



(11) **EP 3 375 897 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
19.09.2018 Bulletin 2018/38

(51) Int Cl.:
C22C 9/00 *(2006.01)* **C22F 1/08** *(2006.01)*
C22F 1/00 *(2006.01)*

(21) Application number: **16863933.4**

(86) International application number:
PCT/JP2016/080082

(22) Date of filing: **11.10.2016**

(87) International publication number:
WO 2017/081969 (18.05.2017 Gazette 2017/20)

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
MA MD

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(30) Priority: **09.11.2015 JP 2015219851**

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(54) **COPPER ALLOY MATERIAL**

(57) A copper alloy material has a composition including: 0.1 mass% or more and 1.5 mass% or less of Cr; 0.05 mass% or more and 0.25 mass% or less of Zr; 0.005 mass% or more and 0.10 mass% or less of P; and a Cu balance including inevitable impurities. The copper alloy material includes a Cr-Zr-P compound containing

Cr, Zr and P and an area ratio of the Cr-Zr-P compound is in a range of 0.5 % or more and 5.0 % or less in a structure observation, and the Cr-Zr-P compound is in a form of a needle shape or a granular shape and a length a longest side of the needle shape or the granular shape is 100 μ m or less.

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Description

Technical Field

[0001] The present invention relates to a copper alloy material suitable for a part used in a high temperature environment such as a molding material for casting and a welding part such as a contact tip.

[0002] Priority is claimed on Japanese Patent Application No. 2015-219851, filed on November 9, 2015, the content of which is incorporated herein by reference.

Background Art

[0003] Conventionally, Cu-Cr-Zr-based alloys such as C18150 are used as a material for casting mold materials and welding members which are used at high temperatures, since they have excellent heat resistance and electrical conductivity as shown in Patent Literatures 1 to 3.

[0004] These Cu-Cr-Zr-based alloy are usually produced by a production process, in which a cast made of Cu-Cr-Zr-based alloy is subjected to a plastic working; a solution treatment, for example in a condition of 950-1050°C of a retention temperature and 0.5-1.5 hours of a retention time, and an aging treatment, for example in a condition of 400-500°C of a retention temperature and 2-4 hours of a retention time, are performed on the plastically worked material; and then the material subjected to the solution and aging treatments is finished into a predetermined shape by machine working in the end. In addition, the solution treatment step in the Cu-Cr-Zr-based alloy can be carried out in combination with the plastic working step instead of the so-called in-line solution treatment. In that case, the solution treatment is performed concurrently with the hot rolling working.

[0005] In the above-described Cu-Cr-Zr-based alloy, Cr and Zr are dissolved in the matrix of Cu by the solution treatment and fine precipitates of Cr and Zr are dispersed by the aging treatment to improve strength and conductivity.

Citation List

Patent Literature

[0006]

[PTL 1] Japanese Examined Patent Application, Second Publication No. S62-182238(A)

[PTL 2] Japanese Examined Patent Application, Second Publication No. S62-182239(A)

[PTL 3] Japanese Unexamined Patent Application, First Publication No. H04-120438

Summary of Invention

Technical Problem

[0007] Although the above-described Cu-Cr-Zr-based alloy has excellent heat resistance, when it is exposed to a use environment with a peak temperature of 500°C or more, occasionally, re-solution of precipitate starts for the strength and the conductivity to be reduced and for coarsening of the crystal grain to occur.

[0008] When coarsening of the crystal grains occurs, the propagation speed of the crack increases and the service life of the product may be shortened. In addition, there has been a problem that mechanical properties such as strength and elongation are remarkably deteriorated due to local occurrence of coarsening of crystal grains.

[0009] The present invention has been made in view of the above-described circumstances. An object of the present invention to provide a copper alloy material which is capable of suppressing coarsening of crystal grains, is stable in characteristics and excellent in service life even when it is used in a high temperature environment of 500°C or more.

Solution to Problem

[0010] To solve the above-described technical problem, an aspect of the present invention is directed to a copper alloy material having a composition including: 0.1 mass% or more and 1.5 mass% or less of Cr; 0.05 mass% or more and 0.25 mass% or less of Zr; 0.005 mass% or more and 0.10 mass% or less of P; and a Cu balance including inevitable impurities, wherein the copper alloy material includes a Cr-Zr-P compound containing Cr, Zr and P and an area ratio of the Cr-Zr-P compound is in a range of 0.5 % or more and 5.0 % or less in a structure observation, and the Cr-Zr-P compound is in a form of a needle shape or a granular shape and a length a longest side of the needle shape or the granular shape is 100μm or less (hereinafter, referred as "a copper alloy material of the present invention").

[0011] In the copper alloy material as configured above, the composition includes 0.1 mass% or more and 1.5 mass% or less of Cr; 0.05 mass% or more and 0.25 mass% or less of Zr; 0.005 mass% or more and 0.10 mass% or less of P; and a Cu balance including inevitable impurities. Thus, by precipitating fine precipitates by the aging treatment, strength (hardness) and conductivity can be improved.

[0012] In addition, in the copper alloy material of the present invention, the copper alloy material includes a Cr-Zr-P compound containing Cr, Zr and P and an area ratio of the Cr-Zr-P compound is in a range of 0.5 % or more and 5.0 % or less in a structure observation. Since the Cr-Zr-P compound containing Cr, Zr and P does not disappear even under a high temperature condition of about 1000°C, even when it is used in a high temperature environment, coarsening of crystal grains is suppressed by the grain boundary pinning effect of the Cr-Zr-P compound.

[0013] In addition, the Cr-Zr-P compound is in a form of a needle shape or a granular shape and a length a longest side of the needle shape or the granular shape is 100μm or less. Thus, the above-described pinning effect can be obtained reliably.

[0014] In the copper alloy material of the present invention, it is preferable that after performing a heat treatment at 1000°C for 30 minutes retention, an average size of crystal grains is 200 μm or less.

[0015] In this case, even after performing the heat treatment at 1000°C for 30 minutes retention, crystal grains are not coarsened. Accordingly, mechanical properties and conductivity are stable even in a case of being used under high temperature condition at 500°C or more.

[0016] In the copper alloy material of the present invention, it is preferable that the composition of the copper alloy material further includes Co in a range of 0.02 mass% or more and 0.15 mass% or less, and an atomic ratio of Co to P, $[Co]/[P]$, is in a range of $0.5 \leq [Co]/[P] \leq 5.0$.

[0017] In this case, since the composition of the copper alloy material further includes Co in a range of 0.02 mass% or more and 0.15 mass% or less, CoP compounds and Co_2P compounds exist in the copper alloy material to exhibit the grain boundary pinning effect with the above-described Cr-Zr-P compound. Accordingly, even when it is used in a high temperature environment, coarsening of crystal grains can be suppressed reliably.

[0018] Further, since the atomic ratio of Co to P, $[Co]/[P]$ is set to the range of $0.5 \leq [Co]/[P] \leq 5.0$, solid-solubility of excessive Co and P can be suppressed. Accordingly, reduction of electrical conductivity can be suppressed.

[0019] In addition, in the copper alloy material of the present invention containing Co, it is preferable that a total content of Ti and Hf in the inevitable impurities is 0.10 mass% or less.

[0020] In this case, since the total content of Ti and Hf in the inevitable impurities is set to 0.10 mass% or less, the CoP compounds and the Co_2P compounds are reliably formed. Accordingly, the grain boundary pinning effect can be exhibited effectively; and the coarsening of the crystal grains can be suppressed.

Advantageous Effects of Invention

[0021] According to the present invention, it is possible to provide a copper alloy material capable of suppressing coarsening of crystal grains and having stable characteristics and excellent service life even when it is used in a high temperature environment of 500°C or more.

Brief Description of Drawings

[0022]

FIG. 1 is a flowchart of a method of manufacturing a copper alloy material that is an embodiment of the present invention.

FIG. 2A is a structural observation photograph of Example 2 of the present invention.

FIG. 2B is a structural observation photograph of Comparative Example 1.

FIG. 3A is a structure observation photograph of Example 2 of the present invention after performing the heat treatment at 1000°C for 30 minutes retention time.

FIG. 3B is a structure observation photograph of Comparative Example 1 after performing the heat treatment at 1000°C for 30 minutes retention time.

FIG. 4A is an SEM image in Example 2 of the present invention.

FIG. 4B is an EPMA (Cr) image in Example 2 of the present invention.

FIG. 4C is an EPMA (Zr) image in Example 2 of the present invention.

FIG. 4D is an EPMA (P) image in Example 2 of the present invention.

FIG. 5A is an SEM image in Comparative Example 1 of the present invention.

FIG. 5B is an EPMA (Cr) image in Comparative Example 1 of the present invention.

FIG. 5C is an EPMA (Zr) image in Comparative Example 1 of the present invention.

FIG. 6 is an example of SEM-EPMA images in calculating the area ratio of the Cu-Zr-P compound.

Description of Embodiments

[0023] Hereinafter, a copper alloy material is an embodiment of the present invention will be described.

[0024] The copper alloy material of the present embodiment is a material for a part used in a high temperature environment such as a molding material for casting and a welding part.

[0025] The copper alloy material according to the present embodiment has a composition including: 0.1 mass% or more and 1.5 mass% or less of Cr; 0.05 mass% or more and 0.25 mass% or less of Zr; 0.005 mass% or more and 0.10 mass% or less of P; and a Cu balance including inevitable impurities.

[0026] The copper alloy material of the present embodiment may further include Co in the range of 0.02 mass% or more and 0.15 mass% or less; and the atomic ratio of Co to P, $[Co]/[P]$, may be set in a range of $0.5 \leq [Co]/[P] \leq 5.0$, as needed. In addition, in the case where Co is included, it is preferable that the total content of Ti and Hf in the inevitable impurities is set to 0.10 mass% or less.

[0027] In addition, in the copper alloy material of the present embodiment, the copper alloy material includes a Cr-Zr-P compound (phase) containing Cr, Zr and P and an area ratio of the Cr-Zr-P compound (phase) is in a range of 0.5 % or more and 5.0 % or less in a structure observation, and the Cr-Zr-P compound is in a form of a needle shape or a granular shape and a length a longest side of the needle shape or the granular shape is 100 μ m or less.

[0028] The "Cr-Zr-P compound (phase)" means a phase consisting of Cr-Zr-P compound with a constant content surrounded by grain boundaries.

[0029] The "needle shape" means that the phase has an aspect ratio of 5 or more. The "granular shape" means the phase has an aspect ratio of 1-3.

[0030] The length of the longest side of the Cr-Zr-P compound (phase) in the needle shape can be obtained by measuring the length in the longitudinal direction of the needle shape.

[0031] The length of the longest side of the Cr-Zr-P compound (phase) in the grain shape can be obtained by measuring the length of the granular shape in the direction in which the longest length can be obtained.

[0032] The area ratio of the Cr-Zr-P compound (phase) is obtained by observing the structure of an arbitrary cross section of the copper alloy material (for example, a cross section parallel to the rolling direction) with SEM or the like after microscopic etching and further observing the cross section by performing element analysis with EPMA or the like.

[0033] Furthermore, in the copper alloy material of the present embodiment, the average crystal grain sizes after heat treatment maintained at 1000°C for 30 minutes is set to 200 μ m or less.

[0034] The reasons why the composition of the copper alloy material according to the present embodiment, the crystal structure and the like are defined as described above will be described below.

(Cr: 0.1 mass% or more and 1.5 mass% or less)

[0035] Cr is an element having an action effect that improves strength (hardness) and electrical conductivity by finely precipitating Cr-based precipitates in crystal grains of the parent phase by means of an aging treatment.

[0036] Here, in a case where the content of Cr is less than 0.1 mass%, the precipitation amount during the aging treatment becomes insufficient, and there is a concern that the strength (hardness) improvement effect cannot be sufficiently obtained. In addition, in a case where the content of Cr exceeds 1.5 mass%, there is a concern that coarsened Cr crystalline materials are formed for workability to be reduced.

[0037] On the basis of what has been described above, in the present embodiment, the content of Cr is set in a range of 0.1 mass% or more and 1.5 mass% or less. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the content of Cr is preferably set to 0.3 mass% or more, and the upper limit of the content of Cr is preferably set to 1.0 mass% or less.

(Zr: 0.05 mass% or more and 0.25 mass% or less)

[0038] Zr is an element having an action effect that improves strength (hardness) and electrical conductivity by finely precipitating Zr-based precipitates in the crystal grain boundaries of the parent phase by means of the aging treatment.

[0039] Here, in a case where the content of Zr is less than 0.05 mass%, the precipitation amount during the aging treatment becomes insufficient, and there is a concern that the strength (hardness) improvement effect cannot be sufficiently obtained. In addition, in a case where the content of Zr exceeds 0.25 mass%, there is a concern that electrical conductivity and thermal conductivity may decrease. In addition, even when more than 0.25 mass% of Zr is included, there is a concern that an additional strength improvement effect cannot be obtained.

[0040] On the basis of what has been described above, in the present embodiment, the content of Zr is set in a range of 0.05 mass% or more and 0.25 mass% or less. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the content of Zr is preferably set to 0.07 mass% or more, and the upper limit of the content of Zr is preferably set to 0.15 mass% or less.

(P: 0.005 mass% or more and 0.10 mass% or less)

[0041] By adding P to the Cu-Cr-Zr alloy, the Cr-Zr-P compound (phase) containing Cr, Zr and P is formed. Since the Cr-Zr-P compound (phase) does not disappear in a high temperature condition such as at 1000°C, addition of P exhibits the grain boundary pinning effect even when the alloy is used in a high temperature condition. Accordingly, coarsening of crystal grains can be suppressed.

[0042] Here, in a case where the content of P is less than 0.005 mass%, there is a concern that the Cr-Zr-P compound (phase) is not formed. On the other hand, in a case where the content of P exceeds 0.10 mass%, there is a concern that the electrical conductivity may decrease and the pinning effect may not be exhibited sufficiently.

[0043] On the basis of what has been described above, in the present embodiment, the content of P is set in a range of 0.005 mass% or more and 0.10 mass% or less. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the content of P is preferably set to 0.01 mass% or more, and the upper limit of the content of P is preferably set to 0.05 mass% or less.

(Co: 0.02 mass% or more and 0.15 mass% or less)

[0044] By adding Co, the CoP compound and the Co₂P compounds are formed. The grain boundary pinning effect is exhibited by these the CoP compound and the Co₂P compounds together with the above-described Cr-Zr-P compound (phase). Accordingly, coarsening of crystal grains are reliably suppressed even when the alloy is used in a high temperature condition.

[0045] Here, in a case where the content of Co is less than 0.02 mass%, there is a concern that the CoP compound and the Co₂P compounds are not formed sufficiently and the pinning effect is not improved further even though Co is added. On the other hand, in a case where the content of Co exceeds 0.15 mass%, there is a concern that the CoP compound and the Co₂P compounds are coarsened and the pinning effect is not improved further even though Co is added.

[0046] On the basis of what has been described above, in the present embodiment, the content of Co is set in a range of 0.02 mass% or more and 0.15 mass% or less in a case where Co is included. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the content of Co is preferably set to 0.03 mass% or more, and the upper limit of the content of Co is preferably set to 0.1 mass% or less. In a case where Co is not added intentionally, less than 0.02 mass% of Co may be included as impurities.

(Atomic ratio of Co to P [Co]/[P]: 0.5 or more and 5.0 or less)

[0047] In a case where Co is added, the atomic ratio of Co to P, [Co]/[P] is set in the range of $0.5 \leq [\text{Co}]/[\text{P}] \leq 5.0$. By setting the atomic ratio of Co to P, [Co]/[P] as described above, reduction of electrical conductivity due to solid-solution of excessive Co and P, which do not contribute to formation of the CoP compound and the Co₂P compounds, in the matrix can be suppressed. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the atomic ratio of Co to P, [Co]/[P] is preferably set to 1.0 or more, and the upper limit of the atomic ratio of Co to P, [Co]/[P] is preferably set to 3.0 or less.

(Total content of Ti and Hf: 0.10 mass% or less)

[0048] Furthermore, in the case where Co is added, it is preferable that the total content of Ti and Hf which are inevitable impurities is set to 0.10 mass% or less. Since elements such as Ti and Hf are likely to form a compound with Co, there is a possibility that CoP compound and Co₂P compound can not be formed sufficiently. Therefore, by setting the total content of inevitable impurities of Ti and Hf as described above, the CoP compound and the Co₂P compound can be reliably formed and the pinning effect can be exhibited. In order to reliably exhibit the above-described action effect, it is preferable to set the total content of Ti and Hf as inevitable impurities to 0.03 mass% or less.

(Other Inevitable Impurities: 0.05 mass% or less)

[0049] Meanwhile, examples of the inevitable impurities other than Cr-Zr-P, Co, Ti, and Hf described above include B, Al, Fe, Sn, Zn, Si, Mg, Ag, Ca, Te, Mn, Ni, Sr, Ba, Sc, Y, Ti, Hf, V, Nb, Ta, Mo, W, Re, Ru, Os, Se, Rh, Ir, Pd, Pt, Au, Cd, Ga, In, Li, Ge, As, Sb, Tl, Pb, Be, N, H, Hg, Tc, Na, K, Rb, Cs, Po, Bi, lanthanoids, O, S, C and the like. Since there is a concern that these inevitable impurities may decrease the electrical conductivity and the thermal conductivity, the total amount thereof is preferably set to 0.05 mass% or less.

(Area ratio of Cr-Zr-P compound (phase): 0.5% or more and 5.0% or less)

[0050] In a case where the area ratio of the Cr-Zr-P compound (phase) is less than 0.5%, the crystal grain boundary pinning effect by the Cr-Zr-P compound (phase) becomes insufficient, and there is a concern that coarsening of crystal grains can not be suppressed. On the other hand, when the area ratio of the Cr-Zr-P compound (phase) exceeds 5.0%, there is a concern that workability is decreased.

[0051] On the basis of what has been described above, in the present embodiment, the area ratio of the Cr-Zr-P compound (phase) is set to be 0.5% or more and 5.0% or less. It is preferable that the lower limit of the area ratio of the Cr-Zr-P compound (phase) is 1.0% or more, the upper limit of the area ratio of the Cr-Zr-P compound (phase) is 3.0% or less.

(Length as the longest side of the Cr-Zr-P compound (phase) in a needle shape or a granular shape: 100 μm or less)

[0052] In a case where the length as the longest side of the Cr-Zr-P compound (phase) in a needle shape or a granular shape exceeds 100 μm, there is a concern that the above-described pinning effect may not be exhibited sufficiently.

[0053] On the basis of what has been described above, in the present embodiment, the length as the longest side of the Cr-Zr-P compound (phase) is set to 100 μm or less. It is preferable that the upper limit of the length as the longest side of the Cr-Zr-P compound (phase) is set to 80 μm or less.

(Average crystal grain sizes after heat treatment at 1000°C for 30 minutes retention: 200 μm or less)

[0054] By setting the average crystal grain sizes after heat treatment at 1000°C for 30 minutes retention to 200 μm or less, coarsening of crystal grains can be suppressed reliably when the alloy is used in a high temperature condition such as at 500°C or more. Accordingly, properties such as strength are stabilized.

[0055] On the basis of what has been described above, in the present embodiment, the average crystal grain sizes after heat treatment at 1000°C for 30 minutes retention is set to 200 μm or less.

[0056] Next, a method for manufacturing the casting mold material according to the embodiment of the present invention will be described with reference to a flowchart of FIG. 1.

(Melting and Casting Step S01)

[0057] First, a copper raw material made of oxygen-free copper having a copper purity of 99.99 mass% or higher is loaded into a carbon crucible and is melted using a vacuum melting furnace, thereby obtaining molten copper. Next, the above-described additive elements are added to the obtained molten metal so as to obtain a predetermined concentration, and components are formulated, thereby obtaining a molten copper alloy.

[0058] Here, as raw materials of Cr, Zr, and P which are the additive elements, Cr, and Zr having a high purity are used, and, for example, Cr having a purity of 99.99 mass% or higher is used as a raw material of Cr, Zr having a purity of 99.95 mass% or higher is used as a raw material of Zr, and P having a purity of 99.99 mass% or higher is used as a raw material of P. In addition, Co is added thereto as necessary. Meanwhile, as raw materials of Cr, Zr, Co and P, parent alloys with Cu may also be used.

[0059] In addition, the component-formulated molten copper alloy is injected into a die, thereby obtaining an ingot.

(Homogenization Treatment Step S02)

[0060] Next, a thermal treatment is carried out in order for the homogenization of the obtained ingot.

[0061] Specifically, a homogenization treatment is carried out on the ingot in the atmosphere under conditions of 950°C or higher and 1,050°C or lower for one hour or longer.

(Hot Working Step S03)

[0062] Next, hot rolling with a working percentage of 50% or higher and 99% or lower is carried out on the ingot in a temperature range of 900°C or higher and 1,000°C or lower, thereby obtaining a rolled material. Meanwhile, the method of the hot working may be hot forging. After this hot working, the rolled material is immediately cooled by means of water cooling.

(Solution Treatment Step S04)

[0063] Next, a heating treatment is carried out on the rolled material obtained in the hot working step S03 under

conditions of 920°C or higher and 1,050°C or lower for 0.5 hours or longer and five hours or shorter, thereby carrying out a solution treatment. The heating treatment is carried out, for example, in the atmosphere or an inert gas atmosphere, and as cooling after the heating, water cooling is carried out.

[0064] Alternatively, by performing the inline solution treatment, the hot working step S03 and the solution treatment step S04 may be performed simultaneously.

[0065] Specifically, hot rolling is performed with respect to the ingot at a reduction ratio of 50% or more and 99% or less in a temperature range of 900°C or more and 1000°C or less, and immediately from a temperature of 920°C or more and 1050°C or less, the solution treatment is performed.

(Aging Treatment Step S05)

[0066] Next, after the solution treatment step S04, an aging treatment is carried out, and precipitates such as Cr-based precipitates and Zr-based precipitates are finely precipitated, thereby obtaining an aging treatment material.

[0067] Here, the first aging treatment is carried out under conditions of, for example, 400°C or higher and 530°C or lower for 0.5 hours or longer and five hours or shorter.

[0068] Meanwhile, the thermal treatment method during the aging treatment is not particularly limited, but the thermal treatment is preferably carried out in an inert gas atmosphere. In addition, the cooling method after the heating treatment is not particularly limited, but water cooling is preferably carried out.

[0069] By means of the above-described steps, the copper alloy material that is the present embodiment is manufactured.

[0070] According to the copper alloy material as configured to the above-described present embodiment, the copper alloy material has the composition including: 0.1 mass% or more and 1.5 mass% or less of Cr; 0.05 mass% or more and 0.25 mass% or less of Zr; 0.005 mass% or more and 0.10 mass% or less of P; and a Cu balance including inevitable impurities. Thus, by precipitating fine precipitates by the aging treatment, strength (hardness) and electrical conductivity can be improved.

[0071] In addition, in the present embodiment, the copper alloy material includes a Cr-Zr-P compound containing Cr, Zr and P and an area ratio of the Cr-Zr-P compound is in a range of 0.5 % or more and 5.0 % or less in a structure observation. Thus, the Cr-Zr-P compound (phase) does not disappear even when it is used under a high temperature environment, and coarsening of crystal grains can be suppressed by the pinning effect of these Cr - Zr - P compound.

[0072] In addition, in the present embodiment, the Cr-Zr-P compound is in a form of a needle shape or a grain shape and a length a longest side of the needle shape or the grain shape is 100 μm or less. Thus, the above-described pinning effect can be obtained reliably.

[0073] Moreover, in the present embodiment, since the average crystal grain sizes after heat treatment at 1000°C for 30 minutes retention is set to 200 μm or less. Thus, crystal grains are not coarsened and mechanical property and electrical conductivity are stabilized even when it is used in a high temperature environment of 500°C or more.

[0074] In addition, in the present embodiment, in the case where Co is further included in the range of 0.02 mass% or more and 0.15 mass% or less, and the atomic ratio of Co to P, $[Co]/[P]$ is $0.5 \leq [Co]/[P] \leq 5.0$, the CoP compound and the Co₂P compound are formed, and the crystal grain boundary pinning effect is exhibited together with the above Cr-Zr-P compound (phase). Accordingly, coarsening of crystal grains is suppressed reliably even when used under a high temperature environment. In addition, since the atomic ratio of Co to P, $[Co]/[P]$ is set to $0.5 \leq [Co]/[P] \leq 5.0$, solid-solubility of excessive Co and P can be suppressed. Accordingly, reduction of electrical conductivity can be suppressed.

[0075] In addition, in the case where the composition of the copper alloy material further includes Co, by setting the total content of Ti and Hf in the inevitable impurities to 0.10 mass% or less, the CoP compounds and the Co₂P compounds are reliably formed. Accordingly, the grain boundary pinning effect can be exhibited effectively; and the coarsening of the crystal grains can be suppressed.

[0076] Hitherto, the embodiment of the present invention has been described, but the present invention is not limited thereto and can be appropriately modified in the scope of the technical concept of the invention.

Examples

[0077] Hereinafter, the results of confirmation tests carried out in order to confirm the effects of the present invention will be described.

[0078] A copper raw material made of oxygen-free copper having a copper purity of 99.99 mass% or higher was prepared, was loaded into a carbon crucible, and was melted using a vacuum melting furnace (with a degree of vacuum of 10^{-2} Pa or lower), thereby obtaining molten copper. A variety of additive elements were added to the obtained molten copper so as to formulate a component composition shown in Table 1, the component composition was maintained for five minutes, and then the molten copper alloy was injected into a cast iron die, thereby obtaining an ingot. The sizes of the ingot were set to a width of approximately 80 mm, a thickness of approximately 50 mm, and a length of approximately

130 mm.

[0079] Meanwhile, as a raw material of Cr which was an additive element, Cr having a purity of 99.99 mass% or higher was used, and as a raw material of Zr, Zr having a purity of 99.95 mass% or higher was used, was used.

[0080] Next, a homogenization treatment was carried out in the atmosphere under conditions of 1,000°C for one hour, and then hot rolling was carried out. The rolling reduction in the hot rolling was set to 80%, thereby obtaining a hot-rolled material having a width of approximately 100 mm, a thickness of approximately 10 mm, and a length of approximately 520 mm.

[0081] In the present Examples, the cooling at the cooling rates shown in Table 1 performed after the end of the hot rolling functioned as the solution treatment as well. In other words, the so-called inline solution treatment was performed.

[0082] Next, a aging treatment was carried out under conditions of 500 (± 15)°C for three hours. By following above-described procedures, the copper alloy materials were obtained.

[0083] For the obtained copper alloy material, the structure of the copper alloy material after the aging treatment was observed, and the Cr-Zr-P compound (phase) was evaluated. In addition, the electrical conductivity and the tensile strength of the copper alloy materials after the aging treatment were measured.

[0084] In addition, the heat treatment at 1000°C for 30 minutes retention was performed on the copper alloy materials after the aging treatment; and after water cooling these copper alloy materials, the average crystal grain sizes and the tensile strength were measured.

[0085] FIGS. 2A and 2B show the structure observation pictures of the copper alloy materials of Example 2 of the present invention and Comparative Example 1, respectively, after the above-described aging treatment and before the heat treatment at 1000°C for 30 minutes retention.

[0086] Similarly, FIG. 3A and FIG. 3B show the structure observation pictures of the copper alloy materials of Example 2 of the present invention and Comparative Example 1, respectively, after the above-described aging treatment and the heat treatment at 1000°C for 30 minutes retention.

(Composition analysis)

[0087] The component composition of the obtained copper alloy material was measured by ICP-MS analysis. The measurement results are shown in Table 1.

(Cr-Zr-P compound (phase))

[0088] A sample of 10 mm \times 15 mm from the central portion of the plate width was cut out from the obtained thickness of the copper alloy material and the surface in the rolling direction (RD direction) was polished and then micro etching was performed.

[0089] The sample was observed by SEM. In the SEM-EPMA image (field of view of 250 μm \times 250 μm), the region where the Cr, Zr, and P concentrations were higher than that of the matrix phase was defined as "Cr-Zr-P compound (phase)." Then, the length of the longest side was measured. Then, the area ratio of the Cu-Zr-P compound was determined by the following formula.

$$\text{Area ratio} = (\text{Area occupied by Cr-Zr-P compound (phase)}) / (250 \mu\text{m} \times 250 \mu\text{m})$$

[0090] FIGS. 4A to 4D show SEM-EPMA images of Example 2 of the present invention, and FIGS. 5A to 5C show SEM-EPMA images of Comparative Example 1. In addition, FIG. 6 shows an example of SEM-EPMA images (visual field of 250 μm \times 250 μm) in calculating the area ratio of the Cu-Zr-P compound.

(Average size of crystal grains)

[0091] A sample of 10 mm \times 15 mm from the central portion of the plate width was cut out from the obtained thickness of the copper alloy material and the surface in the rolling direction (RD direction) was polished and then micro etching was performed.

[0092] This sample was observed and the average crystal grain size was measured by the intercept method prescribed in JIS H 0501.

(Conductivity)

[0093] Using a SIGMA TEST D 2.068 (probe diameter ϕ 6 mm) manufactured by Nippon Felster Co., Ltd., the cross

section center portion of a sample of 10 × 15 mm was measured three times, and the average value thereof was obtained.

(Tensile Strength)

- 5 **[0094]** JIS Z 2241 No. 2 test piece was taken with the rolling direction as the pulling direction and subjected to the test using a 100 kN tensile tester.

[Table 1]

		Composition (mass%)							[Co]/ [P]	Cooling rate after the solution treatment (°C/min)
		Cr	Zr	P	Co	Ti	Hf	Cu		
Example of the present invention	1	0.35	0.14	0.02	-	-	-	balance	0.0	31
	2	0.40	0.14	0.02	0.06	-	-	balance	3.0	1000
	3	0.55	0.07	0.02	-	-	-	balance	0.0	1000
	4	1.00	0.08	0.09	-	-	-	balance	0.0	1000
	5	1.40	0.08	0.05	0.03	-	-	balance	0.6	1000
	6	0.90	0.19	0.03	0.14	-	-	balance	4.7	1000
Comparative Example	1	0.70	0.06	-	-	-	-	balance	-	1000
	2	1.50	0.23	0.08	-	-	-	balance	0.0	13
	3	0.70	0.60	0.06	-	-	-	balance	0.0	800
	4	1.00	0.09	0.03	0.18	-	-	balance	6.0	800
	5	0.40	0.14	0.04	0.15	0.10	0.11	balance	3.75	1000

[Table 2]

		Cr-Zr-P compound in a needle shape or a granular shape			Electrical conductivity (%IACS)	Tensile strength after the aging treatment (MPa)	After the heat treatment at 1000°C for 30 minutes retention	
		Presence or Absence	Length of the longest side (μm)	Area ratio (%)			Average size of crystal grains (μm)	Tensile strength (MPa)
Example of the present invention	1	Present	20	1.20	77.0	435	280	398
	2	Present	25	0.80	75.0	430	263	412
	3	Present	24	1.20	82.0	435	78	424
	4	Present	35	1.40	79.0	443	39	401
	5	Present	51	3.10	83.0	461	51	433
	6	Present	74	4.50	72.0	452	43	427
Comparative Example	1	Absent	-	-	87.0	434	870	341
	2	Present	-	6.50	77.0	463	530	378
	3	Present	160	2.30	63.0	438	510	388
	4	Present	27	0.60	65.0	451	125	412
	5	Present	22	0.10	73.0	442	610	361

[0095] FIGS. 2A and 3A, in Examples 1 to 6 of the present invention, grain coarsening was suppressed even after

being placed in a high-temperature environment.

[0096] On the other hand, as shown in FIGS. 2B and 3B, in Comparative Examples 1 to 3 and 5, the crystal grains coarsened after being placed in a high-temperature environment. In Comparative Example 4, coarsening of crystal grains was not observed, but the conductivity was lower than that of Examples 1 to 6 of the present invention (described later).

[0097] In Comparative Example 1 in which P was not added, Cr-Zr-P compounds (phases) in a needle shape or a granular shape were not produced, so that the tensile strength significantly decreased after the heat treatment at 1000°C for 30 minutes.

[0098] In Comparative Example 2 in which the area ratio of the Cr-Zr-P compound (phase) in a needle shape or a granular shape exceeded the range of the scope of the present invention; and the tensile strength significantly decreased after the heat treatment at 1000 °C for 30 minutes.

[0099] In Comparative Example 3 in which the content of Zr exceeded the scope of the range of the present invention, the electrical conductivity was low and the tensile strength was significantly decreased after the heat treatment at 1000°C for 30 minutes.

[0100] In Comparative Example 4 in which the content of Co exceeded the scope of the range of the present invention, the conductivity was low.

[0101] In Comparative Example 5 in which the area ratio of the Cr-Zr-P compound (phase) in a needle shape or a granular shape was less than the range of the scope of the present invention, and the tensile strength was significantly decreased after the heat treatment at 1000°C for 30 minutes.

[0102] In contrast, in Examples 1-6 of the present invention, electrical conductivity was high and there was no significant reduction of the tensile strength even after the heat treatment at 1000°C for 30 minutes. In addition, in Examples 3-6 of the present invention, in which the crystal grain size was set to 200 μm or less after the heat treatment at 1000°C for 30 minutes, the reduction of the tensile strength after the heat treatment at 1000°C for 30 minutes was suppressed.

[0103] From the above-described results, according to the example of the present invention, it is confirmed that a copper alloy material capable of suppressing coarsening of crystal grains and having stable properties and excellent service life even when it is used under a high temperature environment of 500°C or more was provided.

INDUSTRIAL APPLICABILITY

[0104] It is possible to suppress property deterioration of a part made of the Cu-Cr-Zr-based alloy in a high temperature environment and prolong the service life of the casting molding material, the welding part and the like.

Claims

1. A copper alloy material having a composition including:

0.1 mass% or more and 1.5 mass% or less of Cr;
0.05 mass% or more and 0.25 mass% or less of Zr;
0.005 mass% or more and 0.10 mass% or less of P; and
a Cu balance including inevitable impurities,

wherein the copper alloy material includes a Cr-Zr-P compound containing Cr, Zr and P and an area ratio of the Cr-Zr-P compound is in a range of 0.5 % or more and 5.0 % or less in a structure observation, and the Cr-Zr-P compound is in a form of a needle shape or a granular shape and a length a longest side of the needle shape or the granular shape is 100μm or less.

2. The copper alloy material according to Claim 1,

wherein, after performing a heat treatment at 1000°C for 30 minutes retention, an average size of crystal grains is 200 μm or less.

3. The copper alloy material according to Claim 1 or 2,

wherein, the composition of the copper alloy material further includes Co in a range of 0.02 mass% or more and 0.15 mass% or less, and an atomic ratio of Co to P, $[Co]/[P]$, is in a range of $0.5 \leq [Co]/[P] \leq 5.0$.

4. The copper alloy material according to Claim 3, wherein a total content of Ti and Hf in the inevitable impurities is 0.10 mass% or less.

FIG. 1

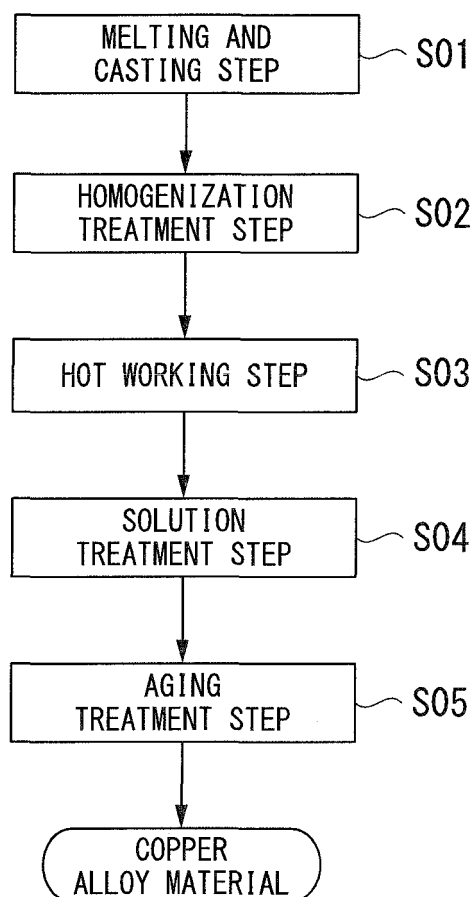


FIG. 2A

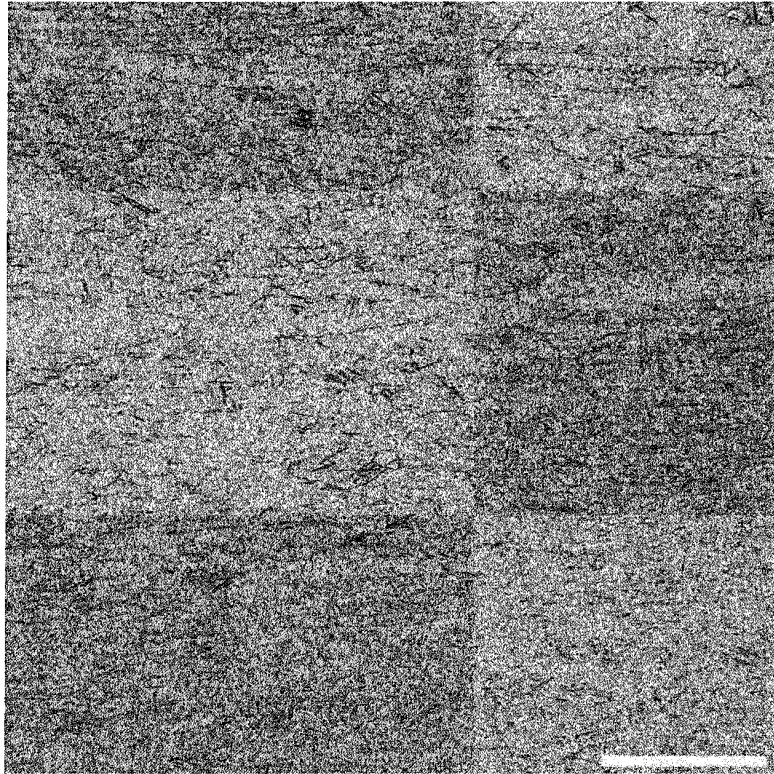


FIG. 2B

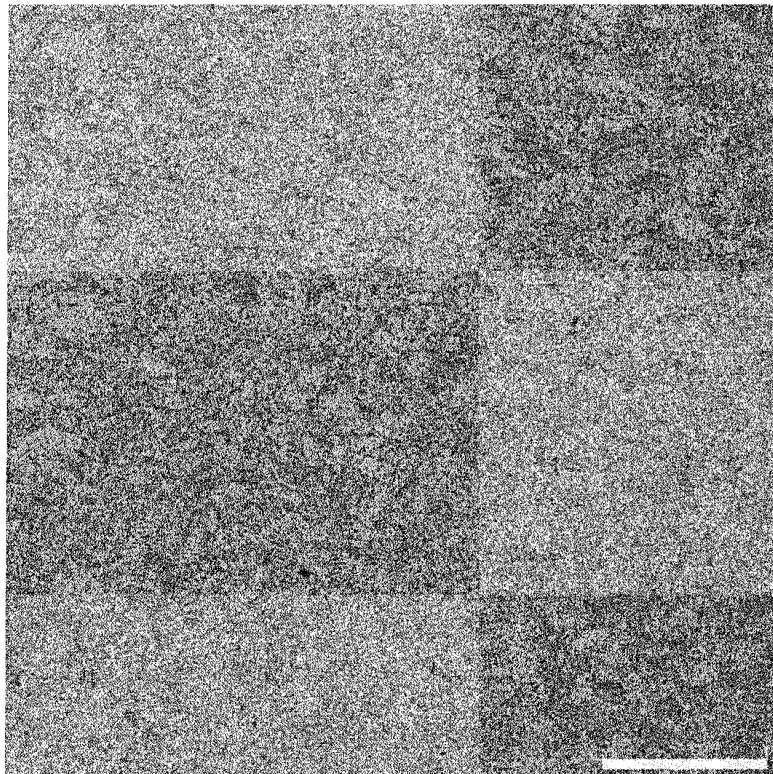


FIG. 3A

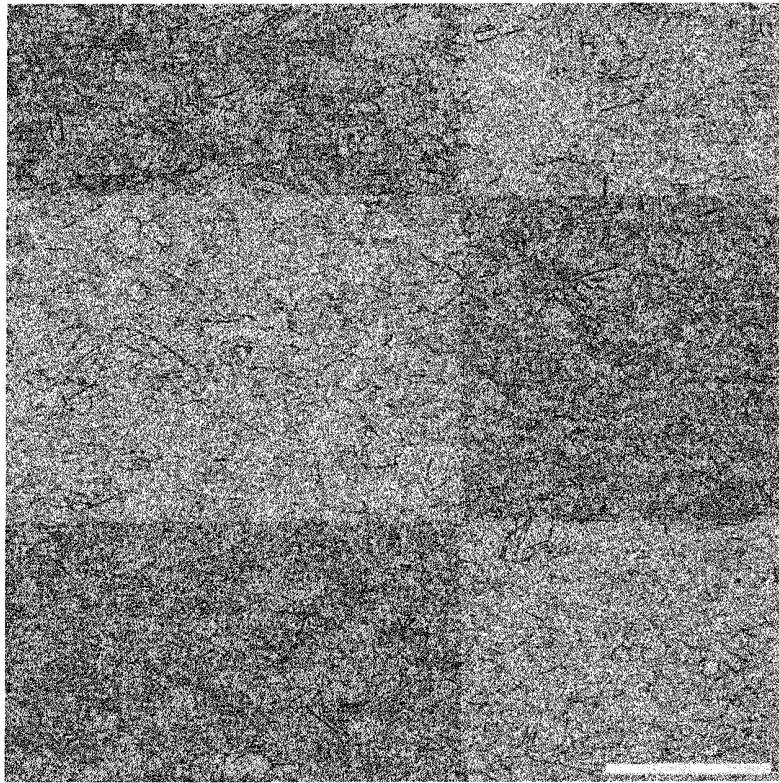


FIG. 3B

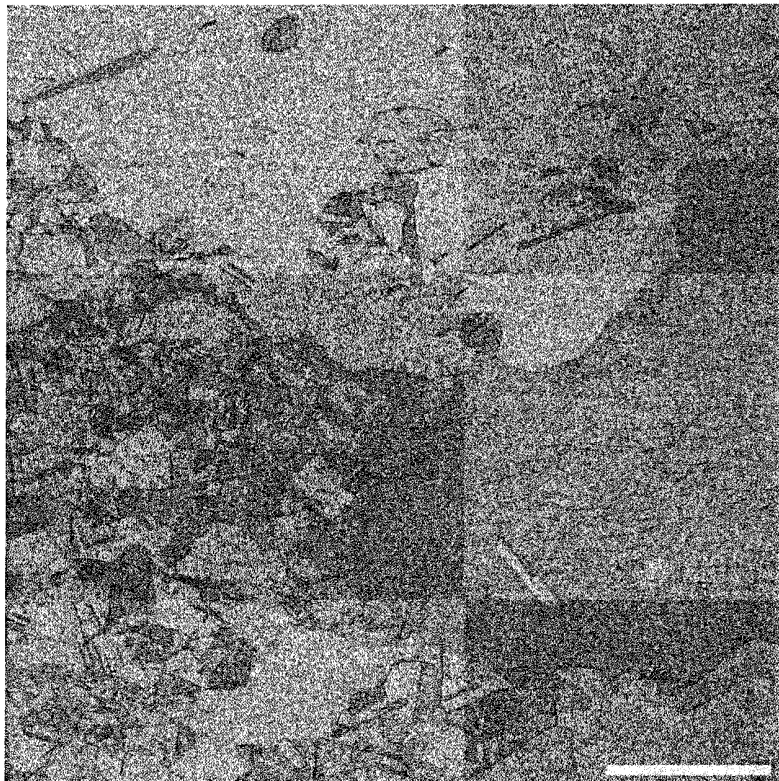


FIG. 4A

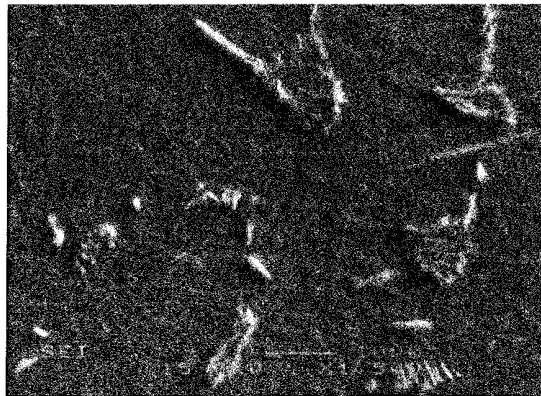


FIG. 4B

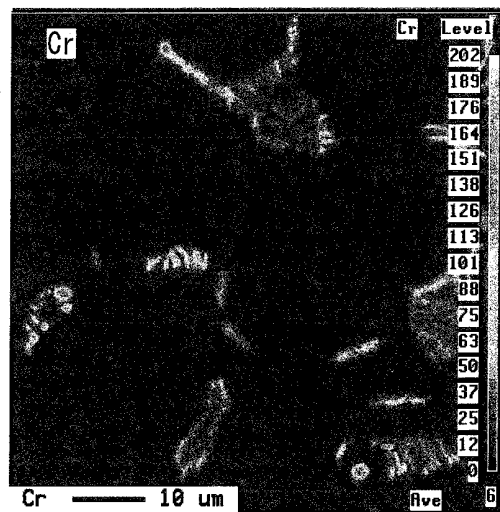


FIG. 4C

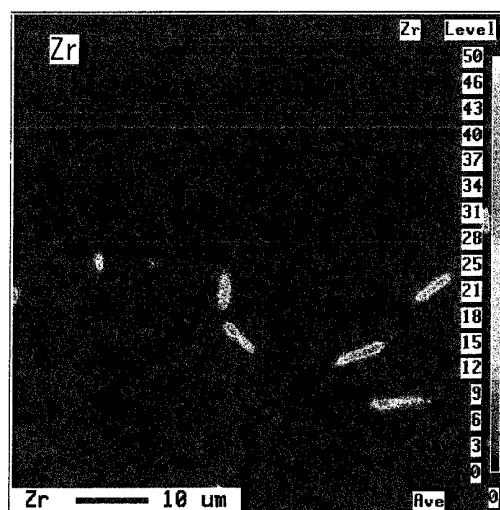


FIG. 4D

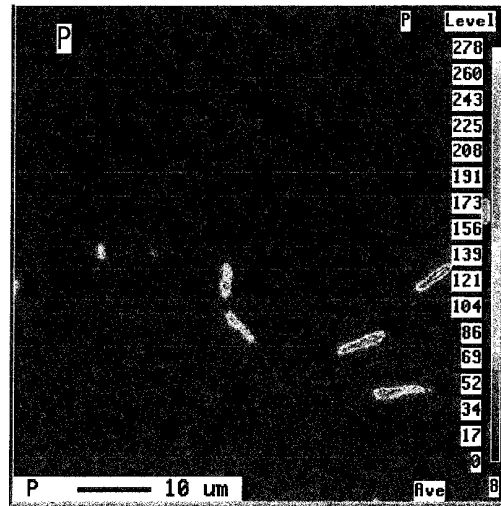


FIG. 5A

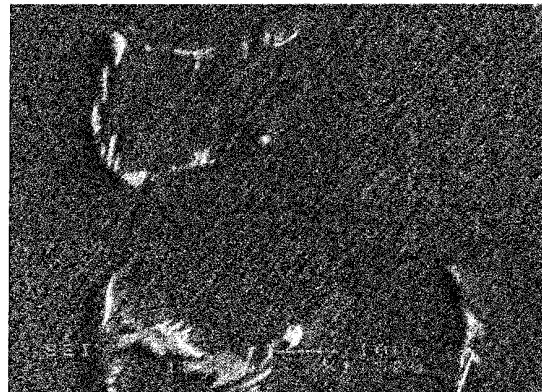


FIG. 5B

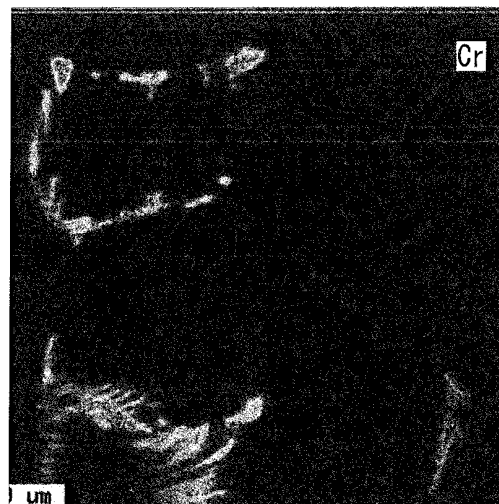


FIG. 5C

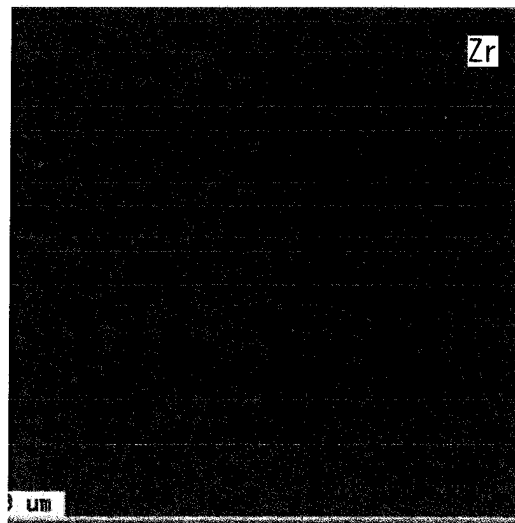
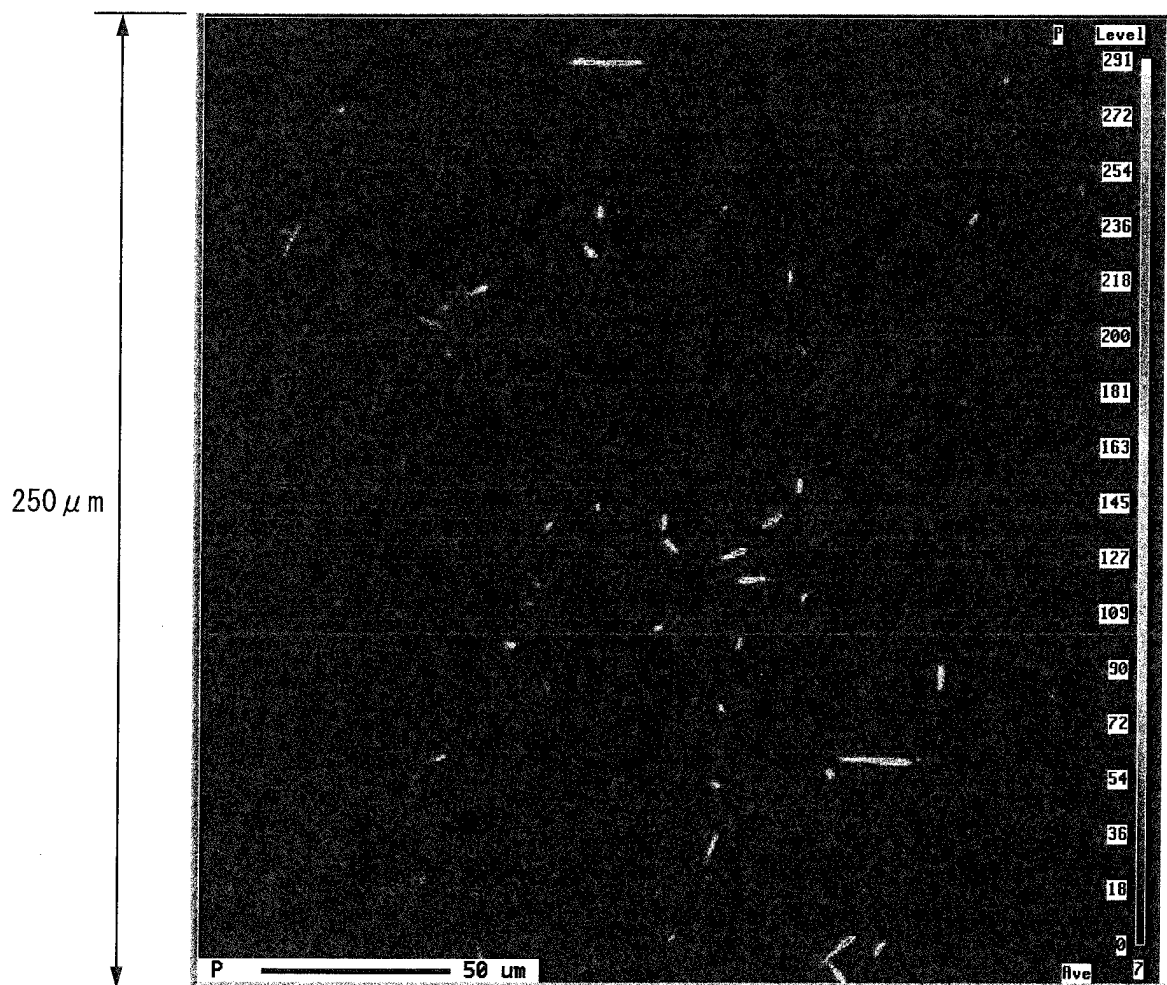


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/080082

A. CLASSIFICATION OF SUBJECT MATTER

C22C9/00(2006.01)i, C22F1/08(2006.01)i, C22F1/00(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C9/00, C22F1/08, C22F1/00

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2016

Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 1-309935 A (Kobe Steel, Ltd.),	1-2
A	14 December 1989 (14.12.1989), examples (Family: none)	3-4
A	JP 5-70867 A (Mitsubishi Materials Corp.), 23 March 1993 (23.03.1993), claim 4; examples (Family: none)	1-4
A	JP 63-143229 A (Nippon Mining Co., Ltd.), 15 June 1988 (15.06.1988), claim 2; examples (Family: none)	1-4

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

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Date of the actual completion of the international search
22 December 2016 (22.12.16)Date of mailing of the international search report
10 January 2017 (10.01.17)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/080082

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 102912178 A (Henan University of Science and Technology), 06 February 2013 (06.02.2013), claim 1 (Family: none)	1-4

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP S62182238 A [0006]
- JP S62182239 A [0006]
- JP H04120438 B [0006]