainder, which comprises components other than the components described above, is Cu and unavoidable impurities. Cu forms the matrix phase of the Cu-Ag alloy wire of the present invention, in which the essential component Ag and any other component may exist in the form of a solid solution or in the form of precipitates. The term "unavoidable impurities" refers to impurities present at levels unavoidable under the conditions of the process of manufacturing the Cu-Ag alloy wire of the present invention. The unavoidable impurities may cause a reduction in electrical conductivity depending on their content. In view of a reduction in electrical conductivity, therefore, it is preferred to reduce the content of the unavoidable impurities. Examples of the unavoidable impurities include Pb, S, and P.

[0025] Hereinafter, the metallographic structure of the Cu-Ag alloy wire of the present invention will be described. The Cu-Ag alloy wire of the present invention has a matrix phase containing multiple Ag phases that are linearly distributed and connected approximately along the longitudinal direction of the Cu-Ag alloy wire and have an atomic concentration of Ag in the range of 0.5 to 50.0%. The Cu-Ag alloy wire has a cross-section in which the number of the Ag phases with an average diameter in the range of 0.5 to 20.0 nm is in the range of 10 to 400 per 10,000 nm^2 area measured perpendicular to the longitudinal direction of the Cu-Ag alloy wire.

[0026] The Ag phases may be measured by three-dimensional atom probe (3DAP) method. FIGS. 1 to 4 show how the Ag phases exist in the matrix phase of the Cu-Ag alloy wire according to an embodiment of the present invention, which is determined by 3DAP method. The metallographic structure regarding how Ag exists in the matrix phase of the Cu-Ag alloy wire can be observed by 3DAP method. The 3DAP method is an analytical technique that allows three-dimensional compositional analysis of nanoprecipitates and clusters in metals and semiconductors. The principles of the 3DAP method are as follows. An about 100 nm-diameter, needle-shaped sample with an approximately conical tip portion is prepared and placed in a 3D atom probe field ion microscope (3DAP system), in which high voltage pulses are then applied to cause one-by-one field evaporation of atoms from the tip of the sample. Laser pulses with a specific wavelength are also applied to the needle tip to assist the field evaporation, which makes it possible to reduce the probability of sample destruction, to improve the mass resolution, and to measure semiconductors and insulators. The two-dimensional coordinate position of each ion generated by the field evaporation resulting from the application of voltage and laser pulses is determined by using a two-dimensional position detector to detect the time-of-flight and position of the ion. The type of the ion reaching the detector is also identifiable since the measurement of the time from its evaporation at the needle tip to its arrival at the detector allows time-of-flight type mass spectrometric analysis. When the laser irradiation is repeated, information on the two-dimensional coordinate position of the ion and on the structure of the sample in the depth direction can be obtained. Data analysis of such information taking the needle tip shape into account allows the acquisition of three-dimensional compositional information.

[0027] Hereinafter, some representative results of the measurement by 3DAP method will be shown. FIG. 1 shows the iso-concentration surfaces of Ag phases with an atomic concentration of Ag of 2.0 at.%, which are data obtained by measuring, with a 3D atom probe field ion microscope (3DAP system), the Ag phases in a tip portion of an approximately conical sample prepared from a Cu-Ag alloy wire (with an Ag concentration of 2.0 mass%) according to an embodiment of the present invention, in which the tip portion is a portion from a first position corresponding to the tip of the sample (0 nm position) to a second position 140 nm distant from the tip (140 nm position), and the data are the results of the measurement from the side of the tip portion. FIG. 2 shows the iso-concentration surfaces of Ag phases with an atomic concentration of Ag of 3.5 at.%, which are data obtained similar to those shown in FIG. 1 by measuring a lower part of the tip portion of the sample, in which the lower part is a portion from a third position 80 nm distant from the first position (80 nm position) to the second position (140 nm position), and the data are the results of the measurement from the top face of the lower part. FIG. 3 is a diagram showing the graphic results of calculating, from the results of the iso-concentration surfaces of Ag phases shown in FIG. 2, the number of the Ag phases and the direction in which each Ag phase extends. FIG. 4 is a diagram showing the graphic results of calculating, from the results of the iso-concentration surfaces of Ag phases shown in FIG. 2, the distances between adjacent ones of Ag phases (and the average diameter of the Ag phases).

[0028] The 3DAP method includes: setting a single Ag concentration threshold for Ag concentrations in a cross-section of the Cu-Ag alloy wire, which is perpendicular to its longitudinal direction; and tentatively determining, to be Ag phases, sites that have been determined to have a concentration distribution beyond the threshold value. As a result, as shown in FIG. 1, the Ag phases with atomic concentrations beyond the predetermined threshold can be imaged in a plane along the longitudinal direction. As shown in FIG. 2, the Ag phases with atomic concentrations beyond the predetermined threshold can also be imaged along the cross-sectional direction.

[0029] In this case, as shown in FIG. 2, the Ag phases are identified (assigned) and counted using a threshold of 3.5 at.% with respect to the Ag iso-concentration surfaces in the cross-section of the alloy wire.

[0030] The average diameter of the Ag phases is determined by a process including: assuming, as circles, the cross-sections of the tentatively determined Ag phases, which are perpendicular to the longitudinal direction; and calculating the average diameter from the areas of the circles. In the Cu-Ag alloy according to the present invention, the Ag phases are selected having an average diameter in the range of 0.5 to 20.0 nm. In the measurement of the Ag atomic concentration, the tentatively determined Ag phases are subjected to profile analysis along the longitudinal direction, and Ag phases are selected that continuously have Ag atomic concentrations of 0.5 to 50% over a length of 60 nm. The number of the Ag phases is determined by a process including: selecting and counting Ag phases that satisfy the above average diameter requirement and the above Ag atomic concentration requirement; and converting the resulting count to a value per 10,000 nm^2 measured area provided that the number of the Ag phases is proportional to area. The average of the shortest distances between most adjacent ones of the Ag phases is calculated by a process including: determine the distance between each pair of target Ag phases whose centers are closest to each other; and averaging the determined distances. FIGS. 3 and 4 show the results of the analysis. FIG. 3 shows the results of assigning the Ag phases in the longitudinal direction of the wire, and FIG. 4 shows the results of assigning the Ag phases in the cross-section of the wire.

[0031] FIG. 5 is a graph showing the results of atomic concentration analysis of the elements Cu, Ag, N, and O in one of the multiple Ag phases identified from FIG. 3 in the lower part of the tip portion (from the third position (80 nm position) to the second position (140 nm position)), in which the atomic concentration analysis is along the longitudinal direction of the Ag phase. FIG. 5 indicates that the atomic concentration of Ag in the Ag phase varies (fluctuates) within the range of 2 to 7 at.%. The amounts of the elements N and O, which may be affected by the noise from the ambient environment, are almost negligible because they are very small and have very little influence on the properties of the Cu-Ag alloy.

[0032] The Cu-Ag alloy wire of the present invention has, in its matrix phase, multiple Ag phases that are linearly distributed and connected approximately along the longitudinal direction of the Cu-Ag alloy wire. As can be seen in FIGS. 1 and 3, the Ag phases are approximately parallel and extend along the longitudinal direction of the wire although they are not completely aligned in the longitudinal direction. In this case, the phases that are connected along the longitudinal direction are not uniform or constant in Ag atomic concentration in the longitudinal direction and vary in Ag atomic concentration as shown in FIG. 5. In this context, the Ag atomic concentration indicates the Ag content, and it is important that there are phases that have Ag atomic concentrations in the range of 0.5 to 50.0% and are connected along the longitudinal direction. An Ag atomic concentration of less than 0.5% makes it impossible to determine whether Ag is in the form of precipitates or a solid solution and to identify the second phase. With an Ag atomic concentration of more than 50.0%, Ag phases will be sufficiently coarse and tend to be so spaced that they will fail to provide high tensile strength. Thus, the Ag phases need to have Ag atomic concentrations in the range of 0.5 to 50.0 at.%. Moreover, the Ag phases need to be connected along the longitudinal direction. Otherwise, the Ag phases will be so spaced that they will fail to provide higher tensile strength or higher bending fatigue resistance. Therefore, the Cu-Ag alloy wire has multiple Ag phases that are linearly distributed and connected approximately along the longitudinal direction of the Cu-Ag alloy wire.

[0033] When measured perpendicular to the longitudinal direction, the cross-section of the Cu-Ag alloy wire has 10 to 400 Ag phases with an average diameter in the range of 0.5 to 20 nm per 10,000 nm^2 measured area, which are continuously or intermittently connected along the longitudinal direction. Ag phases with an average diameter of less than 0.5 nm, which is substantially the same level as the atomic diameter, are difficult to distinguish at the resolution of existing analyzers as to whether Ag is in the form of precipitates or a solid solution. The lower limit 0.5 nm is set because Ag phases with an average diameter of 0.5 nm or more can be adequately identified in relation to properties. On the other hand, Ag phases with an average diameter of more than 20 nm will have almost no contribution to densification because they exist at a low density and are widely spaced from one another. Thus, an average diameter of more than 20 nm is a negligible level for the improvement in tensile strength and bending fatigue resistance and does not need to be taken into account.

[0034] In the cross-section of the Cu-Ag alloy wire, less than 10 Ag phases per 10,000 nm^2 measured area will be so spaced that they cannot provide improved tensile strength or improved bending fatigue resistance. No Cu-Ag alloy wire has been found to have more than 400 Ag phases per 10,000 nm^2 measured area in the cross-section. Thus, the upper limit of the number of Ag phases per 10,000 nm^2 measured area is set at 400.

[0035] In the measured cross-section of the Cu-Ag alloy wire (as shown in FIGS. 2 and 4), the average of the shortest distances between the circumferences of adjacent ones of the Ag phases is preferably in the range of 3 to 30 nm. In FIGS. 2 and 4, the hollow circle indicates the cross-section of each Ag phase. With the shortest distance average of more than 30 nm, the Ag phases may less contribute to the strength of the wire. The lower limit of the average of the shortest distances between the Ag phases is not provided to specify certain properties. The lower limit is provided to specify the range of the average of the shortest distances between the Ag phases in which certain properties can be ensured, although some Ag phases may be unidentifiable for the resolution limit as in the case of the average diameter of the Ag phases. Controlling the average of the shortest distances between the Ag phases within the range according to the present invention will provide higher tensile strength and improved bending fatigue resistance.

[0036] The bending fatigue resistance of metal is resistance to flex fatigue, which is a phenomenon in which the durability of the metal material decreases when the metal undergoes continuous mechanical stress or repeated bending. The bending fatigue resistance of metal depends on variations in the inner metallographic structure. The Cu-Ag alloy wire of the present invention has a unique metallographic structure. Such a metallographic structure will provide both high tensile strength and improved bending fatigue resistance and be less likely to change, for example, when the average of the shortest distances between the circumferences of adjacent ones of the Ag phases is in the range of 3 to 30 nm as measured and analyzed from the side and the cross-section perpendicular to the longitudinal direction.

[0037] The Cu-Ag alloy wire of the present invention having the unique metallographic structure described above will have high tensile strength and excellent bending fatigue resistance while maintaining high electrical conductivity. The Cu-Ag alloy wire preferably has an electrical conductivity of 65% IACS or more, more preferably 75% IACS or more.

[0038] Cu-Ag alloy wires tend to be increasingly used in the form of ultrafine wires with diameters smaller than usual. Even such ultrafine wires need to have high tensile strength and high electrical conductivity. In particular, Cu alloys with high tensile strength are demanded, and thus the Cu-Ag alloy wire of the present invention preferably has a tensile strength of at least 900 MPa or more, more preferably 1,000 MPa or more. With this feature, the Cu-Ag alloy wire of the present invention will resist high tensile loads even when reduced in diameter.

[0039] The Cu-Ag alloy wire of the present invention is preferably a round wire with a diameter of 0.01 mm to 0.08 mm. Regarding part conductors, the market is demanding 0.01 mmϕ to 0.08 mmϕ wires with high tensile strength and high conductivity. To reflect the market's need, the lower limit of the wire diameter is set to 0.01 mmϕ. The Cu-Ag alloy wire of the present invention can address future applications in which there will be a demand for a further reduction in diameter. With a diameter of more than 0.08 mmϕ, the wire will no longer serve as an ultrafine wire.

[0040] The Cu-Ag alloy wire of the present invention is also preferably a ribbon wire having an approximately rectangular cross-section and having a width of 0.02 to 0.32 mm and a thickness of 0.002 to 0.040 mm. Such a wire may be produced, for example, by a method including: forming the above round wire by drawing; and then rolling the round wire into a desired shape. For similar reasons to those for the upper and lower limits of the wire diameter, the ribbon preferably has such dimensions as a width of 0.02 to 0.32 mm and a thickness of 0.002 to 0.040 mm. The width is in the transverse direction of the rolling rolls, and the thickness is in the roll-to-roll direction. The rolling rolls will not come into contact with the transverse ends of the wire and allow them to remain arc-shaped while deforming the wire. In this context, the width and the thickness respectively refer to the longest and shortest sizes of the cross-section of the ribbon wire.

[0041] A method for producing the Cu-Ag alloy wire of the present invention will be described. It should be noted that the production method described below is a mere example and should not be construed as a limitation to the scope of the present invention. A method for producing the Cu-Ag alloy wire of the present invention includes: a casting step including melting and casting a Cu-Ag alloy material with a specific chemical composition and cooling the cast material to obtain an ingot; a first drawing step including drawing the Cu-Ag alloy material ingot; a first heat treatment step including heat-treating the drawn Cu-Ag alloy material; a second drawing step including further drawing the heat-treated material; a second heat treatment step including further heat-treating the drawn material; and a third drawing step including subjecting the heat-treated material to final drawing to obtain a Cu-Ag alloy wire. The drawing steps reduce the size of precipitates and the spacing between precipitates. Thus, each of the heat treatments is performed to control the distribution of precipitates in such a way that the precipitate system and the spacing between phases will fall within the ranges according to the present invention at the stage where the final drawing is completed.

Casting Step

[0042] The casting step may include cooling the cast material at a rate of 10°C/second or more for the purpose of preventing excessive formation of Ag precipitate crystals in the Cu matrix phase. Large precipitate crystals formed during the casting may fail to be turned into Ag phases with an appropriate average size during the subsequent drawing step or may provide Ag phases spaced widely apart, which may cause the final Cu-Ag alloy wire product to have lower tensile strength.

First Drawing Step

[0043] The first drawing step includes drawing the product resulting from the casting step. The reduction ratio is preferably about 50 to about 90% for the purpose of enhancing sufficient precipitation of Ag during heat treatment. At a reduction ratio of less than 50%, Ag may fail to form sufficient precipitates, so that the spacing between Ag phases in the drawn product may fail to be sufficiently narrow and thus the reduction ratio of the second and later drawing steps may provide only a small increase in strength. This may make it difficult to provide high tensile strength to the Cu-Ag alloy wire with a relatively large diameter. The precipitation can be enhanced by drawing at a reduction ratio of 90% or more. In that case, however, a high reduction ratio cannot be set in the later drawing step after the heat treatment, so that high tensile strength may be difficult to achieve. Thus, the upper limit is preferably set to 90%. The reduction ratio is defined by the formula: $\text{reduction ratio} = ((S1 - S2)/S1) \times 100\ (\%)$, where S1 is the cross-sectional area before the drawing, and S2 is the cross-sectional area after the drawing.

First Heat Treatment Step → Second Drawing Step → Second Heat Treatment Step

[0044] In the present invention, it is preferred to perform at least two heat treatment steps, including first and second heat treatment steps, during the process in which the ingot is drawn into the final wire diameter. The first heat treatment step includes performing heat treatment for precipitating Ag in the Cu matrix phase to form Ag phases. The first heat treatment step may include performing heat treatment at a temperature in the range of 350 to 500°C for a time period in the range of 2 to 10 hours. Subsequently, the second drawing step is performed, which may include drawing at a reduction ratio of 5 to 40% for the purpose of promoting the formation of Ag phases from Ag precipitates formed during the second heat treatment. The second heat treatment is then performed, which may include heat treatment at a temperature in the range of 350 to 500°C for a time period in the range of 10 to 20 hours.

[0045] If the first and second heat treatment steps are performed at a temperature lower than the above lower limit or for a time period shorter than the above lower limit, Ag phases may precipitate in a smaller amount, which may make it impossible to obtain a metallographic structure with an Ag phase precipitate density falling within the range according to the present invention, so that the final product may fail to have high tensile strength. If the treatment temperature exceeds the upper limit, the solid solubility limit may decrease and Ag phases may precipitate in a smaller amount. If the treatment time exceeds the upper limit, many of the Ag phase precipitates may have sizes beyond the range according to the present invention, so that the number of the precipitates may decrease to a level below the range according to the present invention and the average of the shortest distances may increase to a level above the upper limit, which may make it impossible to achieve sufficient levels of tensile strength and bending fatigue resistance. If only the first heat treatment is performed, the precipitates with desired sizes may fail to reach a sufficient number density and the average of the shortest distances may also exceed the upper limit, which may result in insufficient levels of strength and bending fatigue resistance. Therefore, further improving the strength and bending fatigue resistance properties will require increasing the number density of the Ag phases, for which the second stretching step and the following second heat treatment step may be added. The optimum heat treatment conditions and the driving force to precipitate the Ag phases significantly vary depending on how much plastic working is carried out before the heat treatment. Thus, there is no need to stick to the above conditions as long as precipitates can be obtained in a sufficient amount that allows the Cu-Ag alloy wire to have the metallographic structure according to the present invention.

Third Drawing Step

[0046] The third drawing step is then performed to provide a sufficient level of strength to the alloy. In the third drawing step, the reduction ratio is preferably about 90% to about 99.9999%. A lower reduction ratio may fail to provide a sufficient increase in strength. The upper limit of the reduction ratio reflects practical limitations with no relation to the properties. The ribbon wire is produced by rolling a round wire, which has been produced in a cylindrical shape, to a specified thickness.

[0047] The process may also include a peeling step for the purpose of improving the surface quality or preventing the wire from breaking or having abnormalities in shape due to external damage. A finishing heat treatment step may also be performed at the final stage of the process to yield a final Cu-Ag alloy wire (the final heat-treated product). Preferred conditions for carrying out the final heat treatment include, but are not limited to, a temperature of 450 to 600°C and a time period of 10 seconds to 30 minutes.

EXAMPLES

[0048] The present invention will be described in detail with reference to the following examples. It should be noted that the following examples are not intended to limit the present invention.

[0049] In the air, each of Cu-Ag alloys with the following chemical compositions was molten and cast: Cu-1.5 mass% Ag (Examples 1-1 to 1-12 and Comparative Examples 1-1 to 1-11); Cu-2.0 mass% Ag (Examples 2-1 to 2-12 and Comparative Examples 2-1 to 2-11); Cu-4.0 mass% Ag (Examples 3-1 to 3-12 and Comparative Examples 3-1 to 3-11); Cu-6.0 mass% Ag (Examples 4-1 to 4-12 and Comparative Examples 4-1 to 4-11); Cu-0.5 mass% Ag, Cu-0.8 mass% Ag, Cu-6.5 mass% Ag, and Cu-8.0 mass% Ag (Comparative Examples 5-1, 5-2, 5-3, and 5-4); and Cu-2.0 mass% Ag-one component selected from Sn, Mg, Zn, In, Ni, Co, Zr, and Cr (Examples 6-1 to 6-8 and Comparative Examples 6-1 to 6-3), and the cast alloy was cooled at a rate of 8 to 50°C/second to produce an ingot with a diameter of 6.3 to 16 mmϕ (casting step) .

[0050] The ingot was then drawn at a reduction ratio of 35 to 95% into a wire with a diameter of 1.0 to 9.5 mmϕ (first drawing step). The wire was then subjected to aging heat treatment at 350 to 550°C for a holding time of 1 to 15 hours for both precipitation and recrystallization (first heat treatment step). Subsequently, the wire was cooled and then drawn at 3 to 99.9% (second drawing step). Subsequently, the wire was held at 350 to 550°C for 5 to 50 hours and then subjected to aging heat treatment at 350 to 550°C for a holding time of 1 to 15 hours (second heat treatment step). Subsequently, the wire was cooled and then cold-drawn at 65 to 99.998% into a diameter of 0.02 to 0.08 mmϕ (third drawing step) .

Performance Evaluation

[0051] The Cu-Ag alloy wires produced as shown above were measured for tensile strength, bending fatigue resistance, and optionally electrical conductivity, and their metallographic structure was analyzed using a 3DAP system and analysis software.

Tensile Strength

[0052] Three test pieces (n = 3) with the original wire shape (not according to JIS Z 2201) were measured for tensile strength under test conditions according to JIS Z 2241. The average (MPa) of the measured tensile strengths was used as the measured value.

Bending Fatigue Resistance

[0053] The bending fatigue resistance was determined by performing the reverse bend test according to JIS H 0500 No. 4100. The fatigue properties depend on wire diameter. Thus, 0.03 mmϕ wire samples were subjected to the test, including products separately produced by drawing, into the same diameter, unfinished samples for products thinner and thicker than 0.03 mmϕ and for rolled products. A jig having a radius R of 6 mm for the bending fulcrum was used. One end of the sample was fixed on the grip, and a 30 g weight was suspended from the other end such that the sample did not undergo deflection. The number of bending cycles was counted until the sample broke, and the average of the counts (n = 5) (average flex life) was evaluated as to whether or not it satisfied the relations of formulas 1 and 2 below. Specifically, the bending fatigue resistance of the sample was evaluated as "excellent" (indicated by bullseye symbol (⊙)), "good" (indicated by circle symbol (o)), and "poor" (indicated by cross symbol (x)), respectively, when the average flex life value satisfied formula 1, when the average flex life value did not satisfy formula 1 but satisfied formula 2, and when the average flex life value neither satisfied formula 1 nor formula 2.

$$\text{Average flex life} \geq 5{,}900 \times (\text{Ag concentration}) + 40{,}000 \qquad \text{Formula 1:}$$

$$\text{Average bending life} \geq 5{,}900 \times (\text{Ag concentration}) + 20{,}000 \qquad \text{Formula 2:}$$

Electrical Conductivity

[0054] Two pieces of each of the samples were measured for electrical conductivity in a thermostatic chamber controlled at 20°C (±1°C) using a four-terminal method based on JIS H 0505-1975, and the average (%IACS) of the measurements was used as the measured value. The distance between the terminals was 100 mm.

Metallographic Structure

[0055] The metallographic structure of the Cu-Ag alloy wire was observed and analyzed using a 3DAP system because the Ag phase (second phase) had a size on the order of sub-nanometers to nanometers. In the 3DAP system, atoms evaporated from the material were detected by a two-dimensional detector, and the detected data were reconstructed to visualize three-dimensional structures on the order of nanometers. The sample for the 3D atom probe measurement was prepared using focused ion beam (FIB).

[0056] The FIB was generated using SII NT-3050TB and Helios G4 (manufactured by FEI Company). The sample was prepared in the shape of a cone with an about 80 nm-diameter circular bottom and a length of about 140 nm using Ga ion beams at an acceleration voltage of 30 kV. For the analysis, the longitudinal direction of the sample was in the longitudinal direction of the Cu-Ag alloy wire. Alternatively, the longitudinal direction of the sample may be in the direction of the diameter of the cross-section perpendicular to the longitudinal direction of the Cu-Ag alloy wire. Final finishing was performed using 5 kV ion beams to reduce any damaged layer as much as possible.

[0057] The 3DAP analysis system consisted of LEAP 4000XSi (manufactured by AMETEK Inc.). Ultraviolet laser pulses with a wavelength of 355 nm were applied for the evaporation. A voltage of 1 to 5 kV was also applied to the sample. Analysis software such as IVAS 3.8.8 (manufactured by CAMECA) or IVAS LT was used to analyze the atomic concentration of Ag phases and the shortest distances between Ag phases.

Measurement of the Average Diameter, the Atomic Concentration, and the Number of Ag Phases

[0058] The sample information collected by the 3DAP method was analyzed using the analysis software IVAS. In the analysis, a single Ag concentration threshold was set for Ag concentrations in a cross-section of the Cu-Ag alloy wire, which was perpendicular to its longitudinal direction, and sites that were determined to have a concentration distribution beyond the threshold value were tentatively determined to be Ag phases. The average diameter of the Ag phases was determined by a process including: assuming, as circles, the cross-sections of the tentatively determined Ag phases, which were perpendicular to the longitudinal direction; and calculating the average diameter from the areas of the circles. Ag phases with an average diameter in the range of 0.5 to 20.0 nm were selected from those tentatively determined. In the measurement of Ag atomic concentration, the tentatively determined Ag phases were subjected to profile analysis along the longitudinal direction, in which Ag phases having Ag atomic concentrations of 0.5 to 50% continuously over a length of 60 nm were selected. Ag phases satisfying both the average diameter requirement and the Ag atomic concentration requirement were selected and counted to determine the number of Ag phases. The area of the sample analyzed was approximately 5,000 nm^2. The count was converted to a value per 10,000 nm^2 area, which was used as the tentative number of Ag phases.

Average of Shortest Distances between Ag Phases

[0059] The shortest distance between Ag phases was defined as the shortest distance between the circumferences of a pair of most adjacent Ag phases. The shortest distances between Ag phases (n ≥ 10) in the bottom cross-section of the sample were averaged.

Examples 1-1 to 1-12 and Comparative Examples 1-1 to 1-10

[0060] The wire samples of Examples 1-1 to 1-12 and Comparative Examples 1-1 to 1-10 were produced using Cu-Ag alloy with the chemical composition of Cu-1.5 mass% Ag under different conditions for varying the Ag atomic concentration of Ag phases, the average diameter of Ag phases, and the number of Ag phases and for varying the average of the shortest distances between Ag phases.

[0061] Table 1 shows the conditions for producing the samples of Examples 1-1 to 1-12 and Comparative Examples 1-1 to 1-10. The sample of Example 1-10 was formed by working a round wire with a final wire diameter of 0.03 mm into a ribbon with a thickness of 0.008 mm and a width of 0.08 mm. In the tables, the underline indicates that the corresponding value is out of the range according to the present invention.

[Table 1]

(Cu-1.5 mass% Ag alloy wire)								
Examples Comparative Examples	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
			Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Example 1	15	65	400	10	10	400	10	99.998
Example 1 - 2	45	65	400	10	5	400	10	99.998
Example 1 - 3	45	50	400	10	10	500	10	99.998
Example 1 - 4	45	65	350	8	20	425	10	99.998
Example 1 - 5	45	65	450	10	10	400	15	99.998
Example 1 - 6	45	65	375	10	10	425	10	99.998
Example 1 - 7	45	65	425	10	5	350	15	99.998
Example 1 - 8	45	65	500	3	10	400	15	99.998
Example 1 - 9	45	65	475	5	10	400	15	99.998
Example 1 - 10	45	65	400	8	35	375	20	99.99
Example 1 - 11	45	65	400	10	25	400	15	99.998
Example 1 -12	45	90	400	10	25	400	15	99.9
Comparative Example 1-1	*5*	65	375	15	50	375	10	99.998
Comparative Example 1 - 2	45	*35*	400	15	50	400	12	99.998
Comparative Example 1 - 3	45	65	*300*	10	50	*250*	10	99.998
Comparative Example 1 - 4	45	65	*550*	10	50	*550*	10	99.998
Comparative Example 1 - 5	45	65	400	*1*	50	400	*6*	99.998
Comparative Example 1 - 6	45	65	500	*15*	50	450	*25*	99.998
Comparative Example 1 - 7	45	65	350	10	*3*	350	10	99.998
Comparative Example 1 - 8	45	65	350	10	50	*250*	18	99.998

(continued)

(Cu-1.5 mass% Ag alloy wire)								
Examples Comparative Examples	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
			Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Comparative Example 1 - 9	45	65	375	10	-	-	-	99.998
Comparative Example 1 - 10	45	*95*	450	10	*99*	500	15	*85*

[0062] Table 2 shows the results of the evaluation of the metallographic structure and the properties of the samples of Examples 1-1 to 1-12 and Comparative Examples 1-1 to 1-10. The evaluation items are the minimum and maximum values of the Ag atomic concentration (%) of the Ag phases, the average diameter of the Ag phases, the number of the Ag phases, and the average of the shortest distances between the Ag phases, which represent the metallographic structure, and the tensile strength and the bending fatigue resistance, which represent the mechanical properties.

[Table 2]

(Cu-1.5 mass% Ag alloy wire)								
Examples Comparative Examples	Final wire diameter (mmφ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Example 1 -1	0.03	1	4	1.0	15	22	1035	◎
Example 1 -2	0.03	1	6	0.8	35	18	1040	◎
Example 1 -3	0.03	2	5	22	25	18	1055	◎
Example 1 -4	0.03	2	4	1.5	15	24	1015	◎
Example 1 - 5	0.03	0.7	2	30	22	18	1030	◎
Example 1 -6	0.03	1	3	2.5	30	20	1040	◎
Example 1 -7	0.03	2.5	5	1.5	28	*34*	1060	○
Example 1 - 8	0.03	3	7	1.0	36	*32*	1025	○
Example 1 -9	0.03	2	5	1.6	44	*35*	1015	○
Example1-10	0.03→ Plate thickness of 0.008 mm Width of 0.08 mm	4	7	20	25	*32*	1020	○
Example 1 -11	0.02	1	3	2.5	18	*35*	1010	○
Example 1 -12	0.08	5	8	1.6	14	*33*	1050	○
Comparative Example 1 -1	0.03	2	7	12	*4*	*51*	*880*	×
Comparative Example 1-2	0.03	3	6	1.5	*3*	*48*	*850*	×
Comparative Example 1-3	0.03	1	5	2.5	*2*	*55*	*870*	×

(continued)

(Cu-1.5 mass% Ag alloy wire)								
Examples Comparative Examples	Final wire diameter (mmφ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Comparative Example 1 -4	0.03	35	45	3	*2*	*62*	*840*	×
Comparative Example 1 - 5	0.03	1	3	0.7	*3*	*53*	*890*	×
Comparative Example 1-6	0.03	32	43	3	*4*	*58*	*820*	×
Comparative Example 1 -7	0.03	1	3	2.5	*1*	*52*	*850*	×
Comparative Example 1-8	0.03	5	8	3	*1*	*50*	*865*	×
Comparative Example 1 - 9	0.03	1	5	1.5	*2*	*50*	*840*	×
Comparative Example 1 - 10	0.08	42	38	1.5	10	*62*	*825*	×

[0063] Table 2 shows that the final wire diameter, the Ag atomic concentration of the Ag phases, the average diameter of the Ag phases, the number of the Ag phases, and the average of the shortest distances between the Ag phases of each of the samples of Examples 1-1 and 1-12 all fall within the ranges according to the present invention. They all have a tensile strength as high as at least 1,000 MPa. The bending fatigue resistance of the samples of Examples 1-7 to 1-12 is evaluated as "good" (indicated by circle symbol (o)). The bending fatigue resistance of the samples of Examples 1-1 to 1-6, in which the average of the shortest distances between the Ag phases is in the range of 3 to 30 nm, is evaluated as "excellent" (indicated by bullseye symbol (0)). Regarding the samples of Comparative Examples 1-1 to 1-9, the final wire diameter, the Ag atomic concentration of the Ag phases, and the average diameter of the Ag phases fall within the ranges according to the present invention, but the number of the Ag phases is relatively small and the average of the shortest distances between the Ag phases is at least 30 nm, so that their tensile strength is relatively low and their bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)). Regarding the sample of Comparative Example 1-10, the number of the Ag phases falls within the range according to the present invention, which should be due to the very low third reduction ratio, but the average of the shortest distances between the Ag phases is at least 30 nm, so that its tensile strength is relatively low and its bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)).

Examples 2-1 to 2-12 and Comparative Examples 2-1 to 2-10

[0064] The wire samples of Examples 2-1 to 2-12 and Comparative Examples 2-1 to 2-10 were produced using Cu-Ag alloy with the chemical composition of Cu-2.0 mass% Ag.

[0065] Table 3 shows the conditions for producing the samples of Examples 2-1 to 2-12 and Comparative Examples 2-1 to 2-10.

[Table 3]

(Cu-2.0 mass% Ag alloy wire)								
Examples Comparative Examples	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
			Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Example 2-1	15	65	400	10	10	400	10	99.998

(continued)

(Cu-2.0 mass% Ag alloy wire)

Examples Comparative Examples	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
			Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Example 2-2	45	65	400	10	5	400	10	99.998
Example 2-3	45	50	400	10	10	500	10	99.998
Example 2-4	45	65	350	8	20	425	10	99.998
Example 2-5	45	65	450	10	10	400	15	99.998
Example 2-6	45	65	375	10	10	425	10	99.998
Example 2-7	45	65	425	10	5	350	15	99.998
Example 2-8	45	65	500	3	10	400	15	99.998
Example 2-9	45	65	475	5	10	400	15	99.998
Example 2-10	45	65	400	8	35	375	20	9999
Example 2-11	45	65	400	10	25	400	15	99.998
Example 2-12	45	90	400	10	25	400	15	99.9
Comparative Example2 -1	5	65	375	15	50	375	10	99.998
Comparative Example2 -2	45	*35*	400	15	50	400	12	99.998
Comparative Example2 -3	45	65	*300*	10	50	*250*	10	99.998
Comparative Example2 -4	45	65	*550*	10	50	*550*	10	99.998
Comparative Example2 -5	45	65	400	*1*	50	400	*6*	99.998
Comparative Example2 -6	45	65	500	*15*	50	450	*25*	99.998
Comparative Example2 -7	45	65	350	10	*3*	350	10	99.998
Comparative Example2 -8	45	65	350	10	50	*250*	18	99.998
Comparative Example2 -9	45	65	375	10	-	-	-	99.998
Comparative Example2 -10	45	*95*	450	10	*99*	500	15	*55*

[0066] Table 4 shows the results of the evaluation of the metallographic structure and the properties of the samples of Examples 2-1 to 2-12 and Comparative Examples 2-1 to 2-10.

[Table 4]

(Cu-2.0 mass% Ag alloy wire)

Examples Comparative Examples	Final wire diameter (mm φ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Example2 -1	0.03	3	7	2.5	30	15	1160	◎
Example2 -2	0.03	2	6	3	35	12	1190	◎
Example2 -3	0.03	2	7	4	25	16	1170	◎
Example2 -4	0.03	4	7	3	15	12	1180	◎
Example2 -5	0.03	7	11	5	22	15	1190	◎
Example2 -6	0.03	6	9	4.5	30	16	1190	◎
Example2 -7	0.03	5	10	4	28	18	1200	◎
Example2 -8	0.03	6	11	7	36	14	1180	◎
Example2 -9	0.03	4	8	5	44	*31*	1190	○
Example2 -10	0.03→ Plate thickness of 0.008 mm Width of 0.08 mm	5	9	6	25	*35*	1160	○
Example 2 -11	0.02	2	5	5	18	*32*	1170	○
Example 2 -12	0.08	8	14	7	14	*42*	1150	○
Comparative Example 2 -1	0.03	2	7	15	*5*	*42*	*1040*	×
Comparative Example 2 -2	0.03	3	6	13	*4*	*38*	*1060*	×
Comparative Example 2 -3	0.03	1	5	12	*3*	*45*	*1080*	×
Comparative Example2 -4	0.03	35	*58*	16	*1*	*50*	*1000*	×
Comparative Example 2 -5	0.03	1	3	15	*5*	*46*	*1075*	×
Comparative Example2 -6	0.03	32	*54*	10	*4*	*48*	*1020*	×
Comparative Example 2 -7	0.03	1	3	10	*2*	*45*	*1050*	×
Comparative Example2 -8	0.03	5	8	15	*3*	*42*	*1060*	×
Comparative Example2 -9	0.03	1	5	15	*4*	*38*	*1100*	×
Comparative Example 2 -10	0.08	42	*65*	12	13	*42*	*1020*	×

[0067] The samples of Examples 2-1 to 2-12 all have a metallographic structure falling within the range according to the present invention. Thus, they all have a tensile strength as high as at least 1,100 MPa. The bending fatigue resistance of the samples of Examples 2-9 to 2-12 is evaluated as "good" (indicated by circle symbol (o)). The bending fatigue resistance of the samples of Examples 2-1 to 2-8, in which the average of the shortest distances between the Ag phases is in the range of 3 to 30 nm, is evaluated as "excellent" (indicated by bullseye symbol (⊙)). Regarding the samples of Comparative Examples 2-1 to 2-10, the final wire diameter, the Ag atomic concentration of the Ag phases, and the average diameter of the Ag phases fall within the ranges according to the present invention, but the number of the Ag phases is relatively small and the average of the shortest distances between the Ag phases is at least 30 nm, so that their tensile strength is relatively low and their bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)). Regarding the sample of Comparative Example 2-10, the number of the Ag phases falls within the range according to the present invention, which should be due to the very low third reduction ratio, but the average of the shortest distances between the Ag phases is at least 30 nm, so that its tensile strength is relatively low and its bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)).

Examples 3-1 to 3-12 and Comparative Examples 3-1 to 3-10

[0068] The wire samples of Examples 3-1 to 3-12 and Comparative Examples 3-1 to 3-10 were produced using Cu-Ag alloy with the chemical composition of Cu-4.0 mass% Ag.

[0069] Table 5 shows the conditions for producing the samples of Examples 3-1 to 3-12 and Comparative Examples 3-1 to 3-10.

[Table 5]

(Cu-4.0 mass% Ag alloy wire)

Examples Comparative Examples	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
			Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Example 3 - 1	15	65	400	10	10	400	10	99.998
Example 3 - 2	45	65	400	10	5	400	10	99.998
Example 3 - 3	45	50	400	10	10	500	10	99.998
Example 3 - 4	45	65	350	8	20	425	10	99.998
Example 3 - 5	45	65	450	10	10	400	15	99.998
Example 3 - 6	45	65	375	10	10	425	10	99.998
Example 3 - 7	45	65	425	10	5	350	15	99.998
Example 3 - 8	45	65	500	3	10	400	15	99.998
Example 3 - 9	45	65	475	5	10	400	15	99.998
Example 3 - 10	45	65	400	8	35	375	20	99.99
Example 3 - 11	45	65	400	10	25	400	15	99.998
Example 3 - 12	45	90	400	10	25	400	15	99.9
Comparative Example 3 - 1	*5*	65	400	15	50	400	10	99.998
Comparative Example 3 - 2	45	*35*	400	15	50	400	12	99.998
Comparative Example 3 - 3	45	65	*300*	10	50	*250*	10	99.998
Comparative Example 3 - 4	45	65	*550*	10	50	*550*	10	99.998

(continued)

(Cu-4.0 mass% Ag alloy wire)								
Examples Comparative Examples	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
			Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Comparative Example 3 - 5	45	65	400	*1*	50	400	*6*	99.998
Comparative Example 3 - 6	45	65	500	*15*	50	450	*25*	99.998
Comparative Example 3 - 7	45	65	350	10	*3*	350	10	99.998
Comparative Example 3 - 8	45	65	350	10	50	*250*	18	99.998
Comparative Example 3 - 9	45	65	375	10	-	-	-	99.998
Comparative Example 3 -10	45	65	450	10	*99.99*	500	15	*85*

[0070] Table 6 shows the results of the evaluation of the metallographic stgructure and the properties of the samples of Examples 3-1 to 3-12 and Comparative Examples 3-1 to 3-10.

[Table 6]

(Cu-4.0 mass% Ag alloy wire)								
Examples Comparative Examples	Final wire diameter (mm φ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Example 3 - 1	0.03	6	14	10	55	12	1380	◎
Example 3 - 2	0.03	7	15	12	43	9	1365	◎
Example 3 - 3	0.03	12	22	8	35	11	1410	◎
Example 3 - 4	0.03	6	12	13	40	8	1400	◎
Example 3 - 5	0.03	13	26	12	48	16	1390	◎
Example 3 - 6	0.03	10	22	8	65	14	1395	◎
Example 3 - 7	0.03	13	23	12	50	10	1370	◎
Example 3 - 8	0.03	16	28	9	52	8	1390	◎
Example 3 - 9	0.03	12	21	11	65	15	1380	◎
Example 3 - 10	0.03→ Plate thickness of 0.008 mm Width of 0.08 mm	25	44	12	50	*35*	1400	○
Example 3 - 11	0.02	10	18	14	36	*33*	1380	○

(continued)

(Cu-4.0 mass% Ag alloy wire)								
Examples Comparative Examples	Final wire diameter (mm φ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Example 3 - 12	0.08	26	38	13	32	*36*	1340	○
Comparative Example 3 - 1	0.03	10	20	22	*8*	*35*	*1120*	×
Comparative Example 3 - 2	0.03	15	25	17	*8*	*33*	*1130*	×
Comparative Example 3 - 3	0.03	14	35	18	*7*	*36*	*1080*	×
Comparative Example 3 - 4	0.03	38	*62*	16	*5*	*32*	*1000*	×
Comparative Example 3 - 5	0.03	5	15	15	*6*	*35*	*1075*	×
Comparative Example 3 - 6	0.03	42	67	17	*7*	*33*	*1020*	×
Comparative Example 3 - 7	0.03	12	25	13	8	*38*	*1050*	×
Comparative Example 3 - 8	0.03	12	28	16	8	*42*	*1060*	×
Comparative Example 3 -9	0.03	4	10	14	*1*	*38*	*1100*	×
Comparative Example 3 - 10	0.03	*52*	*80*	15	14	*35*	*1050*	×

[0071] The samples of Examples 3-1 to 3-12 all have a metallographic structure falling within the range according to the present invention. Thus, they all have a tensile strength as high as at least 1,300 MPa. The bending fatigue resistance of the samples of Examples 3-10 to 3-12 is evaluated as "good" (indicated by circle symbol (o)). The bending fatigue resistance of the samples of Examples 3-1 to 3-9, in which the average of the shortest distances between the Ag phases is in the range of 3 to 30 nm, is evaluated as "excellent" (indicated by bullseye symbol (0)). Regarding the samples of Comparative Examples 3-1 to 3-9, the final wire diameter, the Ag atomic concentration of the Ag phases, and the average diameter of the Ag phases fall within the ranges according to the present invention, but the number of the Ag phases is relatively small and the average of the shortest distances between the Ag phases is at least 30 nm, so that their tensile strength is relatively low and their bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)). Regarding the sample of Comparative Example 3-10, the number of the Ag phases falls within the range according to the present invention, which should be due to the very low third reduction ratio, but the average of the shortest distances between the Ag phases is at least 30 nm, so that its tensile strength is relatively low and its bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)).

Examples 4-1 to 4-12 and Comparative Examples 4-1 to 4-10

[0072] The wire samples of Examples 4-1 to 4-12 and Comparative Examples 4-1 to 4-10 were produced using Cu-Ag alloy with the chemical composition of Cu-6.0 mass% Ag.

[0073] Table 7 shows the conditions for producing the samples of Examples 4-1 to 4-12 and Comparative Examples 4-1 to 4-10.

[Table 7]

(Cu-6.0 mass% Ag alloy wire)								
Examples Comparative Examples	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
			Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Example 4 - 1	15	65	400	10	10	400	10	99.998
Example 4 - 2	45	65	400	10	5	400	10	99.998
Example 4 - 3	45	50	400	10	10	500	10	99.998
Example 4 - 4	45	65	350	8	20	425	10	99.998
Example 4 -5	45	65	450	10	10	400	15	99.998
Example 4 -6	45	65	375	10	10	425	10	99.998
Example 4 - 7	45	65	425	10	5	350	15	99.998
Example 4 - 8	45	65	500	3	10	400	15	99.998
Example 4 - 9	45	65	475	5	10	400	15	99.998
Example 4 - 10	45	65	400	8	35	375	20	99.99
Example 4 - 11	45	65	400	10	25	400	15	99.998
Example 4 - 12	45	90	400	10	25	400	15	99.9
Comparative Example 4 - 1	5	65	400	15	50	400	10	99.998
Comparative Example 4 - 2	45	*35*	400	15	50	400	12	99.998
Comparative Example 4 - 3	45	65	*300*	10	50	*250*	10	99.998
Comparative Example 4 - 4	45	65	*550*	10	50	*550*	10	99.998
Comparative Example 4 - 5	45	65	400	*1*	50	400	6	99.998
Comparative Example 4 - 6	45	65	500	is	50	450	*25*	99.998
Comparative Example 4 - 7	45	65	350	10	*3*	350	10	99.998
Comparative Example 4 - 8	45	65	350	10	50	*250*	18	99.998
Comparative Example4 -9	45	65	375	10	-	-	-	99.998
Comparative Example 4 - 10	45	65	450	10	*99.99*	500	15	*85*

[0074] Table 8 shows the results of the evaluation of the metallographic structure and the properties of the samples of Examples 4-1 to 4-12 and Comparative Examples 4-1 to 4-10.

[Table 8]

(Cu-6.0 mass% Ag alloy wire)

Examples Comparative Examples	Final wire diameter (mm φ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Example 4 - 1	0.03	8	25	14	55	12	1450	◎
Example 4 - 2	0.03	10	32	16	43	9	1420	◎
Example 4 - 3	0.03	15	45	10	35	11	1480	◎
Example 4 - 4	0.03	15	22	18	40	8	1410	◎
Example 4 - 5	0.03	14	30	14	48	16	1460	◎
Example 4 - 6	0.03	15	32	12	65	14	1450	◎
Example 4 - 7	0.03	15	47	16	50	10	1470	◎
Example 4 - 8	0.03	21	35	11	52	8	1480	◎
Example 4 - 9	0.03	18	28	14	65	7	1450	◎
Example 4 - 10	0.03 → Plate thickness of 0.008 mm Width of 0.08 mm	26	44	15	50	13	1435	◎
Example 4 - 11	0.02	15	33	18	36	8	1510	◎
Example 4 - 12	0.08	30	48	19	32	*31*	1420	○
Comparative Example 4 - 1	0.03	10	20	*25*	14	24	*1220*	×
Comparative Example 4 - 2	0.03	16	25	*22*	18	20	*1180*	×
Comparative Example 4 - 3	0.03	2	8	*23*	15	25	*1230*	×
Comparative Example 4 - 4	0.03	38	*62*	*28*	16	18	*1150*	×
Comparative Example 4 - 5	0.03	5	15	*22*	18	18	*1215*	×
Comparative Example 4 - 6	0.03	42	*67*	*21*	25	21	*1290*	×
Comparative Example 4 - 7	0.03	2	8	*26*	15	25	*1170*	×
Comparative Example 4 - 8	0.03	12	28	*30*	12	28	*1130*	×
Comparative Example 4 - 9	0.03	4	10	*25*	16	16	*1250*	×
Comparative Example 4 - 10	0.03	*52*	*80*	*32*	25	18	*1240*	×

[0075] The samples of Examples 4-1 to 4-12 all have a metallographic structure falling within the range according to the present invention. Thus, they all have a tensile strength as high as at least 1,400 MPa. The bending fatigue resistance of the samples of Examples 4-1 to 4-11 is evaluated as "good" (indicated by circle symbol (o)). The bending fatigue resistance of the sample of Example 4-12, in which the average of the shortest distances between the Ag phases is in the range of 3 to 30 nm, is evaluated as "excellent" (indicated by bullseye symbol (0)). Regarding the samples of Comparative Examples 4-1 to 4-10, the final wire diameter, the Ag atomic concentration of the Ag phases, the number of the As phases, and the average of the shortest distances between the Ag phases fall within the ranges according to the present invention, but the average diameter of the Ag phases is at least 30 nm, so that their tensile strength is relatively low and their bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)). Regarding the sample of Comparative Example 4-10, even at the very low third reduction ratio, it was difficult to control the number of the Ag phases within the range according to the present invention and the average diameter of the Ag phases was at least 20 nm. The resulting tensile strength is relatively low and the resulting bending fatigue resistance is evaluated as "poor" (indicated by cross symbol (x)).

Comparative Examples 5-1 to 5-4

[0076] The wire samples of Comparative Examples 5-1 to 5-4 were produced using Cu-Ag alloys having the chemical compositions of Cu-0.5 mass% Ag, Cu-0.8 mass% Ag, Cu-6.5 mass% Ag, and Cu-8.0 mass% Ag, which are out of the range according to the present invention (1.0 to 6.0 mass% Ag).

[0077] Table 9 shows the conditions for producing the samples of Comparative Examples 5-1 to 5-4.

[Table 9]

(Cu-Ag alloy wire)

Examples Comparative Examples	Composition (mass%)	Casting (cooling rate) (°C/s)	First drawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
				Holding temperature(°C)	Holding time(h)	Holding temperature(°C)	Holding time(h)		
Comparative Example 5 -1	Cu-0.5Ag	45	65	400	10	10	400	10	99.998
Comparative Example 5 - 2	Cu-0.8Ag	45	65	400	10	10	400	10	99.998
Comparative Example 5 -3	Cu-6.5Ag	45	50	400	10	10	500	10	99.998
Comparative Example 5 - 4	Cu-8.0Ag	45	65	350	8	20	425	10	99.998

[0078] Table 10 shows the results of the evaluation of the metallographic structure and the properties of the samples of Comparative Examples 5-1 to 5-4.

[Table 10]

(Cu-Ag alloy wire)								
Examples Comparative Examples	Final wire diameter (mmφ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Comparative Example 5 - 1	0.03	-	-	-	-	-	750	×
Comparative Example 5 - 2	0.03	-	-	-	-	-	860	×
Comparative Example 5 - 3	0.03	20	45	15.0	85	5	1390	◎
Comparative Example 5 - 4	0.03	25	48	18.0	110	8	1420	◎

[0079] As shown in Table 10, by the analysis with the 3DAP system, no Ag phase precipitation was observed in the samples of Comparative Examples 5-1 and 5-2 in which the content of Ag was lower than the lower limit 1.0 mass%. Thus, it was not possible to measure the atomic concentration of Ag phases, the average diameter and the number of Ag phases, and the average of the shortest distances between Ag phases. Thus, they had a tensile strength lower than 900 MPa, and their bending fatigue resistance did not satisfy formula 1 and was evaluated as "poor" (indicated by cross symbol (x)). The sample of Comparative Example 5-3, in which the content of Ag was higher than the upper limit 6.0 mass%, had a tensile strength higher than 900 MPa. The bending fatigue resistance of the sample of Comparative Example 5-3, in which the atomic concentration of Ag phases and other properties fell within the ranges according to the present invention, was evaluated as "excellent" (indicated by bullseye symbol (0)). The sample of Comparative Example 5-4, in which the content of Ag was higher than the upper limit 6.0 mass%, had a tensile strength higher than 900 MPa. The bending fatigue resistance of the sample of Comparative Example 5-4, in which the atomic concentration of Ag phases and other properties fell within the ranges according to the present invention, was evaluated as "excellent" (indicated by bullseye symbol (0)). However, there is no difference in the effect on tensile strength or bending fatigue resistance between Comparative Example 5-3 and Example 4-3 or between Comparative Example 5-4 and Example 4-4, and increasing the Ag content may raise the problem of high costs.

Examples 6-1 to 6-8 and Comparative Examples 6-1 to 6-3

[0080] The wire samples of Examples 6-1 to 6-8 and Comparative Examples 6-1 to 6-3 were produced using Cu-Ag alloy having a chemical composition including Cu-2.0 mass% Ag and one selected from Sn, Mg, Zn, In, Ni, Co, Zr, and Cr.

[0081] Table 11 shows the conditions for producing the samples of Examples 6-1 to 6-8 and Comparative Examples 6-1 to 6-3.

[Table 11]

(Cu-2.0 mass% Ag alloy wire)

Examples Comparative Examples	Optional additive element (mass%)	Casting (cooling rate) (°C/s)	Firstdrawing reduction ratio(%)	First heat treatment		Second heat treatment		Second drawing reduction ratio(%)	Third drawing reduction ratio(%)
				Holding temperature(°C)	Holdingtime(h)	Holding temperature(°C)	Holding time(h)		
Example 6 - 1	0.1Sn	15	65	400	10	10	400	10	99.998
Example 6 - 2	0.1Mg	45	65	400	10	5	400	10	99.998
Example 6 - 3	0.3Zn	45	50	400	10	10	500	10	99.998
Example 6 - 4	0.1In	45	65	350	8	20	425	10	99.998
Example 6 - 5	0.2Ni	45	65	450	10	10	400	15	99.998
Example 6 - 6	0.1Co	45	65	375	10	10	425	10	99.998
Example 6 - 7	0.05Zr	45	65	425	10	5	350	15	99.998
Example 6 - 8	0.1Cr	45	65	500	3	10	400	15	99.998
Comparative Example 6 - 1	0.5Sn	Electrical conductivity degradation(60%IACS)							
Comparative Example 6 - 2	0.5Mg	Electrical conductivity degradation(61%IACS)							
Comparative Example 6 - 3	0.5Zr	Ingot cracking							

[0082] Table 12 shows the results of the evaluation of the metallographic structure and the properties of the samples of Examples 6-1 to 6-8 and Comparative Examples 6-1 to 6-3.

[Table 12]

(Cu-2.0 mass% Ag alloy wire)

Examples Comparative Examples	Final wire diameter (mm φ)	Ag atomic concentration of Ag phases(at.%)		Average diameter of Ag phases(nm)	Number of Ag phases (/10,000 nm^2)	Average of shortest distances between Ag phases(nm)	Tensile strength (MPa)	Bending fatigue resistance
		Minimum	Maximum					
Example 6 - 1	0.03	4	8	3.5	31	16	1195	◎
Example 6 - 2	0.03	3	9	4	34	12	1240	◎
Example 6 - 3	0.03	6	12	3	25	15	1200	◎
Example 6 - 4	0.03	5	10	4.5	15	13	1220	◎
Example 6 - 5	0.03	8	14	4	22	12	1220	◎
Example 6 - 6	0.03	3	6	5	30	13	1240	◎
Example 6 - 7	0.03	2	8	2.5	28	11	1215	◎
Example 6 - 8	0.03	5	11	4	36	14	1225	◎
Comparative Example 6 - 1	Electrical conductivity degradation(60%IACS)							
Comparative Example 6 - 2	Electrical conductivity degradation(61%IACS)							
Comparative Example 6 - 3	Ingot cracking							

[0083] The samples of Examples 6-1 to 6-8 all have a metallographic structure falling within the range according to the present invention. Thus, they all have a tensile strength as high as at least 1,100 MPa. The bending fatigue resistance of the samples of Examples 6-1 to 6-8, in which the average of the shortest distances between the Ag phases is in the range of 3 to 30 nm, is evaluated as "excellent" (indicated by bullseye symbol (0)). The sample of Comparative Example 6-1, which contains 0.5 mass% Sn, and the sample of Comparative Example 6-2, which contains 0.5 mass% Mg, have an electrical conductivity of at most 60% IACS. Such a low electrical conductivity may raise a practical problem. In Comparative Example 6-3 where the content of Zr was 0.5 mass%, the ingot cracked during the process, so that it was difficult to produce a round wire or the like, which was unacceptable for production.

Claims

1. A Cu-Ag alloy wire having a chemical composition comprising: 1.0 mass% to 6.0 mass% of Ag; and a remainder of Cu and unavoidable impurities,

    the Cu-Ag alloy wire having a matrix phase containing a plurality of Ag phases that are linearly distributed and connected approximately along a longitudinal direction of the Cu-Ag alloy wire,
    the Ag phases having an atomic concentration of Ag in a range of 0.5% to 50.0%,
    the Cu-Ag alloy wire having a cross-section in which the number of the Ag phases with an average diameter of 0.5 nm to 20.0 nm is in a range of 10 to 400 per 10,000 nm^2 area measured perpendicular to the longitudinal direction of the Cu-Ag alloy wire.

2. The Cu-Ag alloy wire according to claim 1, wherein the average of shortest distances between adjacent ones of the Ag phases in the cross-section measured is in a range of 3 nm to 30 nm.

3. The Cu-Ag alloy wire according to claim 1 or 2, wherein the chemical composition of the Cu-Ag alloy wire further comprises 0.05 mass% to 0.30 mass% of at least one component selected from the group consisting of Sn, Mg, Zn, In,

Ni, Co, Zr, and Cr.

4. The Cu-Ag alloy wire according to any one of claims 1 to 3, wherein the Cu-Ag alloy wire is a round wire having a diameter of 0.01 mm to 0.08 mm.

5. The Cu-Ag alloy wire according to any one of claims 1 to 3, wherein the Cu-Ag alloy wire is a ribbon wire having an approximately rectangular cross-section, a width of 0.02 mm to 0.32 mm, and a thickness of 0.002 mm to 0.040 mm.

FIG. 1

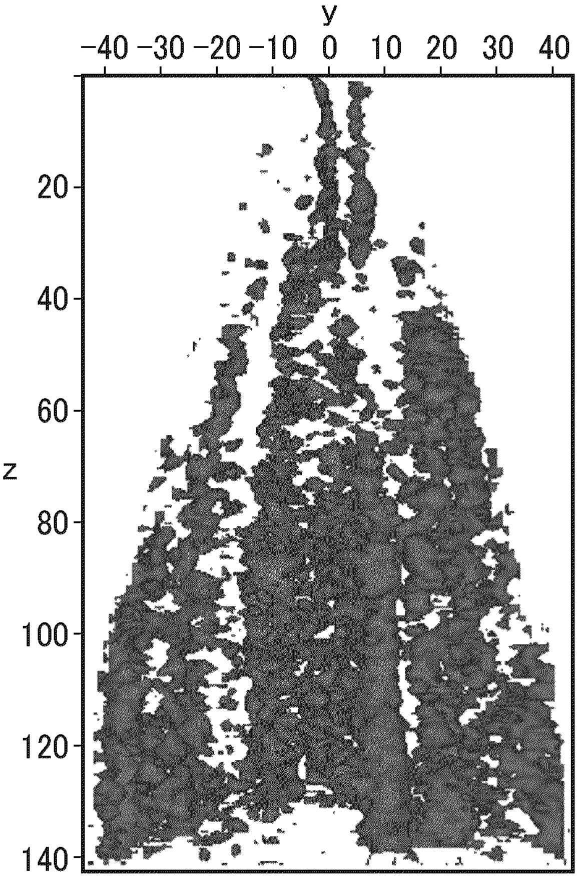
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FIG. 2

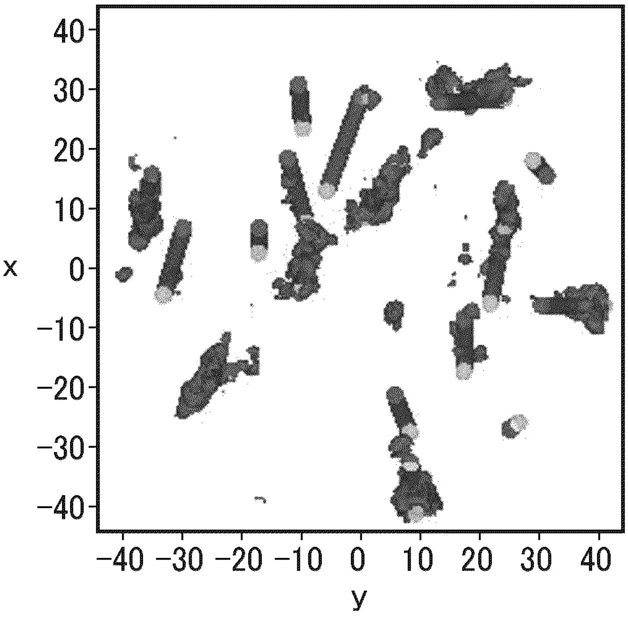
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FIG. 3

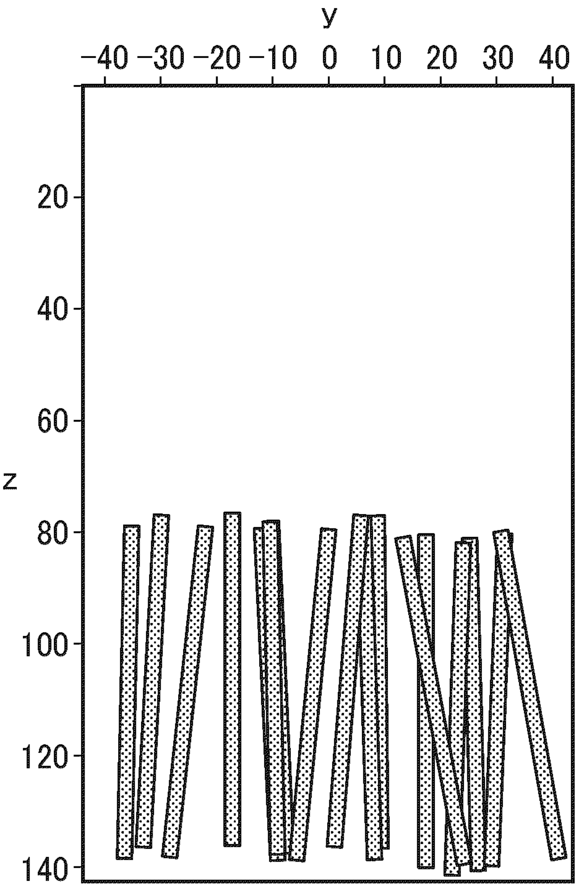
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FIG. 4

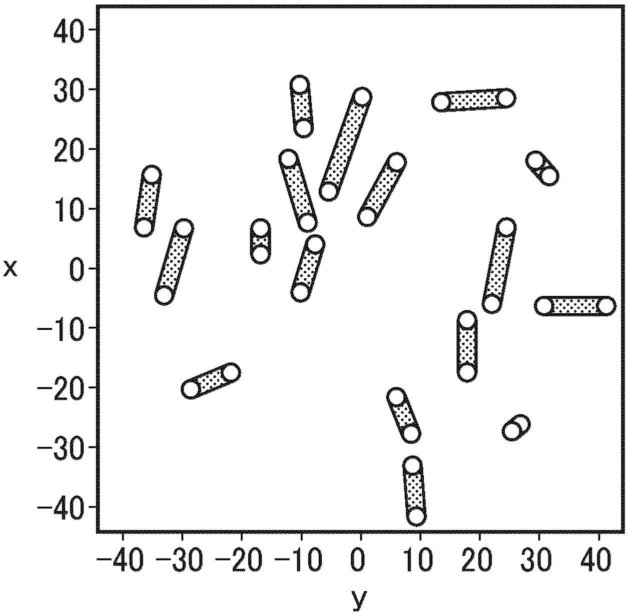
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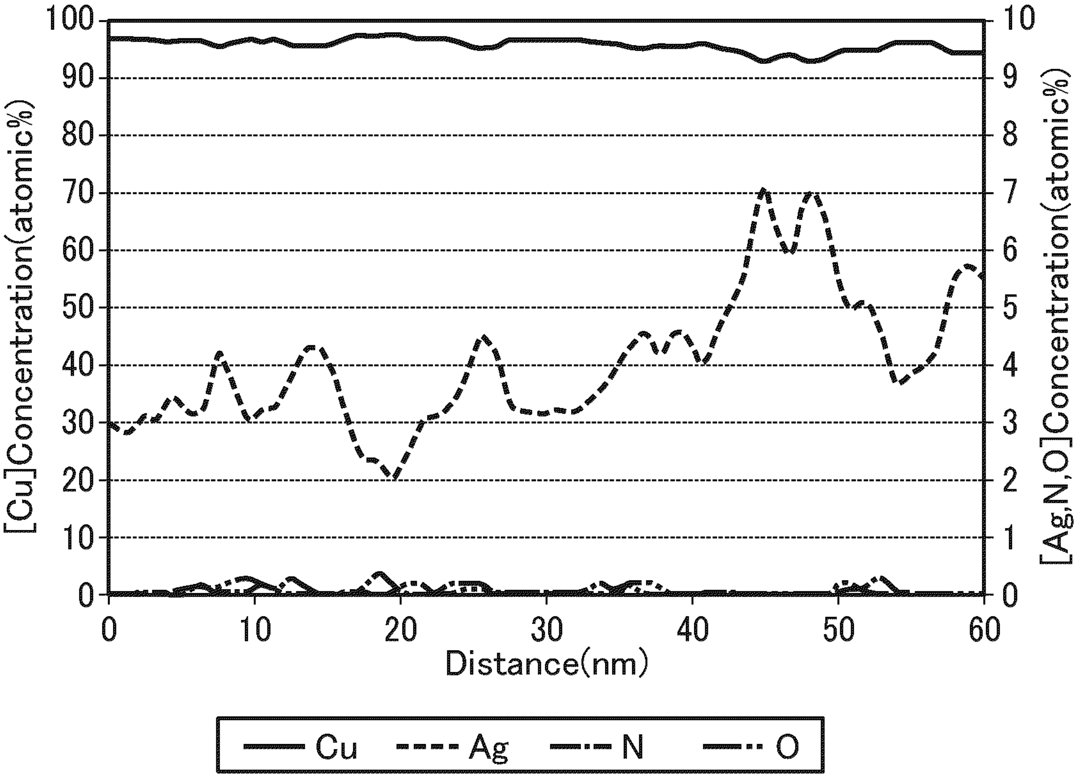
FIG. 5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5
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3
2
1
0
[Ag,N,O]Concentration(atomic%)
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10
20
30
40
50
60
Distance(nm)
Cu
Ag
N
O

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/041681

A. CLASSIFICATION OF SUBJECT MATTER

C22C 9/00(2006.01)i; *C22F 1/00*(2006.01)n; ***C22F 1/08***(2006.01)i; ***H01B 1/02***(2006.01)i
FI: C22C9/00; C22F1/08 C; H01B1/02 A; C22F1/00 602; C22F1/00 622; C22F1/00 625; C22F1/00 630A; C22F1/00 630G; C22F1/00 630K; C22F1/00 661A; C22F1/00 681; C22F1/00 682; C22F1/00 685Z; C22F1/00 686B; C22F1/00 691B; C22F1/00 691C; C22F1/00 692A; C22F1/00 694A

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)

C22C9/00-9/10; C22F1/00; C22F1/08; H01B1/02

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 1971-2022
Registered utility model specifications of Japan 1996-2022
Published registered utility model applications of Japan 1994-2022

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.
A	WO 2011/136284 A1 (SUMITOMO ELECTRIC INDUSTRIES, LTD.) 03 November 2011 (2011-11-03)	1-5
A	JP 2005-336510 A (HITACHI CABLE, LTD.) 08 December 2005 (2005-12-08)	1-5
A	WO 2017/199906 A1 (FURUKAWA ELECTRIC CO., LTD.) 23 November 2017 (2017-11-23)	1-5
A	JP 2017-2337 A (FURUKAWA ELECTRIC CO., LTD.) 05 January 2017 (2017-01-05)	1-5
A	WO 2018/100919 A1 (FURUKAWA ELECTRIC CO., LTD.) 07 June 2018 (2018-06-07)	1-5

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"O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search **15 December 2022**	Date of mailing of the international search report **27 December 2022**
Name and mailing address of the ISA/JP **Japan Patent Office (ISA/JP)** **3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915** **Japan**	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2022/041681

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
WO 2011/136284 A1	03 November 2011	JP 2011-246802 A	
		CN 102869805 A	
		KR 10-2013-0093469 A	
		TW 201142048 A1	
JP 2005-336510 A	08 December 2005	US 2005/0260438 A1	
		CN 1702180 A	
WO 2017/199906 A1	23 November 2017	US 2018/0371580 A1	
		EP 3460080 A1	
		CN 108368565 A	
		KR 10-2018-0102063 A	
JP 2017-2337 A	05 January 2017	(Family: none)	
WO 2018/100919 A1	07 June 2018	US 2018/0322979 A1	
		EP 3550044 A1	
		CN 108463568 A	
		KR 10-2018-0116232 A	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 3325639 B **[0004]**
- JP 5051647 B **[0004]**
- JP 5713230 B **[0004]**