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(54) **CU-AI-MN-BASED ALLOY ROD AND SHEET EXHIBITING STABLE SUPERELASTICITY, METHOD OF PRODUCING THE SAME, VIBRATION DAMPING MATERIAL USING THE SAME, AND VIBRATION DAMPING STRUCTURE CONSTRUCTED BY USING VIBRATION DAMPING MATERIAL**

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(57) **ABSTRACT**

A Cu—Al—Mn-based alloy rod having superelastic characteristics and having a recrystallized microstructure substantially formed of a β single phase, wherein, for a longitudinal direction cross section of the rod, a region, in which a grain size of each of grains is a radius of the rod or more, is 90% or more of the longitudinal direction cross section at any location of the rod, and wherein an average grain size of the grains, in which the grain size is the radius of the rod or more, is 80% or more of a diameter of the rod; a Cu—Al—Mn-based alloy sheet; a production method thereof; a vibration damping material using thereof; a vibration damping structure constructed by using the vibration damping material.

Fig. 1

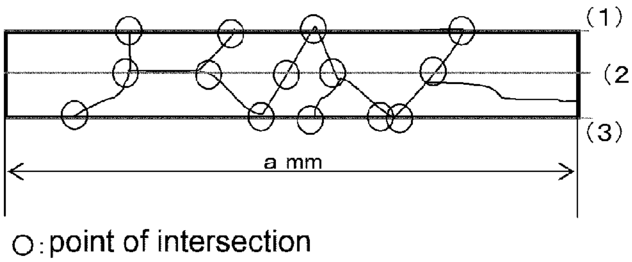

(1)
(2)
(3)
a mm
○: point of intersection

Fig. 2-1

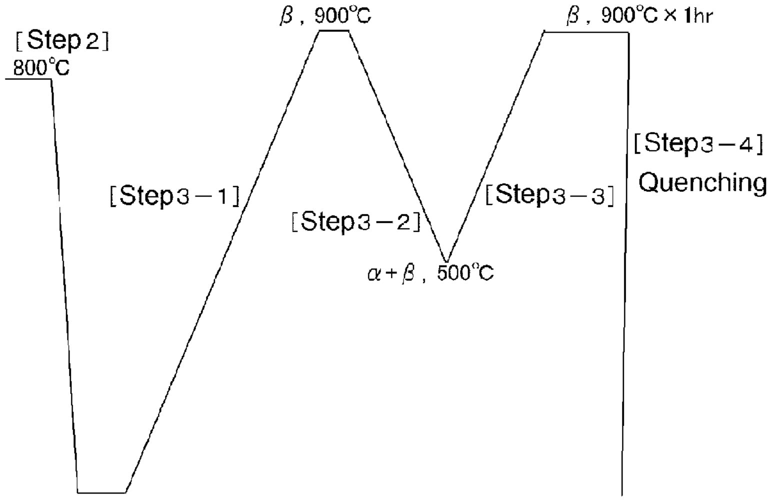

[Step 2]
800°C
β, 900°C
β, 900°C × 1hr
[Step3－1]
[Step3－2]
[Step3－3]
[Step3－4]
Quenching
α+β, 500°C

Fig. 2-2

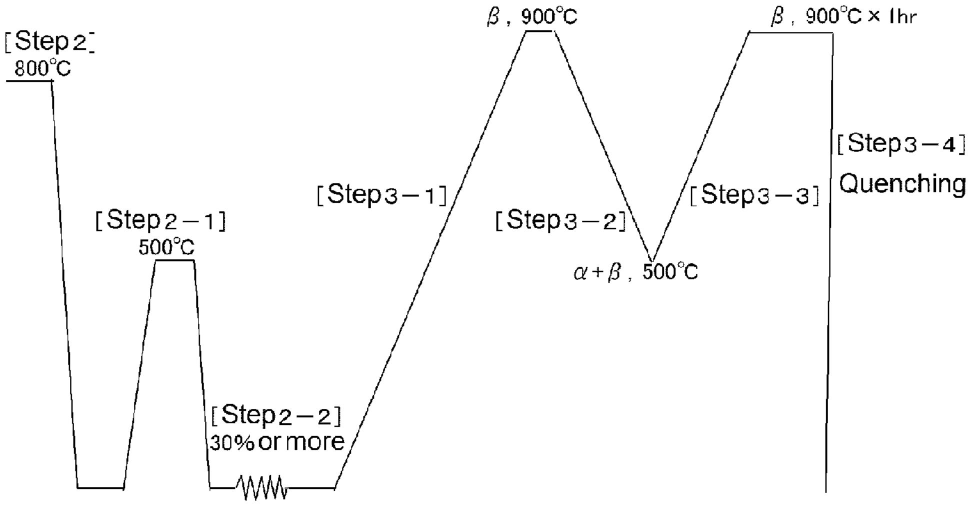

[Step 2]
800°C
[Step 2−1]
500°C
[Step 2−2]
30% or more
[Step 3−1]
β, 900°C
[Step 3−2]
α+β, 500°C
[Step 3−3]
β, 900°C × 1hr
[Step 3−4]
Quenching

Fig. 3a

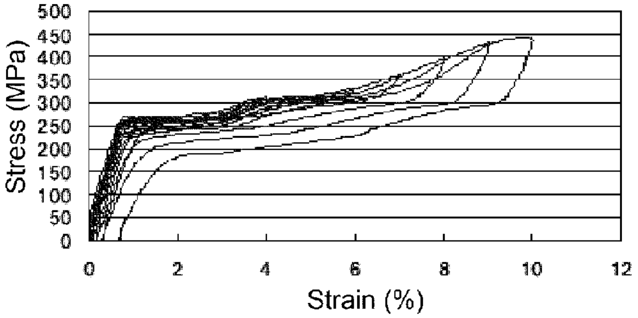

Stress (MPa)
500
450
400
350
300
250
200
150
100
50
0
0
2
4
6
8
10
12
Strain (%)

Fig. 3b

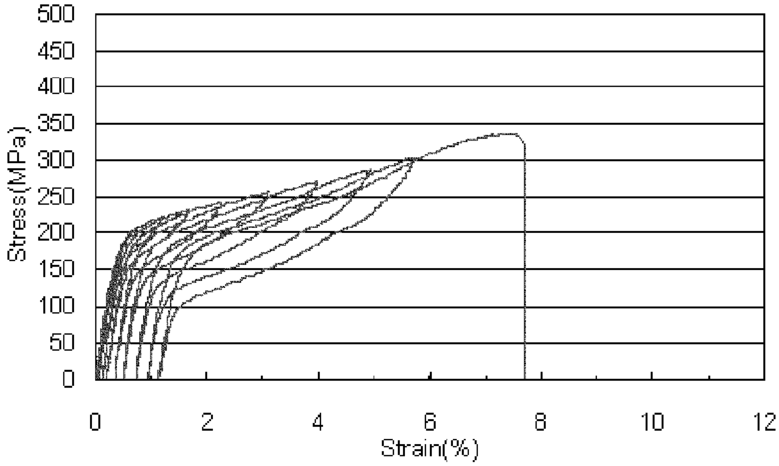
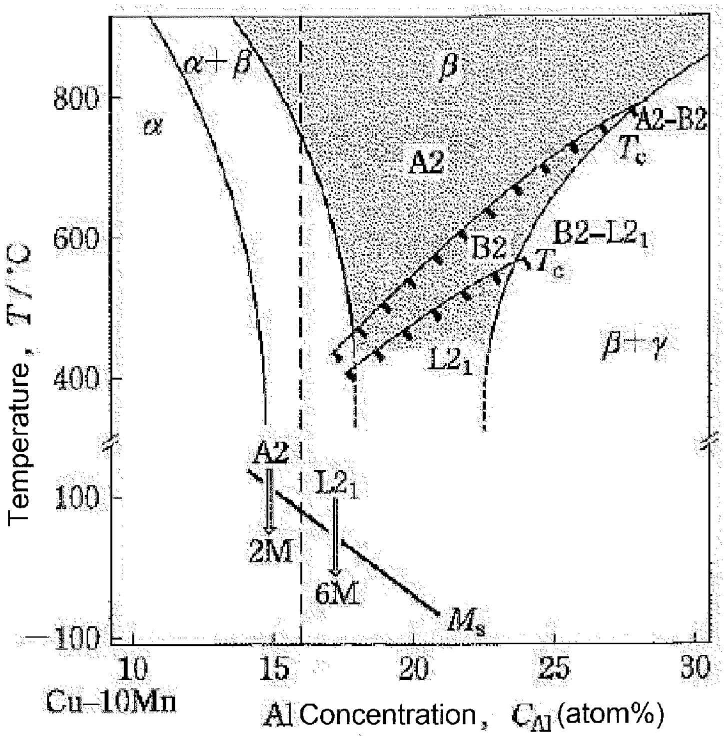

Stress(MPa)
500
450
400
350
300
250
200
150
100
50
0
Strain(%)
0
2
4
6
8
10
12

Fig. 4


Temperature, T/°C
800
600
400
100
−100
10
15
20
25
30
Cu–10Mn
Al Concentration, C_{Al}(atom%)
α
$\alpha+\beta$
β
A2
A2-B2
T_c
B2
B2–$L2_1$
T_c
$L2_1$
$\beta+\gamma$
A2
2M
$L2_1$
6M
M_s

CU-AI-MN-BASED ALLOY ROD AND SHEET EXHIBITING STABLE SUPERELASTICITY, METHOD OF PRODUCING THE SAME, VIBRATION DAMPING MATERIAL USING THE SAME, AND VIBRATION DAMPING STRUCTURE CONSTRUCTED BY USING VIBRATION DAMPING MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Continuation of PCT International Application No. PCT/JP2014/060586 filed on Apr. 14, 2014, which claims priority under 35 U.S.C. §119 (a) to Japanese Patent Application No. 2013-099996 filed in Japan on May 10, 2013. Each of the above applications is hereby expressly incorporated by reference, in its entirety, into the present application.

TECHNICAL FIELD

[0002] The present invention relates to a Cu—Al—Mn-based alloy rod and sheet exhibiting excellent stable superelastic characteristics, a method of producing the same, a vibration damping material, and a vibration damping structure constructed by using the vibration damping material.

BACKGROUND ART

[0003] Shape memory alloys/superelastic alloys exhibit a remarkable shape memory effect and superelastic characteristics concomitantly to reverse transformation of the thermoelastic martensite transformation, and have excellent functions near the living environment temperature. Accordingly, these alloys have been put to practical use in various fields. Representative alloys of the shape memory alloys/superelastic alloys include TiNi alloys and Cu-based alloys. Copper-based shape memory alloys/superelastic alloys (hereinafter, those are simply referred to copper-based alloys) have characteristics inferior to those of TiNi alloys in terms of repetition characteristics, corrosion resistance, and the like. On the other hand, since the cost is inexpensive, there has been a movement to extend the application range of copper-based alloys. However, although the copper-based alloys are advantageous in terms of costs, those alloys are poor in cold workability and low in superelastic characteristics. For those reasons, despite that a variety of studies are being conducted, it is the current situation that practicalization of copper-based alloys has not been necessarily sufficiently progressed.

[0004] Heretofore, various investigations have been conducted on copper-based alloys. For example, Cu—Al—Mn-based shape memory alloys of which a grain size is controlled and which has a β single phase structure with excellent cold workability have been reported in Patent Literatures 1 to 3 described below.

CITATION LIST

Patent Literatures

[0005] Patent Literature 1: JP-A-2005-298952 ("JP-A" means unexamined published Japanese patent application)

Patent Literature 2: JP-A-2001-20026

Patent Literature 3: International Publication WO 2011/152009 A1

SUMMARY OF INVENTION

Technical Problem

[0006] In Patent Literature 1, Cu—Al—Mn—Ni alloys are controlled to be ultrafine crystalline grain microstructure of 10 μm or less. Further, Cu—Al—Mn—Ni alloys described in Patent Literature 1 contain Ni necessarily, and Ni content up to 10 mass % is allowed to be contained. By including Ni, even though crystals are refined, a vibration damping performance is exhibited. Therefore, the crystalline orientation of a β single phase (austenitic single phase) is easily controlled. However, a quenching property is reduced. Herein, the quenching property (or quench-hardening sensitivity) indicates the relationship between the cooling speed in the quenching and the stability of microstructure in the quenching just before the quenching. In detail, when the cooling speed is slow at the time of the quenching, the phenomenon, in which an a phase is precipitated, and thus, superelastic characteristic is poor, is said that the quenching property is sensitive. It is confirmed that since an a phase is started to be precipitated at higher temperature in the Ni-containing copper alloys, a wire diameter becomes thick, and thus, the cooling time period becomes slightly longer, thereby making a quenching property poor, and thereby, satisfactory superelastic characteristic may not be obtained.

[0007] In copper-based alloys described in Patent Literatures 2 and 3, the shape memory characteristics and superelastic characteristics to be manifested by those alloys are less stable, and, from the viewpoint that these characteristics are not stable, the copper-based alloys are at a level having a room for further improvement. In Patent Literature 2, in order to improve the shape memory characteristics and superelastic characteristics of the copper-based alloys, there have been proposed that the crystalline orientations of a β single phase are controlled; in the case of a rod, the average grain size is to be the half of the rod diameter or more or in the case of a sheet, it is to be the sheet thickness or more; and also, the region having the grain diameter is to be 30% or more of the total length of the rod or the total region of the sheet. Further, in Patent Literature 3, in order to improve the shape memory characteristics of the copper-based alloys and also to make the copper-based alloys to have a large cross sectional size that can be applied for a structure, there has been proposed a large crystalline microstructure, in which the maximum grain size is larger than 8 mm. However, with the methods disclosed in Patent Literatures 2 and 3, the grain size distribution of the grains having a predetermined large grain diameter in the Cu—Al—Mn-based alloys is still controlled insufficiently, and shape memory characteristics and superelastic characteristics are still yet insufficiently stable.

[0008] As such, in regard to those shape memory copper-besed alloys that have been hitherto obtained, the investigation on the effect of the control of the grain size distribution of grains having a predetermined large grain size on the superelastic characteristics is insufficient, and thus, the stability and reproducibility of superelastic characteristic are still insufficient.

[0009] The present invention is implemented for providing a Cu—Al—Mn-based alloy rod and sheet which stably exhibits satisfactory superelastic characteristics; for providing a method of producing the same; for providing a vibration damping material using the same; and for providing a vibration damping structure constructed by using the vibration damping material.

Solution to Problem

[0010] The inventors of the present invention conducted a thorough investigation in order to solve the problems of the related art as described above. As a result, the inventors found that, in Cu—Al—Mn-based copper alloys having a coarse crystalline grain microstructure that is close to so-called bamboo microstructure (which is a metal microstructure having a crystalline structure, in which a grain boundary is situated like bamboo joints), with most of the regions thereof being configured by large grains in a predetermined size or more, and the area ratio of the large grains in the predetermined size or more and the average grain size of the large grains in the predetermined size or more being controlled in the proper range, respectively, Cu—Al—Mn-based alloys which stably exhibit satisfactory superelastic characteristics can be obtained. The inventors also found that the controlling of the grain size distribution and average grain size could be obtained by performing the memory heat treatment at the memory heating conditions by a specific slow-lowering speed or raising speed in temperature. The present invention was completed based on these findings.

[0011] That is, the present invention provides the following means:

(1) A Cu—Al—Mn-based alloy rod having superelastic characteristics and having a recrystallized microstructure substantially formed of a β single phase,

[0012] wherein, for a longitudinal direction cross section of the rod, a region, in which a grain size of each of grains is a radius of the rod or more, is 90% or more of the longitudinal direction cross section at any location of the rod, and wherein an average grain size of the grains, in which the grain size is the radius of the rod or more, is 80% or more of a diameter of the rod.

(2) The Cu—Al—Mn-based alloy rod described in the item (1), wherein the average grain size is the diameter of the rod or more.

(3) The Cu—Al—Mn-based alloy rod described in the item (1) or (2), wherein the Cu—Al—Mn-based alloy has a composition containing 3 to 10 mass % of Al; 5 to 20 mass % of Mn; optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities.

(4) A method of producing a Cu—Al—Mn-based alloy rod having a composition containing 3 to 10 mass % of Al, 5 to 20 mass % of Mn, optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities, comprising through [Step **1**] to [Step **3**], in this order:

[0013] melting and casting [Step **1**] an alloy material which gives the composition;

[0014] subjecting to hot working [Step **2**]; and

[0015] performing memory heat treatment [Step **3**],

[0016] wherein, for the memory heat treatment [Step **3**], heating [Step **3-1**] is carried out from a room temperature to a temperature range to be a β phase; heating for maintaining the heating temperature for 1 to 120 minutes; and then, cooling [Step **3-2**] and heating [Step **3-3**] are each repeated once or more; heating is carried out, in which the cooling [Step **3-2**] and the heating [Step **3-3**] are set to a temperature to be an α+β phase at a low temperature and are set to a temperature to be a β phase at a high temperature, and in which a cooling speed and a temperature-raising speed at the time of the cooling [Step **3-2**] and the heating [Step **3-3**] are respectively set to 0.1 to 100° C./minute; and, after final heating, heating for quenching [Step **3-4**] from the temperature to be the β phase is carried out.

(5) The method of producing a Cu—Al—Mn-based alloy rod described in the item (4), wherein, after the hot working [Step **2**], intermediate annealing [Step **2-1**] that is carried out at 400 to 600° C. for 1 to 120 minutes and cold-working [Step **2-2**] at a working ratio of 30% or more are carried out at least one time each in this order, and then, the memory heat treatment [Step **3**] is carried out.

(6) A vibration damping material being composed by using the Cu—Al—Mn-based alloy rod described in any one of the items (1) to (3).

(7) A Cu—Al—Mn-based alloy sheet having superelastic characteristics and having a recrystallized microstructure substantially formed of a β single phase,

[0017] wherein, for a cross section of a sheet thickness direction and a longitudinal direction of the sheet, a region, in which a grain size of each of grains is a half of a sheet thickness or more, is 90% or more of the cross section of the sheet thickness direction and the longitudinal direction at any location of the sheet, and wherein an average grain size of the grains, in which the grain size is the half of the sheet thickness or more, is 80% or more of the sheet thickness.

(8) The Cu—Al—Mn-based alloy sheet described in the item (7), wherein the average grain size is the sheet thickness or more.

(9) The Cu—Al—Mn-based alloy sheet described in the item (7) or (8), wherein the Cu—Al—Mn-based alloy has a composition containing 3 to 10 mass % of Al; 5 to 20 mass % of Mn; optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities.

(10) A method of producing a Cu—Al—Mn-based alloy sheet having a composition containing 3 to 10 mass % of Al, 5 to 20 mass % of Mn, optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities, comprising through [Step **1**] to [Step **3**], in this order:

[0018] melting and casting [Step **1**] an alloy material which gives the composition;

[0019] subjecting to hot working [Step **2**]; and

[0020] performing a memory heat treatment [Step **3**],

[0021] wherein, for the memory heat treatment [Step **3**], heating [Step **3-1**] is carried out from a room temperature to a temperature range to be a β phase; heating for maintaining the heating temperature for 1 to 120 minutes; and then, cooling [Step **3-2**] and heating [Step **3-3**] are each repeated once or more; heating is carried out, in which the cooling [Step **3-2**] and the heating [Step **3-3**] are set to a temperature to be an α+β phase at a low temperature and are set to a temperature to be a β phase at a high temperature, and in which a cooling speed and a temperature-raising speed at the time of the cooling [Step **3-2**] and the heating [Step **3-3**] are respectively set to 0.1 to 100° C./minute; and, after final heating, heating for quenching [Step **3-4**] from the temperature to be the β phase is carried out.

(11) The method of producing a Cu—Al—Mn-based alloy sheet described in the item (10), wherein, after the hot working [Step **2**], intermediate annealing [Step **2-1**] that is carried out at 400 to 600° C. for 1 to 120 minutes and cold-working [Step **2-2**] at a working ratio of 30% or more are carried out at least one time each in this order, and then, the memory heat treatment [Step **3**] is carried out.

(12) A vibration damping material being composed by using the Cu—Al—Mn-based alloy sheet described in any one of the items (7) to (9).

(13) A vibration damping structure constructed by using the vibration damping material described in the items (6) or (12).

[0022] The Cu-Ai-Mn-based alloy rod and sheet of the present invention is preferably such that, as the superelastic characteristics, the residual strain after 6% strain loading is 1.0% or less, and the elongation at breakage is 6% or more.

[0023] Herein, the expression 'having superelastic characteristics' or 'superelastic characteristics are excellent', the strain remaining when a predetermined loading strain or loading stress is applied thereto and then the load is eliminated, is referred to as residual strain, and it is meant that this residual strain is small. It is more desirable as this residual strain is smaller. In the present invention, it is meant that the residual strain after 6% deformation is generally 1.0% or less, preferably 0.5% or less, and more preferably 0.2% or less.

[0024] Also, the expression 'having a recrystallized microstructure substantially formed from a β single phase' means that the proportion occupied by the β phase in the recrystallization structure is generally 90% or more, and preferably 95% or more.

Advantageous Effects of Invention

[0025] The Cu—Al—Mn-based superelastic alloy rod and sheet of the present invention can be used in various applications where superelastic characteristic are required, and applications are expected, for example, in antennas of mobile phones, spectacle frames, as well as orthodontic wires, guide wires, stents, correcting tools for ingrown nails, and orthoses for hallux valgus, as medical products. Further, the Cu—Al—Mn-based superelastic alloy rod and sheet of the present invention is suitable as a vibration damping material, such as a bus bar, due to its excellent superelastic characteristics. Further, a vibration damping structure may be constructed by using such a vibration damping material.

[0026] Other and further features and advantages of the invention will appear more fully from the following description, appropriately referring to the accompanying drawings.

BRIEF DESCRIPTION OF DRAWINGS

[0027] FIG. **1** is a schematic diagram illustrating a method for evaluating a grain size.

[0028] FIG. **2-1** illustrates an example of the process chart of a working and heat treatment. In this example, no intermediate annealing [Step **2-1**] or cold-working [Step **2-2**] are conducted.

[0029] FIG. **2-2** illustrates another example of the process chart of the working and heat treatment. In this example, the intermediate annealing [Step **2-1**] and cold-working [Step **2-2**] after a hot working [Step **2**] are repeatedly carried out at least one time in this order, and then, a memory heat treatment [Step **3**] is carried out.

[0030] FIG. **3***a* is a stress-strain curve (S-S curve) illustrating residual strain as superelastic characteristics in the rod (Example 1) of Examples according to this invention, obtained by the following Examples.

[0031] FIG. **3***b* is a stress-strain curve (S-S curve) illustrating residual strain as superelastic characteristics in the rod (Comparative Example 2) of Comparative Examples, obtained by the following Examples.

[0032] FIG. **4** is a phase diagram illustrating Cu—Al-10 atom % Mn alloys.

MODE FOR CARRYING OUT THE INVENTION

[0033] For the Cu—Al—Mn-based alloy rod and sheet of the present invention, the cooling and heating in the memory heat treatment (also called a shape memory heat treatment) before the quenching are carried out at the predetermined slow temperature lowering and slow temperature raising, respectively, and thus, the grains thereof are sufficiently grown to the predetermined large size, and also, the grain size distribution thereof can be properly controlled. As a result, satisfactory superelastic characteristic can be stably exhibited.

<Definitions of Grain Size and Grain Size Distribution and Controls Thereof>

[0034] In the Cu—Al—Mn-based copper alloys constituting the rod and sheet of the present invention, a small amount of the grains having a small grain size may be present, but the most grains have a large grain size.

[0035] In other words, in the case of a rod, in the longitudinal direction cross section of the rod, the region, in which the grain size of the respective grains is the radius of the rod or more, is 90% or more of the longitudinal direction cross section at any locations of the rod, and the average grain size of the grains, in which the grain size is the radius of the rod or more, is 80% or more of the diameter of the rod. It is preferable that the average grain size is the diameter of the rod or more.

[0036] On the other hand, in the case of a sheet, in the cross section of the longitudinal direction and the sheet thickness direction of the sheet, the region, in which the grain size of the respective grains is the half of the sheet thickness or more, is 90% or more of the cross section of the sheet thickness direction and the longitudinal direction at any locations of the sheet, and the average grain size of the grains, in which the grain size is the half of the sheet thickness or more, is 80% or more of the sheet thickness. It is preferable that the average grain size is the sheet thickness or more.

[0037] Herein, when the present ratio of the large grains in the predetermined range is expressed, it is defined as the area ratio, in which the grains in the predetermined size or more occupy the rod or sheet. Further, by defining the average grain size of the grains in the predetermined size or more, the structural characteristics are defined.

[0038] Unlike the rod, the shape of the sheet is not a round-shaped cross section, and thus, has a low symmetric property. Thus, the standard of the grain size is a sheet thickness, not a sheet width. The reason is based on the fact that, after the grains penetrate through the sheet thickness or sheet width, the driving force of the growth of the grain boundary interface by the grains is lowered, and thus, the grains are increased in their sizes, but it is difficult to penetrate through the sheet width as well as the sheet thickness.

[0039] In the Cu—Al—Mn-based alloy rod and sheet of the present invention, the average grain size of the matrix (the base material) is to be the proper size. This is because in the Cu—Al—Mn-based alloys, when the average grain size is too small, the restriction between the grains is generated from the surrounding grains at the time of being deformed, and thus, the resistance to the deformation becomes larger, thereby deteriorating the superelastic characteristics. In the present invention, the upper limit of the average grain size is not particularly limited, and for example, there are particularly no problems as long as the upper limit is practically obtained (for example, about 150 mm). Further, even when the grains having a large grain size are unevenly distributed, and thus, the non-uniform distribution is generated, the deformation of the copper alloy rod and sheet of the present invention becomes unevenness, which is undesirable. Therefore, in the present invention, as described above, “the region, in which the grain size of the respective grains is the radius of the rod or more, is 90% or more of the longitudinal direction cross section at any locations of the rod” or “the region, in which the grain size of the respective grains is the half of the sheet thickness or more, is 90% or more of the cross section of the sheet thickness direction and the longitudinal direction at any locations of the sheet,” and the grain size distribution is defined by the respective area ratio.

[0040] In the present invention, for the wire (rod) and sheet, by controlling the grain size distribution and average grain size as described above, it is possible to stabilize the superelastic characteristics. In the present invention, because of the difference of the shapes of the rod or sheet products, the rod and sheet are defined as different product inventions. However, in terms of the wrought alloy of Cu—Al—Mn-based superelastic alloys, the rod and sheet are different each other in that the grain size is defined to the diameter of the rod or the grain size is defined to the sheet thickness, but the special technical features of both inventions are common, and thus, both the inventions have the common technical significance (features). Further, in the inventions of the method of producing a rod and the method of producing a sheet, the same can be said to the product inventions. Therefore, it can be interpreted that both the inventions have the common technical significance.

[0041] For the Cu—Al—Mn-based alloy rod and sheet of the present invention, the grains in the predetermined grain size distribution and the predetermined size or more have the average grain size in the predetermined size or more. This is because the effect of the grains each having the size that is considered less than the predetermined size may be ignored, since the grain size of the grains each having the size that is the predetermined size or more is defined, the amount of the grains each having the size that is less than the predetermined size is conspicuously low as compared to the grains each having the size that is the predetermined size or more, and the effect to the superelastic characteristics is small.

[0042] Further, the Cu—Al—Mn-based alloy rod and sheet of the present invention is substantially composed of a β single phase. Herein, the expression ‘being substantially composed of a β single phase’ means that the existence ratio of a phase other than the β phase, for example, an a phase, is generally 10% or less, and preferably 5% or less.

[0043] For example, a Cu-8.1 mass % Al-11.1 mass % Mn alloy is a β (BCC) single phase at 900° C., but is the two phases of an a (FCC) phase+the β phase at 700° C. or less.

<Method of Producing Cu—Al—Mn-Based Superelastic Alloy Rod and Sheet>

[0044] In regard to the Cu—Al—Mn-based superelastic copper-based alloy rod and sheet of the present invention, a production process such as described below may be mentioned, in connection with the production conditions for obtaining the superelastic alloy rod and sheet which stably exhibit satisfactory superelastic characteristics such as described above. Further, a preferred example of the production process is illustrated in FIGS. **2-1** and **2-2**. The treatment temperatures and treatment times (maintaining time periods) in the heat treatments illustrated in the figures, and the working ratio in the cold-working are representatively represented as the values utilized in the Examples, but the present invention is not limited thereto.

[0045] In the entire production process, particularly by controlling both the temperature lowering speed in the memory heat treatment and the temperature raising speed after the cooling each in the predetermined slow ranges, the grains can be sufficiently grown to the predetermined large sizes, and also, by controlling properly the grain size distribution thereof, a Cu—Al—Mn-based alloy is obtained, which stably exhibits satisfactory superelastic characteristics.

[0046] Furthermore, the intermediate annealing at 400 to 600° C. for 1 to 120 minutes and the cold-working, in which the working ratio of the cold-rolling or cold-drawing is in the range of 30% or more, may be repeatedly performed at least each one time after the hot working and before the memory heat treatment. Alternatively, after the hot working, the intermediate annealing is only performed at 400 to 600° C. for 1 to 120 minutes, and after the intermediate annealing, the memory heat treatment may be performed without performing the cold working.

[0047] Herein, for the memory heat treatment, the heating may be performed to raise the temperature to the temperature range of the transformation temperature or more in the β phase, in which the α+β phase is first changed to the β phase, and such a heating temperature is maintained for 1 to 120 minutes. At that time, the heating to the temperature range of the transformation temperature or more, in which the initial α+β phase is changed into the β phase at the time of memory heat treatment, is performed from a room temperature after cooling the temperature to a room temperature in general. However, alternatively, the heating may be performed, just after the hot working without cooling the temperate to the room temperate after the hot working, or the heating may be performed, in the cooling process after the hot working. Herein, the transformation temperature from the α+β phase to the β phase is the boundary temperature between the α+β phase and the β phase in the phase diagram as illustrated in FIG. **4**. Such a temperature is determined, for example, by measuring the caloric change at the time of heating the materials from a low temperature to a high temperature by a differential scanning calorimetry (DSC) measuring device, and the like. Then, the heat treatment cycle, in which the temperature is lowered by the cooling to be the temperature range that is less than the transformation temperature, and then, immediately, the temperature is raised by the heating to be the temperature range that is to be the β phase, is repeated at least one time, such that the β phase becomes the α+β phase. Further, in order to make the microstructure to be a β single phase and make the grains grow to satisfy the definition of the present invention, the heating temperature is preferably higher than the transformation temperature by 50° C. or more. Further, in the case where the temperature is lowered by the cooling to be the temperature range that is less than the transformation temperature for the α+β phase, the temperature is preferably lower than the transformation temperature by 50° C. or less. Herein, the temperature lowering speed at the time of cooling to less than the transformation temperature (the cooling of [Step **3-2**]), and the temperature raising speed at the time of heating to the transformation temperature or more (the heating of [Step **3-3**]) are preferably slow as described below. Then, finally, the solid-solution treatment including the quenching (the quenching of [Step **3-4**]) is performed.

[0048] Herein, for the memory heat treatment, the temperature lowering speed (the temperature lowering speed at the cooling of [Step **3-2**]) and the temperature raising speed (the temperature raising speed at the heating of [Step **3-3**]) are both set to be slow (in this specification, called a temperature slow-lowering speed and a temperature slow-raising speed). The temperature lowering speed at the time of the temperature slow-lowering and the temperature raising speed at the time of the temperature slow-raising each are generally 0.1 to 100° C./minutes, preferably 0.1 to 10° C./minutes, more preferably 0.1 to 3° C./minutes, and particularly preferably 0.2 to 1° C./minutes. Further, in the memory heat treatment, in order for the solid-solution treatment after the heat treatment (the temperature raising to the β single phase (in the figures, abbreviated as “6”, and the same is applied to as above)→the temperature lowering to the α+β phase (α+β)→the temperature raising to the β single phase (β)→), the quenching is performed. For example, such a quenching may be performed by the water-cooling, in which the Cu—Al—Mn-based alloys subjected to the heat treatment are put into the cooling water.

[0049] Preferably, the production process such as follows may be mentioned.

[0050] As an example, after melting and casting [Step **1**] of an alloy raw material to give the following predetermined composition and hot working [Step **2**] of hot rolling or hot forging, the memory heat treatment [Step **3**] is carried out in this order. Then, after the memory heat treatment [Step **3**], aging-heating [Step **4**] may be carried out.

[0051] As another example, the melting and casting [Step **1**] and the hot working [Step **2**] are carried out; then, the intermediate annealing [Step **2-1**] and cold-working [Step **2-2**] are carried out each at least one time; and then, the memory heat treatment [Step **3**] is carried out, in this order. After the memory heat treatment [Step **3**], the aging-heating [4] may be carried out.

[0052] Further, as still another example, the melting and casting [Step **1**] and the hot working [Step **2**] are carried out; then, the intermediate annealing [Step **2-1**] is carried out; and then, the memory heat treatment [Step **3**] is carried out, in this order. After the memory heat treatment [Step **3**], the aging-heating [4] may be carried out.

[0053] The memory heat treatment [Step **3**] contains the steps of: heating by the temperature range to be the β phase; maintaining such a heating temperature for 1 to 120 minutes; temperature-raising treatment [Step **3-1**] for making such a heating temperature to be the β single phase temperature range, for example, 700 to 950° C. (preferably, 800 to 920° C.); temperature-lowering treatment [Step **3-2**] for cooling the temperature from such a heating temperature to the temperature range to be the α+β phase at the temperature-lowering speed, for example, 300 to 700° C. (preferably, 400 to 550° C.); temperature-raising treatment [Step **3-3**] for heating the temperature from such a temperature-lowering temperature to the temperature range to be the β phase at the temperature-raising speed, and maintaining such a heating temperature for certain time periods (preferably, 1 to 120 minutes); and then quenching [Step **3-4**], for example, by cold water. For the temperature-raising treatment [Step **3-1**], the temperature-raising speed is not particularly limited, but the temperature-raising speed in the temperature-raising treatment [Step **3-3**] may be used or a faster speed than the above speed may be used. When the heating maintaining time at the β phase in the temperature-raising treatment [Step **3-1**] is less than 1 minute, the heating is insufficient, and when it exceeds 120 minutes, the heating is already sufficient, and even if maintaining over the time, there are no newly improvement and also a waste of thermal energy. Therefore, the heating maintaining time at the β phase in the temperature-raising treatment [Step **3-1**] is set to be 1 to 120 minutes. Herein, the heat treatment cycle including the temperature-lowering treatment [Step **3-2**] and the temperature-raising treatment [Step **3-3**] may be repeatedly carried out each at least one time as described above. The cooling speed at the time of quenching [Step **3-4**] is generally 30° C./second or more, preferably 100° C./second or more, and more preferably, 1,000° C./second or more.

[0054] In the present invention, the intermediate annealing [Step **2-1**] and the cold-working [Step **2-2**] may be carried out or may not be carried out. Even if any intermediate annealing [Step **2-1**] and cold-working [Step **2-2**] are to be carried out, they may be carried out each once in this order or may be repeatedly carried out once two times in this order.

[0055] Alternatively, the cold-working [Step **2-2**] may not be carried out, but the intermediate annealing [Step **2-1**] may be only carried out.

[0056] After the memory heat treatment [Step **3**], the aging-heating [Step **4**] at 80 to 250° C. for 5 to 60 minutes may be carried out. Any aging-heating [Step **4**] may be preferably carried out. When the aging temperature is too low, the 6 phase is unstable, and when putting at a room temperature, the martensite transformation temperature may be changed. On the other hand, when the aging temperature is too high, the precipitation of a phase may be carried out, and thus, there may be a trend that the shape memory characteristic and superelastic characteristics are conspicuously lowered.

[0057] The intermediate annealing [Step **2-1**] and cold-rolling or cold-wire-drawing [Step **2-2**] may be repeatedly carried out at a plurality of times, and thereby, grain growth may be more stable. The repetition number of intermediate annealings [Step **2-1**] and cold-rollings or cold-wire-drawings [Step **2-2**] is preferably 2 times or more, and more preferably 3 times or more. This repetition number is not particularly limited in terms of the upper limit, but generally 10 times or less, and preferably 7 times or less. As the repetition number of intermediate annealings [Step **2-1**] and cold-rollings or cold-wire-drawings [Step **2-2**] is high, the driving force of the grain growth becomes high, and thus, it is easy to uniformly make the size of the grain coarse.

[0058] Preferred conditions for the steps are as follows.

[0059] The intermediate annealing [Step **2-1**] is preferably carried out at 400 to 600° C. for 1 minute to 120 minutes. It is preferable that this intermediate annealing temperature be set to a lower temperature within this range; and the intermediate annealing temperature is more preferably set to 400 to 550° C., further preferably 400 to 500° C., and particularly preferably 400° C. to 450° C. The annealing time is more preferably 30 minute to 120 minutes, and even if the influence of the sample size is considered, an annealing time of 60 minutes is sufficient for a round rod with diameter ϕ20 mm.

[0060] For the cold-rolling or cold-wire-drawing [Step **2-2**], it is preferable to carry out the step at a working ratio of 30% or higher, more preferably 40% or higher, further preferably from 45 to 75%, and particularly preferably from 45 to 60%. Herein, the working ratio is a value defined by formula:

$$\text{Working ratio}(\%)=\{(A_1-A_2)/A_1\}\times 100$$

wherein A_1 represents the cross-sectional area (mm^2) obtained before cold-rolling or cold-wire-drawing; and A_2 represents the cross-sectional area (mm^2) obtained after cold-rolling or cold-wire-drawing.

<Composition of Cu—Al—Mn-Based Superelastic Alloy Rod and Sheet>

[0061] The Cu—Al—Mn-based alloy rod and sheet of the present invention is formed of a copper alloy which has the β single phase at a high temperature, and a two-phase microstructure of β+α at a low temperature, and is formed of a copper-based alloy containing at least Al and Mn. The Cu—Al—Mn-based alloy that forms the rod and sheet of the present invention has a composition containing 3 to 10 mass % of Al and 5 to 20 mass % of Mn, with the balance being Cu and unavoidable impurities. If the content of elemental Al is too small, the β single phase cannot be formed, and if the content is too large, the resultant alloy becomes very brittle. The content of elemental Al may vary depending onto the content of elemental Mn, but a preferred content of elemental Al is 6 to 10 mass %. When the alloy contains elemental Mn, the range of existence of the β phase extends to a lower Al-content side, and cold workability is markedly enhanced, for thereby making the form-working readily. If the amount of addition of elemental Mn is too small, satisfactory workability is not obtained, and the region of the β single phase cannot be formed. Also, if the amount of addition of elemental Mn is too large, sufficient shape recovery characteristics are not obtained. A preferred content of Mn is 8 to 12 mass %. The Cu—Al—Mn alloy having the above-described composition has high hot workability and cold workability, and enables to obtain a working ratio of 20 to 90% or higher in cold working. Thus, the alloy can be readily worked by forming into sheets and wires (rods), as well as fine wires, foils, pipes and the like that have been conventionally difficult to produce.

[0062] In addition to the essential alloying elements described above, the Cu—Al—Mn-based alloy that forms the rod and sheet of the present invention can further contain, as an optionally adding alloying element(s), at least one selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag. These elements enhance the physical strength of the resultant Cu—Al—Mn-based alloy, while maintaining cold workability. The content in total of these elements is preferably 0.001 to 10 mass %, and particularly preferably 0.001 to 5 mass %. If the content of these elements is too large, the martensite transformation temperature is lowered, and the β single phase microstructure becomes unstable. Regarding these optionally adding alloying elements, use can be made of the aforementioned elements that are generally used by being contained into copper-base alloys, for example, for the purpose of strengthening of copper alloys.

[0063] Co, Fe and Sn are elements that are effective for strengthening of the matrix microstructure. Co makes the grains coarse by forming CoAl; however, Co in an excess amount causes lowering of toughness of the alloy. A preferred content of Co is 0.001 to 2 mass %. A preferred content of Fe is 0.001 to 3 mass %. A preferred content of Sn is 0.001 to 1 mass %.

[0064] Ti is bonded to N and O, which are inhibitory elements, and forms oxynitride. A preferred content of Ti is 0.001 to 2 mass %.

[0065] V, Nb, Mo and Zr have an effect of enhancing hardness, and enhance abrasion resistance. Further, since these elements are hardly solid-solubilized into the matrix, the elements precipitate as the β phase (bcc crystals), for thereby enhancing the physical strength. Preferred contents of V, Nb, Mo and Zr are respectively 0.001 to 1 mass %.

[0066] Cr is an element effective for retaining abrasion resistance and corrosion resistance. A preferred content of Cr is 0.001 to 2 mass %.

[0067] Si has an effect of enhancing corrosion resistance. A preferred content of Si is 0.001 to 2 mass %.

[0068] W is hardly solid-solubilized into the matrix, and thus has an effect of precipitation strengthening. A preferred content of W is 0.001 to 1 mass %.

[0069] Mg eliminates N and O, which are inhibitory elements, fixes S that is an inhibitory element as sulfide, and has an effect of enhancing hot workability or toughness. Addition of a large amount of Mg brings about grain boundary segregation, and causes embrittlement. A preferred content of Mg is 0.001 to 0.5 mass %.

[0070] P acts as a de-oxidation agent, and has an effect of enhancing toughness. A preferred content of P is 0.01 to 0.5 mass %.

[0071] Be, Sb, Cd, and As have an effect of strengthening the matrix microstructure. Preferred contents of Be, Sb, Cd and As are respectively 0.001 to 1 mass %.

[0072] Zn has an effect of raising the shape memory treatment temperature. A preferred content of Zn is 0.001 to 5 mass %.

[0073] Ag has an effect of enhancing cold workability. A preferred content of Ag is 0.001 to 2 mass %.

[0074] The superelastic Cu—Al—Mn-based alloy that forms the rod and sheet of the present invention preferably has a Ni content of 1 mass % or less, and more preferably 0.15 mass % or less, and it is particularly preferable that the alloy does not contain Ni. It is because if the alloy contains Ni in a large amount, but the quench-hardening property previously explained is deteriorated.

<Physical Properties>

[0075] The superelastic Cu—Al—Mn-based alloy rod and sheet of the present invention has the following physical properties.

[0076] Regarding the superelastic characteristics, the residual strain after 6% deformation is generally 1.0% or less, preferably 0.5% or less, and more preferably 0.2% or less.

[0077] The elongation (elongation at breakage) is generally 6% or more, preferably 8% or more, and more preferably 10% or more.

[0078] Further, the residual strain as the superelastic characteristics and the elongation have no unevenness in the performance, even if specimens are cut out from at any sites from a same alloy and analyzed. Herein, the expression 'having unevenness' means that, in regard to the residual strain and elongation, for example, when three specimens are cut out from a same alloy and analyzed, one or more specimens have a residual strain value of more than 1.0%, or have an elongation value of less than 6%.

<Size of Rod and Sheet>

[0079] There are also no particular limitations on the sizes of the Cu—Al—Mn-based alloy rod and sheet of the present invention, and, for example, in the case of the rod, the diameter thereof is generally 8 mm or more, and for example, 8 mm to 50 mm may also be employed. The diameter of the rod may be the size of 8 mm to 16 mm depending on the use thereof. Further, the sheet may have the thickness of generally 1 mm or more, and for example, 1 mm to 15 mm.

[0080] Further, the rod of the present invention may have the shape of a tube having a tube wall and a hollow shape.

<Vibration Damping Material>

[0081] The vibration damping material of the present invention is constituted of the rod or sheet. Examples of the vibration damping material are not particularly limited, but for example, may include brace, fastener, anchor bolt, and the like.

<Vibration Damping Structure>

[0082] The vibration damping structure of the present invention is constructed of the vibration damping material. Examples of the vibration damping structure are not particularly limited, but any kinds of the structures may be used as long as the structures are constructed of using the above-described brace, fastener, anchor bolt, and the like.

EXAMPLES

[0083] The present invention will be described in more detail based on examples given below, but the invention is not meant to be limited by these.

Example 1

[0084] Samples (specimen) of rods (wires) were produced under the following conditions.

[0085] As the copper alloys that give the compositions as indicated in Table 1-1 and Table 1-2, pure copper, pure Mn, pure Al, and materials of other optionally adding alloying elements were subjected respectively to melting in a high-frequency induction furnace. The copper alloys thus melted were cooled, to obtain ingots with diameter of 80 mm×length of 300 mm. The ingots thus obtained were subjected to hot forging at 800° C., to obtain round rods with diameter 20 mm.

[0086] The round rods were again subjected to (1) hot forging or (2) cold-wire-drawing, if necessary, to obtain the rods having the diameters as indicated in Table 2-1 and Table 2-2 with the conditions as follows.

[0087] That is, according to the respective working and heat treatment process as illustrated in FIG. **2-1** or FIG. **2-2**, the working and heat treatment were carried out at the conditions listed in Table 2-1 and Table 2-2. In detail, after the hot working [Step **1**], the intermediate annealing [Step **2-1**] and the cold-wire-drawing [Step **2-2**] were not carried out, and the memory heat treatment [Step **3**] was carried out (Examples 1 to 23, Example 28, respective Comparative Examples) (Process of FIG. **2-1**), or after the hot working [Step **1**], the intermediate annealing [Step **2-1**] at 500° C. for 1 hour and then the cold-wire-drawing [Step **2-2**] were carried out once each or were repeatedly carried out at a plurality of times (Examples 24 to 27) (Process of FIG. **2-2**). For all the cases subjected to any kinds of those processes, then, the rods in Examples and Comparative Examples, which have the diameters listed in Table 2-1 and Table 2-2, were prepared by: temperature-raising at the temperature-raising speed of 30° C./minutes to be 900° C. (the temperature to the β single phase); maintaining this temperature for 5 minutes; temperature-lowering at the temperature-lowering speed listed in Table 2-1 and Table 2-2 to be 500° C. (the temperature to the α+β phase); immediately, temperature-raising at the temperature-raising speed listed in Table 2-1 and Table 2-2 to be 900° C. (the temperature to the β single phase); maintaining this temperature for 1 hour; and finally, quenching from 900° C. by cold water cooling.

[0088] FIG. **2-1** and FIG. **2-2** are charts illustrating the examples of respective process, and the working ratio of cold-working and the numbers of repetition cycles of the cold-workings and intermediate annealings were changed to be as listed in Table 2-1 and Table 2-2, to carry out the respective process. In Table 2-1 and Table 2-2, the working ratios in the respective cold workings (the working ratio by cold-wire-drawing in Examples) indicates one time working ratio→second time working ratio→third time working ratio→ . . . working ratios, in order, from the left side to the right side in the column of "cold-working ratio (%)". Further, the numbers of repetition cycles of the intermediate annealings and cold-workings indicate "the numbers of cycles of cold-workings". In other words, before the respective cold-wire-drawings [Step **2-2**], the intermediate annealing [Step **2-1**] at 500° C. for 1 hour was carried out, and then, the respective cold-wire-drawings [Step **2-2**] in the numbers of cycles (the numbers of cycles in Tables) of cold-working ratios and cold-workings listed in Table 2-1 and Table 2-2 were carried out. Further, in FIG. **2-1** and FIG. **2-2**, the aging-heating [Step **4**] was omitted, but was carried out as the following conditions to all Test Examples.

[0089] As described above, there were Test Examples without carrying out neither of intermediate annealing [Step **2-1**] nor cold-working [Step **2-2**], and also, there were Test examples that the second or third intermediate annealings and cold-workings were carried out or were not carried out.

[0090] Hereinafter, representative working process examples will be described along with the rod diameters and working ratios.

Rod Working Process Example 1

[0091] Round rod with diameter ϕ20 mm×length L 500 mm (hot forged up)

[0092] Round rod with diameter ϕ15 mm×length L 890 mm (hot forged up) (working ratio of 43%)

[0093] Round rod with diameter ϕ12 mm×length L 1,390 mm (cold-wire-drawn up) (working ratio of 36%)

[0094] Round rod with diameter ϕ10 mm×length L 2,000 mm (cold-wire-drawn up) (working ratio of 36%→31→%)

[0095] Round rod with diameter ϕ8 mm×length L 3,120 mm (cold-wire-drawn up) (working ratio of 36%→31%→36%)

Rod Working Process Example 2

[0096] Round rod with diameter ϕ20 mm×length L 500 mm (hot forged up)

[0097] Round rod with diameter ϕ17 mm×length L 690 mm (hot forged up) (working ratio of 28%)

[0098] Round rod with diameter ϕ12 mm×length L 1,380 mm (cold-wire-drawn up) (working ratio of 50%)

Rod Working Process Example 3

[0099] Round rod with diameter ϕ20 mm×length L 500 mm (hot forged up)

[0100] Round rod with diameter ϕ18.7 mm×length L 570 mm (hot forged up) (working ratio of 13%)

[0101] Round rod with diameter ϕ15 mm×length L 885 mm (cold-wire-drawn up) (working ratio of 36%)

[0102] Round rod with diameter ϕ12 mm×length L 1,380 mm (cold-wire-drawn up) (working ratio of 36%→36%)

[0103] Rod specimens thus obtained, which were subjected through the working and heat treatment processes, and to final quenching (rapid cooling) by water cooling, thereby for obtaining samples of the β (BCC) single phase.

[0104] The respective sample was, then, subjected to age-heating at 200° C. for 15 minutes.

[0105] Among Comparative Examples, the rods of Comparative Examples 3 to 8 were obtained in the same manner as in Examples 1 to 23, except for Comparative Examples 4 and 5, in which the productions were stopped due to the forging cracks occurred in the mid way of productions. On the other hand, the rods of Comparative Examples 1 and 2 were obtained in the same manner as in Examples 1 to 23, except that, in the memory heat treatment of Examples 1 to 23, the temperature-lowering step [Step **3-2**] (β→α+β) was carried out at the temperature-lowering speed of 150° C./minute of the rapid temperature-lowering (Comparative Example 2) or the temperature-raising step [Step **3-3**] (α+β→β) was carried out at the temperature-raising speed of 150° C./minute of the rapid temperature-raising (Comparative Example 1).

[0106] Among those, Comparative Examples 1 and 2 are Test Examples simulating JP-A-2001-20026 (Patent Literature 2) and WO 2011/152009 A1 (Patent Literature 3), respectively. In JP-A-2001-20026 (Patent Literature 2) and WO 2011/152009 A1 (Patent Literature 3), any kinds of reviews are not carried out on the temperature-lowering speed or temperature-raising speed at the time of carrying the memory heat treatment out, and thus, in detail, there are no disclosures in that the tests are carried out using what kinds of the temperature-raising speed or temperature-lowering speed. Thus, as the temperature-raising speed or temperature-lowering speed that is conventionally and generally used, the tests were carried out at rapid speeds (rapid temperature-raising or rapid temperature-lowering) that is outside of the slow temperature-raising or slow cooling as defined in the present invention.

[0107] As another Comparative Examples, the rods listed in Table 2-2 (Comparative Examples 7 and 8) were obtained in the same manner as the present invention but using copper alloys containing Ni in the too high contents that were outside of the range defined in the present invention as indicated in Table 1-1. It was confirmed that the Comparative Examples 7 and 8 were poor in quench-hardening sensitivity, and also poor in superelastic characteristics.

[0108] For evaluating the superelastic characteristics, the stress loading-unloading by a tensile test was carried out, to obtain a stress-strain curve (S-S curve), thereby for obtaining and evaluating a residual deformation and an elongation. For the tensile test, three test pieces (N=3) were cut out from one specimen, to test. In the following test results, the residual strain and elongation were the average value obtained from those three values.

[0109] The methods for tests and evaluations are described in detail below.

a-1. Grain Size of Rod

[0110] The samples were prepared by cutting each of the rods at any locations of longitudinal direction and then cutting the half of the cut rod. The cut length a (mm) was not particularly defined, but was five times or more of the diameter thereof. The cross sections of the samples were polished, and then, etched with aqueous ferric chloride solution, and the microstructures thereof were photographed. The schematic diagram is illustrated in FIG. **1**. When the number of points, in which the edge lines ((1) and (3)) and center line ((2)) of the longitudinal direction of the cross section intersect with the grain boundary, is defined as n, the grain size d (mm) is determined by the following formula.

$$d=3\times a/n$$

[0111] Among the grains of the rods, in which the grain size was measured by the above-described method, the case where the region, in which the grain sizes were the radius of the rod or more, was 90% or more of the whole length, was judged excellent and was rated as “A”; and the case where the region was less than 90%, was judged poor and was rated as “D”.

[0112] The case where the grain average size (the average grain size to the grains satisfying the following size) of the respective grains of the rod, which was the diameter of the rod or more, in which the grain size was the radius of the rod or more, was judged excellent and was rated as “A”; the case where the average grain size was 80% of the diameter of the rod or more and was less than the diameter of the rod, was determined good and was rated as “B”; and the case where the average grain size was less than 80% of the diameter of the rod, was judged poor and was rated as “D”.

b. Superelastic Characteristics [Residual Strain (%) after 6% Deformation]

[0113] A stress-strain curve (S-S curve) was determined by performing a tensile test, and the residual strain was determined and evaluated.

[0114] Three test pieces each having a length of 150 mm were cut out from each of the specimens and supplied to the test. The residual strain after 6% deformation was determined from the stress-strain curve (S-S curve), and the values are presented in the tables.

[0115] Regarding the test conditions, the tensile test of alternately repeating strain loading and elimination by repeatedly loading predetermined strains of different levels over a gauge length of 25 mm, while temporarily increasing the amount of strain from 1% to 8% by 1% in each step, was carried out at a test rate of 2%/min. The cycle of strain loading used herein was as follows: as 0 MPa (strain at zero load) →1%→0 MPa→2%→0 MPa→3%→0 MPa→4% MPa→5%→0 MPa→6%→0 MPa→7%→0 MPa→8%→0 MPa, the loading and unloading of the load were repeated by turns alternately, and while the strain at the time of loading was increased from 1% by 1% each, the loading and unloading of eight strain were repeated till adding 8% of the loading strain.

[0116] The case where the residual strain was 0.2% or less, was judged to have excellent superelastic characteristics and was rated as “A”; the case where the residual strain was more than 0.2% but not more than 0.5%, was judged to have satisfactory superelastic characteristics and was rated as “B”; the case where the residual strain was more than 0.5% but not more than 1.0%, was judged to have acceptable superelastic characteristics and was rated as “C”; and the case where the residual strain was large such as more than 1.0%, was judged to have unacceptable superelastic characteristics and was rated as “D”.

[0117] For the representative residual strain, a stress-strain curve (S-S curve) was illustrated in FIG. **3***a* and FIG. **3***b*. FIG. **3***a* illustrates the rod of Example (Example 1), and FIG. **3***b* illustrates the rod of Comparative Example (Comparative Example 2), respectively.

c. Elongation (El) (%)

[0118] The elongation at breakage was measured, according to the method defined in JIS H7103.

[0119] The case where the elongation was 10% or more, was judged excellent and was rated as “A”; the case where the elongation was 8% or more but less than 10%, was judged satisfactory and was rated as “B”; the case where the elongation was 6% or more but less than 8%, was judged acceptable and was rated as “C”; and the case where the elongation was less than 6%, was judged poor and was rated as “D”.

d. Quench-Hardening Sensitivity

[0120] For the quench-hardening sensitivity, the amount of precipitation of the α phase obtained when a sample was cooled at a cooling speed of 300° C./sec after heating, was evaluated as the volume proportion based on an image analysis of SEM images.

[0121] The case where the volume proportion of the α phase was 10% or less, was judged to be excellent in quench-hardening sensitivity and was rated as “A”; and the case where the volume proportion was more than 10%, was judged to be poor in quench-hardening sensitivity and was rated as “D”.

[0122] The results are shown in Tables 2-1 to 2-2.

TABLE 1-1

Alloy No.	Alloying elements (mass %) Al	Mn	Others	Remarks
1	8.1	10.7	—	This invention
2	8.1	11.1	—	
3	8.2	19.5	—	
4	8.1	5.5	—	
5	3.5	10.1	—	
6	9.5	11.0	—	
7	8.1	10.2	Co 0.5	
8	8.1	10.2	Fe 0.5	
9	8.1	9.0	Ni 1.0	
10	2.0	11.0	—	Comparative example
11	12.0	11.0	—	
12	8.0	4.0	—	
13	8.0	24.0	—	
14	8.0	9.0	Ni 2.0	
15	8.0	9.0	Ni 2.0, Fe 0.5	

Note:
‘—’ means not contained
The balance was Cu and unavoidable impurities

TABLE 1-2

Alloy No.	Alloying elements (mass %) Al	Mn	Ti	V	Cr	Si	Sn	Zn	Remarks
16	8.1	10.2	0.5	—	—	—	—	—	This invention
17	8.1	10.2	—	0.5	—	—	—	—	
18	8.1	10.2	—	—	0.5	—	0.1	—	
19	8.1	10.2	0.3	—	—	0.05	—	—	
20	8.1	10.2	—	0.1	—	—	0.5	—	
21	8.1	10.2	—	0.1	—	—	—	0.5	
22	8.1	10.2	—	—	0.4	—	0.1	—	
23	8.1	10.2	0.2	—	0.3	—	—	—	

Note:
‘—’ means not contained
The balance was Cu and unavoidable impurities

TABLE 2-1

Remarks	Alloy No.	Cold-working ratio (%)	The number (times) of cycles in cold-working	Rod diameter of specimen (mm)	Shape memory heat-treatment Temp.-lowering speed to α → β + α (° C./min)	Temp.-raising speed to β + α → β (° C./min)
Ex 1	1	—	—	15	1	1
Ex 2	1	—	—	15	1	3
Ex 3	1	—	—	15	3	1
Ex 4	1	—	—	15	1	10
Ex 5	1	—	—	15	10	1
Ex 6	1	—	—	15	100	100
Ex 7	1	—	—	15	1	1
Ex 8	2	—	—	15	1	1
Ex 9	3	—	—	15	1	1
Ex 10	4	—	—	15	1	1
Ex 11	5	—	—	15	1	1
Ex 12	6	—	—	15	1	1
Ex 13	7	—	—	15	1	1
Ex 14	8	—	—	15	1	1
Ex 15	9	—	—	15	1	1
Ex 16	16	—	—	15	1	1
Ex 17	17	—	—	15	1	1
Ex 18	18	—	—	15	1	1
Ex 19	19	—	—	15	1	1
Ex 20	20	—	—	15	1	1
Ex 21	21	—	—	15	1	1

TABLE 2-1-continued

Ex 22	22	—	—	15	1	1
Ex 23	23	—	—	15	1	1
Ex 24	1	36	1	12	1	3
Ex 25	1	50	1	12	1	3
Ex 26	1	36 + 36	2	12	1	3
Ex 27	1	36 + 31 + 36	3	8	1	3
Ex 28	1	—	—	20	1	1

Remarks	Region (%) in which the respective grain size is a rod radius or more		Ratio of av. grain size [grain size/rod diameter]		Super-elasticity performance [Residual strain (%) when 6% deformed]		El (%)		Quench-hardening sensitivity [α-phase occupied ratio]	
Ex 1	A	99	A	1.3	A	0.13	A	16.2	A	0.1%
Ex 2	A	94	B	0.8	B	0.43	B	9.5	A	0.1%
Ex 3	A	95	B	0.9	B	0.26	B	9.8	A	0.1%
Ex 4	A	92	B	0.8	C	0.64	B	8.9	A	0.1%
Ex 5	A	94	B	0.9	B	0.35	B	9.4	A	0.1%
Ex 6	A	91	B	0.8	C	0.90	B	8.2	A	0.1%
Ex 7	A	99	A	1.3	A	0.10	A	15.8	A	0.1%
Ex 8	A	99	A	1.4	A	0.17	A	16.0	A	0.1%
Ex 9	A	99	A	1.0	A	0.18	A	10.4	A	0.1%
Ex 10	A	99	A	1.2	A	0.10	A	11.9	A	0.1%
Ex 11	A	99	A	1.1	A	0.17	A	10.5	A	0.1%
Ex 12	A	99	A	1.0	A	0.13	A	10.6	A	0.1%
Ex 13	A	99	A	1.3	A	0.12	A	12.4	A	0.1%
Ex 14	A	99	A	1.2	A	0.14	A	12.7	A	0.1%
Ex 15	A	99	A	1.2	A	0.12	A	13.1	A	1.7%
Ex 16	A	99	A	1.1	A	0.15	A	11.2	A	0.1%
Ex 17	A	99	A	1.4	A	0.16	A	12.0	A	0.1%
Ex 18	A	99	A	1.3	A	0.14	A	12.5	A	0.1%
Ex 19	A	99	A	1.2	A	0.15	A	14.6	A	0.1%
Ex 20	A	99	A	1.4	A	0.11	A	12.9	A	0.1%
Ex 21	A	99	A	1.2	A	0.15	A	13.1	A	0.1%
Ex 22	A	99	A	1.3	A	0.13	A	12.1	A	0.1%
Ex 23	A	99	A	1.2	A	0.17	A	11.8	A	0.1%
Ex 24	A	97	A	1.1	A	0.14	A	12.1	A	0.1%
Ex 25	A	99	A	1.4	A	0.10	A	15.4	A	0.1%
Ex 26	A	99	A	1.4	A	0.09	A	14.8	A	0.1%
Ex 27	A	99	A	1.6	A	0.07	A	16.3	A	0.1%
Ex 28	A	99	A	1.0	A	0.14	A	14.7	A	0.1%

Note:
'Ex' means example according to this invention.

TABLE 2-2

				Rod	Shape memory heat-treatment	
Remarks	Alloy No.	Cold-working ratio (%)	The number (times) of cycles in cold-working	diameter of specimen (mm)	Temp.-lowering speed to β → β + α (° C./min)	Temp.-raising speed to β + α → β (° C./min)
CEx 1	1	—	—	15	1	150
CEx 2	1	—	—	15	150	1
CEx 3	10	—	—	15	1	1
CEx 4	11		Cracked in forging, impossible to work			
CEx 5	12		Cracked in forging, impossible to work			
CEx 6	13	—	—	15	1	1
CEx 7	14	—	—	15	1	1
CEx 8	15	—	—	15	1	1

Remarks	Region (%) in which the respective grain size is a rod radius or more		Ratio of av. grain size [grain size/rod diameter]		Super-elasticity performance [Residual strain (%) when 6% deformed]		El (%)		Quench-hardening sensitivity [α-phase occupied ratio]	
CEx 1	D	42	D	0.4	D	1.88	C	6.2	A	0.1%
CEx 2	D	59	D	0.7	D	1.20	C	7.8	A	0.1%
CEx 3	A	93	B	0.8	D	4.29	A	18.1	A	0.1%
CEx 4			Cracked in forging, impossible to work							
CEx 5			Cracked in forging, impossible to work							

TABLE 2-2-continued

CEx 6	A	95	B	0.9	D	4.73	A	19.5	A	0.1%
CEx 7	A	97	A	1.1	D	3.09	A	12.5	D	20.3%
CEx 8	A	96	A	1.2	D	2.98	A	12.1	D	19.4%

Note:
'CEx' means comparative example.

[0123] Examples 1 to 12 were Test Examples to the alloy compositions, in which essentially adding elements were only contained and their contents (composition ratio) were variously changed. Examples 13 to 15 and 16 to 23 were Test Examples to various alloy compositions, in which optionally adding elements (small amounts of optionally adding elements) were added to the essentially adding elements. Further, Examples 1 to 6 and 24 to 28 were Test Examples, in which the production conditions were variously changed to Examples 7 to 23.

[0124] As is apparent from the results shown in the tables, and as shown from the results of Examples 1 to 28, the materials (rods), each of which satisfy the grain size distribution of the given large grain size and the average grain size thereof as defined in the present invention, can be obtained, by satisfying the given production conditions (for example, the temperature-lowering speed and temperature-raising speed at the time of the memory heat treatment, and the like) as defined in the present invention, and also making the alloy compositions to be in the preferred range of the present invention, regardless of whether the intermediate annealing after hot working or the cold-working thereafter was carried out, or not. Thus, the desired excellent superelastic characteristics can be obtained, and also the elongation and quench-hardening sensitivity can become excellent.

[0125] On the other hand, for Comparative Examples 1 and 2, since the temperature-raising speed in [Step **3-3**] or the temperature-lowering speed in [Step **3-2**] in the memory heat treatment was too fast, it was difficult to satisfy the grain size distribution of the grain having the predetermined large grain size as defined in the present invention, and also it was difficult to satisfy the average grain size thereof. Thus, each of Comparative Examples 1 and 2 did not exhibit desired superelastic characteristics, and also, was small in improvement of elongation. For Comparative Example 3, the content of Al was too small, and for Comparative Example 6, the content of Mn was too much. Thus, each of Comparative Examples 3 and 6 satisfied the grain size distribution of the grain of the predetermined large grain size as defined in the present invention and the average grain size thereof, but did not exhibit the desired superelastic characteristics. For Comparative Example 4, the content of Al was too large, and for Comparative Example 5, the content of Mn was too small. Thus, with respect to Comparative Examples 4 and 5, the workability was poor, the cracks were occurred in the forging-working, and it was impossible to produce the samples. For Comparative Examples 7 and 8, Ni was contained in the alloy component at a too large content, and thus, they satisfied the grain size distribution of the grain of the predetermined large grain size as defined in the present invention and the average grain size thereof. However, in the microstructures of those materials (rods) of Comparative Examples 7 and 8, it was confirmed that the precipitation of the α phase was occurred, the quench-hardening sensitivity was poor, and the desired superelastic characteristics was impossible to exhibit.

[0126] Further, the test results were omitted but not shown. However, for the case of the rod, in which after the hot working, only the intermediate annealing was carried out, and after the intermediate annealing, the cold working was not carried out and the memory heat treatment was carried out, the similar results as those Examples can be obtained.

Example 2

[0127] Samples (specimens) of sheets were produced under the following conditions.

[0128] As the copper alloys that give the compositions as indicated in Table 1-1 and Table 1-2, pure copper, pure Mn, pure Al, and materials of other optionally adding alloying elements were subjected respectively to melting in a high-frequency induction furnace. The copper alloys thus melted were cooled, to obtain ingots with diameter of 80 mm×length of 300 mm. The ingots thus obtained were subjected to hot forging at 800° C., to obtain sheets with sheet thickness 15 mm and sheet width 30 mm.

[0129] The sheets were further subjected to hot rolling, to obtain sheets with sheet thickness of 10 mm, and if necessary, the sheets were subjected to cold rolling, to obtain sheets with the sheet thicknesses as indicated in Table 2-3 and Table 2-4 with the conditions as follows.

[0130] In the similar manner as the rods, according to the respective working and heat treatment process as illustrated in FIG. **2-1** or FIG. **2-2**, the working and heat treatment were carried out at the conditions listed in Table 2-3 and Table 2-4. In detail, after the hot working [Step **1**], the intermediate annealing [Step **2-1**] and the cold-wire-drawing [Step **2-2**] were not carried out, and the memory heat treatment [Step **3**] was carried out (Examples 29 to 51, Example 56, respective Comparative Examples) (Process of FIG. **2-1**), or after the hot working [Step **1**], the intermediate annealing [Step **2-1**] at 500° C. for 1 hour and then the cold-wire-drawing [Step **2-2**] were carried out once each or were repeatedly carried out at a plurality of times (Examples 52 to 55) (Process of FIG. **2-2**). For all the cases subjected to any kinds of those processes, then, the sheets in Examples and Comparative Examples, which have the sheet thicknesses listed in Table 2-3 and Table 2-4, were prepared by: temperature-raising at the temperature-raising speed of 30° C./minutes to be 900° C. (the temperature to the β single phase); maintaining this temperature for 5 minutes; temperature-lowering at the temperature-lowering speed listed in Table 2-3 and Table 2-4 to be 500° C. (the temperature to the α+β phase); immediately, temperature-raising at the temperature-raising speed listed in Table 2-3 and Table 2-4 to be 900° C. (the temperature to the (3 single phase); maintaining this temperature for 1 hour; and finally, quenching from 900° C. by cold water cooling.

[0131] The explanations about FIG. **2-1** and FIG. **2-2** and Table 2-3 and Table 2-4 were the same as FIG. **2-1** and FIG. **2-2** and Table 2-1 and Table 2-2 in the case of the rods.

[0132] As described above, there were Test Examples without carrying out neither of intermediate annealing [Step **2-1**] nor cold-working [Step **2-2**], and also, there were Test examples that the second or third intermediate annealings and cold-workings were carried out or were not carried out.

[0133] Hereinafter, representative working process examples will be described along with the sheet thicknesses and working ratios.

Sheet Working Process Example 1

[0134] Sheet thickness 15 mm×sheet width 30 mm×length L 500 mm (hot forged up)

[0135] Sheet thickness 10 mm×sheet width 33 mm×length L 680 mm (hot rolled up)

[0136] Sheet thickness 6 mm×sheet width 35 mm×length L 1,070 mm (hot rolled up)

[0137] Sheet thickness 4 mm×sheet width 35 mm×length L 1,600 mm (cold rolled up, working ratio of 33%)

[0138] Sheet thickness 2.5 mm×sheet width 35 mm×length L 2,560 mm (cold rolled up, working ratio of 33%→37%)

[0139] Sheet thickness 1.5 mm×sheet width 35 mm×length L 4,270 mm (cold rolled up, working ratio of 33%→37%→40%)

Sheet Working Process Example 2

[0140] Sheet thickness 6 mm×sheet width 35 mm×length L 1,070 mm (hot forged up)

[0141] Sheet thickness 3 mm×sheet width 35 mm×length L 2,140 mm (cold rolled up, working ratio of 50%)

[0142] Sheet specimens thus obtained, which were subjected through the working and heat treatment processes, and to final quenching (rapid cooling) by water cooling, thereby for obtaining samples of the 6 (BCC) single phase.

[0143] The respective sample was, then, subjected to age-heating at 200° C. for 15 minutes.

[0144] Among Comparative Examples, the sheets of Comparative Examples 11 to 16 were obtained in the same manner as in Examples 29 and the like, except for Comparative Examples 12 and 13, in which the productions were stopped due to the forging cracks occurred in the mid way of productions. On the other hand, the sheets of Comparative Examples 9 and 10 were obtained in the same manner as in Examples 29 to 51, except that, in the memory heat treatment of Examples 29 and the like, the temperature-lowering step [Step **3-2**] (6→α+6) was carried out at the temperature-lowering speed of 150° C./minute of the rapid temperature-lowering (Comparative Example 10) or the temperature-raising step [Step **3-3**] (α+β→β) was carried out at the temperature-raising speed of 150° C./minute of the rapid temperature-raising (Comparative Example 9).

[0145] Among those, Comparative Examples 9 and 10 are Test Examples simulating JP-A-2001-20026 (Patent Literature 2) and WO 2011/152009 A1 (Patent Literature 3), respectively. In JP-A-2001-20026 (Patent Literature 2) and WO 2011/152009 A1 (Patent Literature 3), any kinds of reviews are not carried out on the temperature-lowering speed or temperature-raising speed at the time of carrying the memory heat treatment out, and thus, in detail, there are no disclosures in that the tests are carried out using what kinds of the temperature-raising speed or temperature-lowering speed. Thus, as the temperature-raising speed or temperature-lowering speed that is conventionally and generally used, the tests were carried out at rapid speeds (rapid temperature-raising or rapid temperature-lowering) that is outside of the slow temperature-raising or slow cooling as defined in the present invention.

[0146] As another Comparative Examples, the sheets listed in Table 2-4 (Comparative Examples 15 and 16) were obtained in the same manner as the present invention but using copper alloys containing Ni in the too high contents that were outside of the range defined in the present invention as indicated in Table 1-1. It was confirmed that the Comparative Examples 15 and 16 were poor in quench-hardening sensitivity, and also poor in superelastic characteristics.

[0147] The characteristics of the thus-obtained sheet samples were tested and evaluated in the same manner as in the rod samples, except the following explanations.

a-2. Gain Size of Sheet

[0148] The samples were prepared by cutting each of the sheets in the sheet thickness direction at any locations of longitudinal direction and then cutting the half of the cut sheet. The cut length a (mm) was not particularly defined, but five times or more of the sheet width. The cross sections of the samples were polished, and then, etched with aqueous ferric chloride solution, and the microstructures thereof were photographed. In the same manner as in the rod samples, the schematic diagram is illustrated in FIG. **1** and the grain size d (mm) is determined in the same manner as in the rod samples.

[0149] Among the respective grains of the sheets, in which the grain size was measured by the above-described method, the case where the region, in which the grain sizes were the half of the sheet thickness or more, was 90% or more of the whole length, was judged excellent and was rated as “A”; and the case where the region was less than 90%, was judged poor and was rated as “D”.

[0150] The case where the grain average size (the average grain size to the grains satisfying such a size) of each of the grains of the sheet, in which the grain size was the half of the sheet thickness or more, was the thickness of the sheet or more, was judged excellent and was rated as “A”; and the case where the average grain size was 80% of the sheet thickness or more but less than the sheet thickness, was determined good and was rated as “B”; and the case where the average grain size was less than 80% of the sheet thickness, was judged poor and was rated as “D”.

[0151] The results are shown in Tables 2-3 to 2-4.

TABLE 2-3

				Sheet	Shape memory heat-treatment	
Remarks	Alloy No.	Cold-working ratio (%)	The number (times) of cycles in cold-working	thickness of specimen (mm)	Temp.-lowering speed to $\beta \rightarrow \beta + \alpha$ (° C./min)	Temp.-raising speed to $\beta + \alpha \rightarrow \beta$ (° C./min)
Ex 29	1	—	—	6	1	1
Ex 30	1	—	—	6	1	3
Ex 31	1	—	—	6	3	1
Ex 32	1	—	—	6	1	10
Ex 33	1	—	—	6	10	1

TABLE 2-3-continued

Ex 34	1	—	—	6	100	100
Ex 35	1	—	—	6	1	1
Ex 36	2	—	—	6	1	1
Ex 37	3	—	—	6	1	1
Ex 38	4	—	—	6	1	1
Ex 39	5	—	—	6	1	1
Ex 40	6	—	—	6	1	1
Ex 41	7	—	—	6	1	1
Ex 42	8	—	—	6	1	1
Ex 43	9	—	—	6	1	1
Ex 44	16	—	—	6	1	1
Ex 45	17	—	—	6	1	1
Ex 46	18	—	—	6	1	1
Ex 47	19	—	—	6	1	1
Ex 48	20	—	—	6	1	1
Ex 49	21	—	—	6	1	1
Ex 50	22	—	—	6	1	1
Ex 51	23	—	—	6	1	1
Ex 52	1	33	1	4	1	3
Ex 53	1	50	1	3	1	3
Ex 54	1	33 + 37	2	2.5	1	3
Ex 55	1	33 + 37 + 40	3	1.5	1	3
Ex 56	1	—	—	10	1	1

Remarks	Region (%) in which the respective grain size is the half of sheet thickness or more		Ratio of av. grain size [grain size/sheet thickness]		Super-elasticity performance [Residual strain (%) when 6% deformed]		El (%)		Quench-hardening sensitivity [α-phase occupied ratio]	
Ex 29	A	99	A	1.2	A	0.14	A	14.0	A	0.1%
Ex 30	A	93	B	0.8	B	0.38	B	9.1	A	0.1%
Ex 31	A	94	B	0.8	B	0.27	B	9.6	A	0.1%
Ex 32	A	93	B	0.9	C	0.71	B	8.4	A	0.1%
Ex 33	A	95	B	0.9	B	0.45	B	9.1	A	0.1%
Ex 34	A	92	B	0.8	C	0.88	B	8.3	A	0.1%
Ex 35	A	98	A	1.4	A	0.08	A	16.0	A	0.1%
Ex 36	A	99	A	1.3	A	0.15	A	15.4	A	0.1%
Ex 37	A	99	A	1.1	A	0.14	A	12.8	A	0.1%
Ex 38	A	99	A	1.3	A	0.11	A	10.8	A	0.1%
Ex 39	A	99	A	1.1	A	0.16	A	11.2	A	0.1%
Ex 40	A	98	A	1.2	A	0.15	A	10.9	A	0.1%
Ex 41	A	99	A	1.3	A	0.11	A	11.9	A	0.1%
Ex 42	A	99	A	1.3	A	0.13	A	11.5	A	0.1%
Ex 43	A	99	A	1.3	A	0.14	A	12.9	A	1.9%
Ex 44	A	99	A	1.4	A	0.18	A	11.9	A	0.1%
Ex 45	A	99	A	1.5	A	0.18	A	14.1	A	0.1%
Ex 46	A	99	A	1.4	A	0.17	A	11.3	A	0.1%
Ex 47	A	99	A	1.3	A	0.13	A	12.2	A	0.1%
Ex 48	A	99	A	1.2	A	0.18	A	14.0	A	0.1%
Ex 49	A	99	A	1.4	A	0.14	A	13.0	A	0.1%
Ex 50	A	99	A	1.4	A	0.17	A	14.7	A	0.1%
Ex 51	A	99	A	1.3	A	0.12	A	13.2	A	0.1%
Ex 52	A	96	A	1.1	A	0.11	A	11.6	A	0.1%
Ex 53	A	99	A	1.5	A	0.08	A	16.8	A	0.1%
Ex 54	A	99	A	1.4	A	0.08	A	15.1	A	0.1%
Ex 55	A	99	A	1.8	A	0.06	A	18.3	A	0.1%
Ex 56	A	98	A	1.1	A	0.13	A	13.9	A	0.1%

TABLE 2-4

				Sheet	Shape memory heat-treatment	
Remarks	Alloy No.	Cold-working ratio (%)	The number (times) of cycles in cold-working	thickness of specimen (mm)	Temp.-lowering speed to β → β + α (° C./min)	Temp.-raising speed to β + α → β (° C./min)
CEx 9	1	—	—	6	1	150
CEx 10	1	—	—	6	150	1
CEx 11	10	—	—	6	1	1
CEx 12	11	Cracked in forging, impossible to work				
CEx 13	12	Cracked in forging, impossible to work				

TABLE 2-4-continued

CEx 14	13	—	—	6	1	1
CEx 15	14	—	—	6	1	1
CEx 16	15	—	—	6	1	1

Remarks	Region (%) in which the respective grain size is the half of sheet thickness or more		Ratio of av. grain size [grain size/sheet thickness]		Super-elasticity performance [Residual strain (%) when 6% deformed]		El (%)		Quench-hardening sensitivity [α-phase occupied ratio]	
CEx 9	D	49	D	0.5	D	1.69	C	6.4	A	0.1%
CEx 10	D	60	D	0.7	D	1.31	C	7.6	A	0.1%
CEx 11	A	96	B	0.8	D	4.75	A	18.6	A	0.1%
CEx 12	Cracked in forging, impossible to work									
CEx 13	Cracked in forging, impossible to work									
CEx 14	A	92	A	1.0	D	4.63	A	18.8	A	0.1%
CEx 15	A	98	A	1.2	D	2.76	A	13.4	D	18.6%
CEx 16	A	98	A	1.1	D	2.81	A	12.9	D	19.6%

[0152] Examples 29 to 40 were Test Examples to the alloy compositions, in which essentially adding elements were only contained and their contents (composition ratio) were variously changed. Examples 41 to 43 and 44 to 51 were Test Examples to various alloy compositions, in which optionally adding elements (small amounts of optionally adding elements) were added to the essentially adding elements. Further, Examples 29 to 34 and 52 to 56 were Test Examples, in which the production conditions were variously changed to Examples 35 to 51.

[0153] As is apparent from the results shown in the tables, and as shown from the results of Examples 29 to 56, the materials (sheets), each of which satisfy the grain size distribution of the given large grain size and the average grain size thereof as defined in the present invention, can be obtained, by satisfying the given production conditions (for example, the temperature-lowering speed and temperature-raising speed at the time of the memory heat treatment, and the like) as defined in the present invention, and also making the alloy compositions to be in the preferred range of the present invention, regardless of whether the intermediate annealing after hot working or the cold-working thereafter was carried out, or not. Thus, the desired excellent superelastic characteristics can be obtained, and also the elongation and quench-hardening sensitivity can become excellent.

[0154] On the other hand, for Comparative Examples 9 and 10, since the temperature-raising speed in [Step **3-3**] or the temperature-lowering speed in [Step **3-2**] in the memory heat treatment was too fast, it was difficult to satisfy the grain size distribution of the grain having the predetermined large grain size as defined in the present invention, and also it was difficult to satisfy the average grain size thereof. Thus, each of Comparative Examples 9 and 10 did not exhibit desired superelastic characteristics, and also, was small in improvement of elongation. For Comparative Example 11, the content of Al was too small, and for Comparative Example 14, the content of Mn was too much. Thus, each of Comparative Examples 11 and 14 satisfied the grain size distribution of the grains of the predetermined large grain size as defined in the present invention and the average grain size thereof, but did not exhibit the desired superelastic characteristics. For Comparative Example 12, the content of Al was too large, and for Comparative Example 13, the content of Mn was too small. Thus, with respect to Comparative Examples 12 and 13, the workability was poor, the cracks were occurred in the forging-working, and it was impossible to produce the samples. For Comparative Examples 15 and 16, Ni was contained in the alloy component at a too large content, and thus, they satisfied the grain size distribution of the grain of the predetermined large grain size as defined in the present invention and the average grain size thereof. However, in the microstructures of those materials (sheets) of Comparative Examples 15 and 16, it was confirmed that the precipitation of the α phase was occurred, the quench-hardening sensitivity was poor, and the desired superelastic characteristics was impossible to exhibit.

[0155] Further, the test results were omitted but not shown. However, for the case of the sheet, in which after the hot working, only the intermediate annealing was carried out, and after the intermediate annealing, the cold working was not carried out and the memory heat treatment was carried out, the similar results as those Examples can be obtained.

[0156] Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

1. A Cu—Al—Mn-based alloy rod having superelastic characteristics and having a recrystallized microstructure substantially formed of a β single phase,

wherein, for a longitudinal direction cross section of the rod, a region, in which a grain size of each of grains is a radius of the rod or more, is 90% or more of the longitudinal direction cross section at any location of the rod, and wherein an average grain size of the grains, in which the grain size is the radius of the rod or more, is 80% or more of a diameter of the rod.

2. The Cu—Al—Mn-based alloy rod as claimed in claim **1**, wherein the average grain size is the diameter of the rod or more.

3. The Cu—Al—Mn-based alloy rod as claimed in claim **1**, wherein the Cu—Al—Mn-based alloy has a composition containing 3 to 10 mass % of Al; 5 to 20 mass % of Mn; optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities.

4. A method of producing a Cu—Al—Mn-based alloy rod having a composition containing 3 to 10 mass % of Al, 5 to 20 mass % of Mn, optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities, comprising through [Step **1**] to [Step **3**], in this order:

melting and casting an alloy material which gives the composition [Step **1**];

subjecting to hot working [Step **2**]; and

performing memory heat treatment [Step **3**],

wherein, for the memory heat treatment [Step **3**], heating is carried out from a room temperature to a temperature range to be a β phase [Step **3-1**]; heating for maintaining the heating temperature for 1 to 120 minutes; and then, cooling [Step **3-2**] and heating [Step **3-3**] are each repeated once or more; heating is carried out, in which the cooling [Step **3-2**] and the heating [Step **3-3**] are set to a temperature to be an α+β phase at a low temperature and are set to a temperature to be a β phase at a high temperature, and in which a cooling speed and a temperature-raising speed at the time of the cooling [Step **3-2**] and the heating [Step **3-3**] are respectively set to 0.1 to 100° C./minute; and, after final heating, heating for quenching from the temperature to be the β phase [Step **3-4**] is carried out.

5. The method of producing a Cu—Al—Mn-based alloy rod as claimed in claim **4**, wherein, after the subjecting to hot working [Step **2**], intermediate annealing that is carried out at 400 to 600° C. for 1 to 120 minutes [Step **2-1**] and cold-working at a working ratio of 30% or more [Step **2-2**] are carried out at least one time each in this order, and then, the memory heat treatment [Step **3**] is carried out.

6. A vibration damping material being composed of the Cu—Al—Mn-based alloy rod as claimed in claim **1**.

7. A vibration damping structure constructed of the vibration damping material as claimed in claim **6**.

8. A Cu—Al—Mn-based alloy sheet having superelastic characteristics and having a recrystallized microstructure substantially formed of a β single phase,

wherein, for a cross section of a sheet thickness direction and a longitudinal direction of the sheet, a region, in which a grain size of each of grains is a half of a sheet thickness or more, is 90% or more of the cross section of the sheet thickness direction and the longitudinal direction at any location of the sheet, and wherein an average grain size of the grains, in which the grain size is the half of the sheet thickness or more, is 80% or more of the sheet thickness.

9. The Cu—Al—Mn-based alloy sheet as claimed in claim **8**, wherein the average grain size is the sheet thickness or more.

10. The Cu—Al—Mn-based alloy sheet as claimed in claim **8**, wherein the Cu—Al—Mn-based alloy has a composition containing 3 to 10 mass % of Al; 5 to 20 mass % of Mn; optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities.

11. A method of producing a Cu—Al—Mn-based alloy sheet having a composition containing 3 to 10 mass % of Al, 5 to 20 mass % of Mn, optionally 1 mass % or less of Ni; and optionally 0.001 to 10 mass % in total of at least one element selected from the group consisting of Co, Fe, Ti, V, Cr, Si, Nb, Mo, W, Sn, Mg, P, Be, Sb, Cd, As, Zr, Zn, and Ag, with the balance being Cu and unavoidable impurities, comprising through [Step **1**] to [Step **3**], in this order:

melting and casting an alloy material which gives the composition [Step **1**];

subjecting to hot working [Step **2**]; and

performing a memory heat treatment [Step **3**],

wherein, for the memory heat treatment [Step **3**], heating is carried out from a room temperature to a temperature range to be a β phase [Step **3-1**]; heating for maintaining the heating temperature for 1 to 120 minutes; and then, cooling [Step **3-2**] and heating [Step **3-3**] are each repeated once or more; heating is carried out, in which the cooling [Step **3-2**] and the heating [Step **3-3**] are set to a temperature to be an α+β phase at a low temperature and are set to a temperature to be a β phase at a high temperature, and in which a cooling speed and a temperature-raising speed at the time of the cooling [Step **3-2**] and the heating [Step **3-3**] are respectively set to 0.1 to 100° C./minute; and, after final heating, heating for quenching from the temperature to be the β phase [Step **3-4**] is carried out.

12. The method of producing a Cu—Al—Mn-based alloy sheet as claimed in claim **11**, wherein, after the subjecting to the hot working [Step **2**], intermediate annealing that is carried out at 400 to 600° C. for 1 to 120 minutes [Step **2-1**] and cold-working at a working ratio of 30% or more [Step **2-2**] are carried out at least one time each in this order, and then, the memory heat treatment [Step **3**] is carried out.

13. A vibration damping material being composed of the Cu—Al—Mn-based alloy sheet as claimed in claim **8**.

14. A vibration damping structure constructed of the vibration damping material as claimed in claim **13**.

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