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(54) **CASTING MOLD MATERIAL AND CU-CR-ZR-AL ALLOY STARTING MATERIAL**

(57) A casting mold material used in casting a metal material has a composition including 0.3 mass% or more and less than 0.5 mass% of Cr, 0.01 mass% or more and 0.15 mass% or less of Zr, 0.1 mass% or more and less

than 2.0 mass% of Al; and a Cu balance including inevitable impurities and has precipitates in a needle shape or precipitates in a plate shape.

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Description

Technical Field

[0001] The present invention relates to a casting mold material used in casting metal such as steel materials and a Cu-Cr-Zr-Al alloy material suitable for the casting mold material.

[0002] Priority is claimed on Japanese Patent Application No. 2015-203581, filed on October 15, 2015, the content of which is incorporated herein by reference.

Background Art

[0003] In the related art, for casting mold materials used in casting steel materials and the like, there is a demand for excellent characteristics such as high-temperature strength enabling the casting mold materials to withstand strong thermal stress, high-temperature elongation enabling the casting mold materials to withstand severe thermal fatigue environments, and wear resistance (hardness) at a high temperature. Therefore, Cu-Cr-Zr-based alloys being favorable in terms of the above-described characteristics are used as continuous casting mold materials. It is known that the above-described characteristics are enhanced by further adding additive elements to the Cu-Cr-Zr-based alloys.

[0004] In addition, in mold materials for electromagnetic stirring, the depth of penetration δ of a magnetic field is represented by the following expression where the magnetic permeability is represented by μ , the frequency of the applied magnetic field is represented by f , and the electrical conductivity is represented by σ .

$$\delta = (1/\pi \cdot \mu \cdot f \cdot \sigma)^{0.5}$$

[0005] As is clear from this expression, the electrical conductivity σ of the mold material is preferably low in order to increase the depth δ of the magnetic field. However, there is a concern that an excess decrease in the electrical conductivity σ may decrease the thermal conductivity and cause insufficient cooling.

[0006] Therefore, for mold materials, it is proposed to adjust the electrical conductivity σ to approximately 30% to 60% IACS by adding additive elements other than Cr and Zr thereto.

[0007] For example, PTL 1 discloses a mold material for precipitation hardening-type continuous casting which contains Cr: 0.3% to 1.5% and Zr: 0.03% to 0.6% in terms of mass ratio and to which Al and an element such as Si, Ni, Sn, Zn, or Mn are further added.

[0008] In addition, PTL 2 discloses a mold material for metal casting which contains Cr: 0.3 to 1.2 wt% and Zr: 0.05 to 0.25 wt% and to which Sn, Al, Ag, Ni, Ti, Co, Fe, and the like are further added.

[0009] In the Cu-Cr-Zr-based alloys described in PTL 1 and 2, when a supersaturated solid solution of Cr and Zr which turns into a non-equilibrium phase by a solution treatment is formed, and Cr and Zr are dispersed and precipitated by the subsequent aging treatment, mechanical characteristics such as high-temperature strength, high-temperature elongation, and wear resistance (hardness), electrical conductivity, and thermal conductivity are improved. Meanwhile, in order to form the above-described supersaturated solid solution, it is necessary to carry out rapid cooling after the solution treatment.

Citation List

Patent Literature

[0010]

[PTL 1] Japanese Examined Patent Application, Second Publication No. S62-041302

[PTL 2] Japanese Unexamined Patent Application, First Publication No. H05-339688

Summary of Invention

Technical Problem

[0011] Meanwhile, generally, casting mold materials are used after the durability is improved by thermal spraying a Ni-Cr alloy or the like having excellent thermal resistance and wear resistance on the surface thereof. When the above-described thermal spraying treatment is carried out, since the casting mold materials are slowly cooled instead of water

cooling or the like after a thermal treatment is carried out in a high temperature range of, for example, approximately 1,000°C, there has been a problem in that the strength (hardness) or the electrical conductivity does not sufficiently improve even when an aging treatment is carried out after the thermal spraying treatment.

[0012] In detail, in a case where the casting mold materials are slowly cooled to, for example, 800°C at a cooling rate of 25°C/min or lower after a thermal treatment is carried out in a high temperature range of approximately 1,000°C, granular Cr-containing precipitates (Cr-based precipitates) and granular Zr-containing precipitates (Zr-based precipitates) are precipitated during the slow cooling. In addition, in the subsequent aging treatment, Cr and Zr which have formed solid solutions around these granular precipitates as nuclei are precipitated, and thus the precipitates grow and coarsen, it becomes impossible to sufficiently ensure fine precipitates which contribute to the precipitation strengthening mechanism, and it becomes impossible to improve the strength (hardness).

[0013] The present invention has been made in consideration of the above-described circumstances, and an object of the present invention is to provide a casting mold material capable of sufficiently improving the strength (hardness) and the electrical conductivity by means of the subsequent aging treatment even in a case where the casting mold material is slowly cooled after a thermal spraying treatment and a Cu-Cr-Zr-Al alloy material suitable for this casting mold material.

Solution to Problem

[0014] In order to achieve the above-described object, a casting mold material according to an aspect of the present invention (hereinafter, referred to as "the casting mold material of the present invention") used in casting a metal material, the casting mold material including a composition includes: 0.3 mass% or more and less than 0.5 mass% of Cr; 0.01 mass% or more and 0.15 mass% or less of Zr; 0.1 mass% or more and less than 2.0 mass% of Al; and a Cu balance including inevitable impurities, wherein the casting mold material comprises precipitates in a needle shape or precipitates in a plate shape.

[0015] In the casting mold material having this constitution, since the composition includes 0.3 mass% or more and less than 0.5 mass% of Cr, 0.01 mass% or more and 0.15 mass% or less of Zr, 0.1 mass% or more and less than 2.0 mass% of Al, and a Cu balance including inevitable impurities, it is possible to improve the strength (hardness) and the electrical conductivity by precipitating fine precipitates by means of an aging treatment. In addition, it is possible to adjust the electrical conductivity to approximately 30% to 60% IACS, and the casting mold material is particularly suitable for mold materials in electromagnetic stirring uses.

[0016] In addition, since the casting mold material of the present invention has precipitates in a needle shape or precipitates in a plate shape containing Cr, granular precipitates being formed during slow cooling after a thermal spraying treatment are suppressed. Therefore, in the aging treatment after the thermal spraying treatment, Cr and Zr being precipitated around granular precipitates as nuclei are suppressed, it is possible to sufficiently disperse the fine precipitates, and it is possible to sufficiently improve the strength (hardness) and the electrical conductivity by means of the precipitation strengthening mechanism.

[0017] Here, in the casting mold material of the present invention, a maximum size of the precipitates in a needle shape or the precipitates in a plate shape is preferably 100 μm or less. Meanwhile, the maximum size of the precipitates in a needle shape or the precipitates in a plate shape refers to the diameter of the minimum circumscribed circle drawn for the observed precipitates.

[0018] In this case, the maximum size of the precipitates in a needle shape or the precipitates in a plate shape is set to be as relatively small as 100 μm or less, and thus Cr sufficiently forms a solid solution in the parent phase of Cu, it is possible to sufficiently disperse the fine precipitates during the subsequent aging treatment, and it is possible to sufficiently improve the strength (hardness) and the electrical conductivity by means of a precipitation strengthening mechanism.

[0019] In addition, the composition of the casting mold material according to the present invention preferably further includes 0.01 mass% or more and 0.15 mass% or less of one or more elements selected from Fe, Si, Co, and P as a total.

[0020] In this case, since the casting mold material includes elements of Fe, Si, Co, and P in the above-described range, granular precipitates being formed during slow cooling after the thermal spraying treatment are suppressed, and the generation of the precipitates in a needle shape or precipitates in a plate shape containing Cr is accelerated. Therefore, it is possible to sufficiently precipitate fine Cr-based and Zr-based precipitates by means of the aging treatment after the thermal spraying treatment, and it is possible to reliably improve the strength (hardness) and the electrical conductivity.

[0021] The Cu-Cr-Zr-Al alloy material according to the present invention includes: 0.3 mass% or more and less than 0.5 mass% of Cr; 0.01 mass% or more and 0.15 mass% or less of Zr; 0.1 mass% or more and less than 2.0 mass% of Al; and a Cu balance including inevitable impurities, wherein the Cu-Cr-Zr-Al alloy material satisfies a relationship of $B/A > 1.1$ where an electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is maintained at 1,000°C for one hour and is then cooled from 1,000°C to 600°C at a cooling rate of 10°C/min is defined by A and an electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is further maintained at 500°C for three hours is defined by B.

[0022] In the Cu-Cr-Zr-Al alloy material having the above-described constitution, since the Cu-Cr-Zr-Al alloy material satisfies a relationship of $B/A > 1.1$ where the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is maintained at 1,000°C for one hour and is then cooled from 1,000°C to 600°C at a cooling rate of 10°C/min is defined by A and the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is further maintained at 500°C for three hours is defined by B, even in a case where the Cu-Cr-Zr-Al alloy material is slowly cooled from 1,000°C to 600°C at a cooling rate of 10°C/min, the electrical conductivity is improved by the subsequent thermal treatment at 500°C for three hours, and it becomes possible to improve the strength by means of precipitation hardening.

[0023] Therefore, the Cu-Cr-Zr-Al alloy material is particularly suitable for the above-described casting mold material.

[0024] Here, the composition of the Cu-Cr-Zr-Al alloy material according to the present invention preferably further includes 0.01 mass% or more and 0.15 mass% or less of one or more elements selected from Fe, Si, Co, and P as a total.

[0025] In this case, since the Cu-Cr-Zr-Al alloy material includes elements of Fe, Si, Co, and P in the above-described range, even in a case where the Cu-Cr-Zr-Al alloy material is heated to a high temperature range of, for example, approximately 1,000°C and is then slowly cooled, it is possible to suppress unnecessary precipitation of Cr and Zr and thus ensure the solid solution amount of Cr and Zr. Therefore, it is possible to sufficiently precipitate fine precipitates by means of the aging treatment after the slow cooling, and it is possible to reliably improve the strength (hardness) and the electrical conductivity.

Advantageous Effects of Invention

[0026] According to the present invention, it is possible to provide a casting mold material capable of sufficiently improving the strength (hardness) and the electrical conductivity by means of the subsequent aging treatment even in a case where the casting mold material is slowly cooled after a thermal spraying treatment and a Cu-Cr-Zr-Al alloy material suitable for this casting mold material.

Brief Description of Drawings

[0027]

FIG. 1 is a flowchart of a method for manufacturing a casting mold material that is an embodiment of the present invention.

FIG. 2 illustrates structural observation photographs of Invention Example 2 and Comparative Example 4.

FIG. 3(a) is a view illustrating precipitates in a needle shape or precipitates in a plate shape observed in an SEM image in Invention Example 2.

FIG. 3(b) is a view illustrating an element mapping result of the precipitates in a needle shape or the precipitates in a plate shape observed in EPMA (Cr) in Invention Example 2.

FIG. 3(c) is a view illustrating the element mapping result of the precipitates in a needle shape or the precipitates in a plate shape observed in EPMA (Zr) in Invention Example 2.

FIG. 4 is an explanatory view illustrating a Vickers hardness measurement location in the examples.

Description of Embodiments

[0028] Hereinafter, a casting mold material and a Cu-Cr-Zr-Al alloy material that are an embodiment of the present invention will be described.

[0029] The casting mold material that is the present embodiment is used as a continuous casting die for continuously casting steel materials and the like. In addition, in the present embodiment, the Cu-Cr-Zr-Al alloy material is used as a material for the casting mold material.

[0030] The casting mold material and the Cu-Cr-Zr-Al alloy material that are the present embodiment have a composition including 0.3 mass% or more and less than 0.5 mass% of Cr, 0.01 mass% or more and 0.15 mass% or less of Zr, 0.1 mass% or more and less than 2.0 mass% of Al, and a Cu balance including inevitable impurities, and further including 0.01 mass% or more and 0.15 mass% or less of one or more elements selected from Fe, Si, Co, and P as a total.

[0031] Here, the reasons for specifying the component compositions of the casting mold material and the Cu-Cr-Zr-Al alloy material as described above will be described below.

(Cr: 0.3 mass% or more and less than 0.5 mass%)

[0032] 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.

[0033] Here, in a case where the content of Cr is less than 0.3 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 is 0.5 mass% or more, for example, when the casting mold material and the Cu-Cr-Zr-Al alloy material are slowly cooled from a high temperature range of approximately 1,000°C to a temperature of 800°C or lower at a cooling rate of 25°C/min or lower, granular Cr-based and Zr-based precipitates are precipitated, these granular precipitates further grow in the aging treatment after a slow cooling, and thus there is a concern that it may become impossible to ensure fine precipitates that contribute to the precipitation strengthening mechanism.

[0034] On the basis of what has been described above, in the present embodiment, the content of Cr is set in a range of 0.3 mass% or more and less than 0.5 mass%. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the content of Cr is preferably set to 0.35 mass% or more, and the upper limit of the content of Cr is preferably set to 0.45 mass% or less.

(Zr: 0.01 mass% or more and 0.15 mass% or less)

[0035] 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.

[0036] Here, in a case where the content of Zr is less than 0.01 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 0.15 mass%, there is a concern that electrical conductivity and thermal conductivity may decrease. In addition, even when more than 0.15 mass% of Zr is included, there is a concern that an additional strength improvement effect cannot be obtained.

[0037] On the basis of what has been described above, in the present embodiment, the content of Zr is set in a range of 0.01 mass% or more and 0.15 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 0.05 mass% or more, and the upper limit of the content of Zr is preferably set to 0.13 mass% or less.

Al: 0.1 mass% or more and less than 2.0 mass%

[0038] Al is an element having an action effect that decreases electrical conductivity by forming a solid solution in copper alloys. Therefore, it is possible to adjust the electrical conductivity of the casting mold material to approximately 30% to 60% IACS by controlling the amount of Al added, and the casting mold material becomes particularly suitable for mold materials in electromagnetic stirring uses.

[0039] Here, in a case where the content of Al is less than 0.1 mass%, it becomes difficult to suppress the electrical conductivity at a low level, and there is a concern that it may become impossible to ensure the depth of penetration of a magnetic field. In addition, in a case where the content of Al is 2.0 mass% or more, there is a concern that the electrical conductivity may significantly decrease and the thermal conductivity may become insufficient.

[0040] On the basis of what has been described above, in the present embodiment, the content of Al is set in a range of 0.1 mass% or more and less than 2.0 mass%. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the content of Al is preferably set to 0.5 mass% or more, and the upper limit of the content of Al is preferably set to 1.5 mass% or less.

(One or More Elements Selected from Fe, Si, Co, and P: Total of 0.01 mass% or more and 0.15 mass% or less)

[0041] Elements of Fe, Si, Co, and P have an action effect that suppresses granular Cr-based and Zr-based precipitates being precipitated and accelerates the precipitation of precipitates in a needle shape or precipitates in a plate shape containing Cr when, for example, the casting mold material and the Cu-Cr-Zr-Al alloy material are slowly cooled from a high temperature range of approximately 1,000°C to a temperature of 800°C or lower at a cooling rate of 25°C/min or lower.

[0042] Here, in a case where the total content of one or more elements selected from Fe, Si, Co, and P is less than 0.01 mass%, there is a concern that the above-described action effect cannot be exhibited. On the other hand, in a case where the total content of one or more elements selected from Fe, Si, Co, and P exceeds 0.15 mass%, there is a concern that the electrical conductivity and the thermal conductivity may decrease.

[0043] On the basis of what has been described above, in the present embodiment, the total content of one or more elements selected from Fe, Si, Co, and P is set in a range of 0.01 mass% or more and 0.15 mass% or less. Meanwhile, in order to reliably exhibit the above-described action effect, the lower limit of the total content of one or more elements selected from Fe, Si, Co, and P is preferably set to 0.02 mass% or more, and the upper limit of the total content of one or more elements selected from Fe, Si, Co, and P is preferably set to 0.1 mass% or less.

(Other Inevitable Impurities: 0.05 mass% or less)

[0044] Meanwhile, examples of the inevitable impurities other than Cr, Zr, Al, P, Fe, Si, and Co described above include B, Ag, Sn, Zn, Ti, 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, lanthanides, 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.

[0045] In addition, the casting mold material that is the present embodiment has precipitates in a needle shape or precipitates in a plate shape containing Cr in the parent phase of Cu. The maximum size of these precipitates in a needle shape or precipitates in a plate shape is set to 100 μm or less.

[0046] Whether or not "the precipitates in a needle shape or the precipitates in a plate shape containing Cr are present" is determined on the basis of a standard described below.

[0047] An observation sample is taken from the casting mold material, structural observation is carried out on a polished cross section after a polishing treatment using a scanning electron microscope, and the presence or absence of precipitates in a needle shape or precipitates in a plate shape containing Cr is confirmed.

[0048] Whether or not "Cr is contained" is detectable from an analysis of the composition by means of EPMA.

[0049] Whether or not "the precipitates are precipitates in a needle shape or precipitates in a plate shape" is determined from the shapes of precipitates on a cross section which serves as the target of the structural observation. First, the longest diameter of the precipitates is obtained as the longitudinal direction size from the shapes of the precipitates. In addition, among diameters in a direction intersecting the longitudinal direction size, the longest diameter of the precipitates is obtained as the transverse direction size. When the value of the aspect ratio (the longitudinal direction size/the transverse direction size) is 5 or more, the precipitates are determined as "precipitates in a needle shape or precipitates in a plate shape".

[0050] Furthermore, in the casting mold material that is the present embodiment, for example, fine Cr-based and Zr-based precipitates having a grain size of 5 μm or smaller are dispersed. Meanwhile, these fine Cr-based and Zr-based precipitates are precipitated in the aging treatment after the slow cooling.

[0051] The precipitates in a needle shape or the precipitates in a plate shape are formed during the slow cooling after a thermal spraying treatment in which a Ni-Cr alloy having excellent thermal resistance or wear resistance is thermal sprayed in the manufacturing of the casting mold material. In detail, in the present embodiment, the precipitates in a needle shape or the plate-like precipitate containing Cr are precipitated when a copper alloy containing 0.3 mass% or more and less than 0.5 mass% of Cr, 0.01 mass% or more and 0.15 mass% or less of Zr, 0.1 mass% or more and less than 2.0 mass% of Al, and a Cu balance including inevitable impurities is heated to, for example, 1,000°C or higher during the thermal spraying treatment and is then slowly cooled from a high temperature region of approximately 1,000°C to a temperature of 600°C or lower at a cooling rate of 10°C/min or less. Therefore, granular Cr-based and Zr-based precipitates being precipitated during the slow cooling are suppressed.

[0052] In addition, the Cu-Cr-Zr-Al alloy material that is the present embodiment has the same composition as the casting mold material and satisfies a relationship of $B/A > 1.1$ where the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is maintained at 1,000°C for one hour and is then cooled from 1,000°C to 600°C at a cooling rate of 10°C/min is defined by A and the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is further maintained at 500°C for three hours is defined by B.

[0053] That is, in the Cu-Cr-Zr-Al alloy material that is the present embodiment, even in a case where the Cu-Cr-Zr-Al alloy material is slowly cooled from 1,000°C to 600°C at a cooling rate of 10°C/min after maintained at 1,000°C for one hour, the electrical conductivity is improved by the subsequent thermal treatment of maintaining the Cu-Cr-Zr-Al alloy material at 500°C for three hours.

[0054] 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)

[0055] 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. Here, as raw materials of Cr, Zr, and Al which are the additive elements, Cr, Zr, and Al 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, Al having a purity of 99.95 mass% or higher is used as a raw material of Al. In addition, Fe, Si, Co, and P are added thereto as necessary. Meanwhile, as raw materials of Cr, Zr, Fe, Si, Co, and P, parent alloys with Cu may also be used.

[0056] In addition, the component-formulated molten copper alloy is injected into a die, thereby obtaining an ingot.

(Homogenization Treatment Step S02)

[0057] Next, a thermal treatment is carried out in order for the homogenization of the obtained ingot.

[0058] 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)

[0059] 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)

[0060] 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.

(First Aging Treatment Step S05)

[0061] Next, after the solution treatment step S04, a first aging treatment is carried out, and precipitates such as Cr-based precipitates and Zr-based precipitates are finely precipitated, thereby obtaining a first aging treatment material.

[0062] 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.

[0063] 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.

[0064] By means of the above-described steps, the Cu-Cr-Zr-Al alloy material that is the present embodiment is manufactured.

(Thermal Spraying Treatment Step S06)

[0065] Next, after the first aging treatment step S05, a Ni-Cr alloy or the like is thermal sprayed onto predetermined places on the surface of the Cu-Cr-Zr-Al alloy material, thereby forming a coating layer on the predetermined places on the surface of the Cu-Cr-Zr-Al alloy material. In addition, after this thermal spraying, a thermal treatment is carried out on the Cu-Cr-Zr-Al alloy material on which the coating layer is formed at 900°C or higher and 1,000°C or lower for 15 minutes or longer and 180 minutes or shorter.

[0066] This thermal treatment is carried out in order for the diffusion joining between the Cu-Cr-Zr-Al alloy material and the coating layer.

[0067] As cooling after the thermal spraying and the subsequent thermal treatment, slow cooling having a relatively low cooling rate, for example, furnace cooling, is carried out. Here, regarding the cooling rate in the slow cooling, the cooling rate in a range from the thermal treatment temperature to 800°C or lower is 5°C/minute or higher and 70°C/minute or lower.

(Second Aging Treatment Step S07)

[0068] Next, after the thermal spraying treatment step S06, a second aging treatment is carried out, and precipitates such as Cr-based precipitates and Zr-based precipitates are finely precipitated.

[0069] Here, the 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.

[0070] 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 thermal treatment is not particularly limited, but water cooling is preferably carried out.

[0071] By means of the above-described steps, the casting mold material that is the present embodiment is manufactured.

tured.

[0072] According to the casting mold material of the present invention provided with the above-described constitution, since the casting mold material is provided with a composition including 0.3 mass% or more and less than 0.5 mass% of Cr, 0.01 mass% or more and 0.15 mass% or less of Zr, 0.1 mass% or more and less than 2.0 mass% of Al, and a Cu balance including inevitable impurities, in the second aging treatment step S07, Cr-based and Zr-based precipitates are finely precipitated, whereby it is possible to improve the strength (hardness) and the electrical conductivity. In addition, since Al is included in a range of 0.1 mass% or more and less than 2.0 mass%, it is possible to adjust the electrical conductivity to approximately 30% to 60% IACS, and the casting mold material is particularly suitable for mold materials in electromagnetic stirring uses.

[0073] In addition, since the casting mold material according to the present embodiment has the precipitates in a needle shape or the precipitates in a plate shape containing Cr, granular precipitates being formed during the slow cooling after the thermal spraying treatment step S06 are suppressed, it is possible to sufficiently disperse the fine precipitates by means of the second aging treatment step S07 after the thermal spraying treatment step S06, and it is possible to sufficiently improve the strength (hardness) by means of the precipitation strengthening mechanism.

[0074] Furthermore, in the casting mold material according to the present embodiment, the maximum size of the precipitates in a needle shape or the precipitates in a plate shape containing Cr is set to be as relatively small as 100 μm or less, and thus Cr sufficiently forms a solid solution in the parent phase of Cu, it is possible to sufficiently disperse the fine precipitates by means of the second aging treatment step S07 after the thermal spraying treatment step S06, and it is possible to sufficiently improve the strength (hardness) and the electrical conductivity by means of a precipitation strengthening mechanism.

[0075] In addition, since the composition of the casting mold material according to the present embodiment further includes 0.01 mass% or more and 0.15 mass% or less of one or more elements selected from Fe, Si, Co, and P as a total, granular precipitates being formed during the slow cooling after the thermal spraying treatment step S06 are suppressed, and the generation of the precipitates in a needle shape or the precipitates in a plate shape containing Cr is accelerated. Therefore, it is possible to sufficiently precipitate the fine precipitates by means of the second aging treatment step S07 after the thermal spraying treatment step S06, and it is possible to reliably improve the strength (hardness) and the electrical conductivity.

[0076] Furthermore, since the Cu-Cr-Zr-Al alloy material according to the present embodiment satisfies a relationship of $B/A > 1.1$ where the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is maintained at 1,000°C for one hour and is then cooled from 1,000°C to 600°C at a cooling rate of 10°C/min is defined by A and the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is further maintained at 500°C for three hours is defined by B, even in a case where the Cu-Cr-Zr-Al alloy material is heated to a high temperature range of, for example, approximately 1,000°C and is then slowly cooled in the thermal spraying treatment step S06, in the second aging treatment step S07 after the slow cooling, the electrical conductivity improves, and it is possible to improve the strength (hardness) by means of precipitation hardening.

[0077] 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.

[0078] In the present embodiment, the total content of one or more elements selected from Fe, Si, Co, and P is described to be 0.01 mass% or more and 0.15 mass% or less, but is not limited thereto, and these elements may not be added thereto intentionally.

Examples

[0079] Hereinafter, the results of confirmation tests carried out in order to confirm the effects of the present invention will be described.

[0080] 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.

[0081] Meanwhile, as a raw material of Cr which was an additive element, Cr having a purity of 99.99 mass% or higher was used, as a raw material of Zr, Zr having a purity of 99.95 mass% or higher was used, and, as a raw material of Al, Al having a purity of 99.99 mass% or higher was used.

[0082] 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.

[0083] A solution treatment was carried out on this hot-rolled material under conditions of 1,000°C for 1.5 hours, and then water cooling was carried out.

[0084] Next, a first aging treatment was carried out under conditions of 500 (± 15)°C for three hours, thereby obtaining a Cu-Cr-Zr-Al alloy material.

[0085] Next, a thermal treatment was carried out on the obtained Cu-Cr-Zr-Al alloy material under conditions of 1,000°C for one hour as a simulation of a thermal spraying treatment, and then slow cooling was carried out from 1,000°C to 600°C at a cooling rate of 10°C/minute.

[0086] After that, a second aging treatment was carried out under conditions of 500°C for three hours, thereby obtaining a casting mold material.

[0087] For the obtained Cu-Cr-Zr-Al alloy material, the Vickers hardness (rolled surface) and the electrical conductivity were evaluated.

[0088] Furthermore, for the casting mold material after the thermal spraying treatment and after the second aging treatment, the Vickers hardness (rolled surface) and the electrical conductivity were evaluated. Furthermore, structural observation was carried out, and the presence or absence of precipitates in a needle shape or precipitates in a plate shape containing Cr was evaluated.

(Composition Analysis)

[0089] The component compositions of the obtained Cu-Cr-Zr-Al alloy material and the obtained casting mold material were measured by means of an ICP-MS analysis. The measurement results are shown in Table 1.

(Structural Observation)

[0090] An observation sample was taken from the obtained casting mold material, structural observation was carried out after a polishing treatment using a scanning electron microscope, and the presence or absence of precipitates in a needle shape or precipitates in a plate shape containing Cr was confirmed. The observation results are shown in Table 2. Meanwhile, for the specimens of Invention Example 3 and Comparative Example 2, the results of structural observation carried out after the first aging treatment, after the thermal spraying treatment and the slow cooling, and after the second aging treatment are illustrated in FIG. 2. Furthermore, the enlarged observation results of the precipitates in a needle shape or the precipitates in a plate shape containing Cr which were observed in Invention Example 3 are illustrated in FIG. 3A to FIG. 3C.

(Maximum Size of Precipitates)

[0091] For the precipitates in a needle shape or the precipitates in a plate shape observed as described above, the minimum circumscribed circle was drawn, and the diameter of the minimum circumscribed circle was considered as the maximum size of the precipitates.

(Vickers Hardness Measurement)

[0092] Vickers hardness was measured using a Vickers hardness tester manufactured by Akashi Co., Ltd. at nine places in a test specimen as illustrated in FIG. 4 according to JIS Z 2244, and the average value of seven measurement values excluding the maximum value and the minimum value was obtained. The measurement results after the first aging treatment and after the thermal spraying treatment and the second aging treatment are shown in Table 2.

(Electrical Conductivity Measurement)

[0093] The cross-sectional center portion of a 10×15 mm sample was measured three times using SIGMA TEST D2.068 (having a probe diameter ϕ of 6 mm) manufactured by Foerster Japan Limited, and the average value thereof was obtained. The measurement results after the first aging treatment and after the thermal spraying treatment and the second aging treatment are shown in Table 2.

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[Table 1]

		Composition (mass%)							
		Cr	Zr	Al	Fe	Si	Co	P	Cu
Invention Example	1	0.35	0.13	0.59	-	-	-	-	Balance
	2	0.38	0.14	0.63	-	0.02	-	-	Balance
	3	0.39	0.14	0.93	-	0.02	-	-	Balance
	4	0.50	0.10	0.90	0.04	-	-	-	Balance
	5	0.48	0.06	1.10	-	-	-	0.05	Balance
	6	0.50	0.02	1.90	-	-	0.07	0.02	Balance
Comparative Example	1	0.93	0.11	0.62	-	-	-	-	Balance
	2	0.98	0.12	0.93	-	-	-	-	Balance
	3	0.20	0.09	0.90	-	-	-	-	Balance
	4	0.70	0.08	0.58	-	-	-	-	Balance
	5	0.70	0.17	0.58	-	-	-	-	Balance

[Table 2]

	Presence or absence of precipitates in a needle shape or a plate shape	Maximum size of precipitates (μm)	After first aging treatment		After thermal spraying treatment (after slow cooling)		After second aging treatment		Electrical conductivity ratio B/A
			Vickers hardness (Hv)	Electrical conductivity (%IACS)	Vickers hardness (Hv)	Electrical conductivity A (%IACS)	Vickers hardness (Hv)	Electrical conductivity B (%IACS)	
Invention Example	1	Present	50	40	55	39	76	48	1.23
	2	Present	55	44	54	38	77	46	1.21
	3	Present	54	38	55	34	73	39	1.15
	4	Present	49	35	60	32	79	37	1.16
	5	Present	51	35	58	30	80	35	1.17
	6	Present	59	25	59	24	79	30	1.25
Comparative Example	1	Absent	-	46	49	42	53	43	1.02
	2	Absent	-	39	49	37	52	37	1.00
	3	Absent	-	38	48	35	63	38	1.09
	4	Absent	-	47	44	42	55	44	1.05
	5	Absent	-	44	45	41	57	44	1.07

[0094] As shown in Table 2, it is confirmed that the invention examples satisfied a relationship of $B/A > 1.1$ where the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material was maintained at 1,000°C for one hour and was then cooled from 1,000°C to 600°C at a cooling rate of 10°C/min (after the thermal spraying treatment) is defined by A and the electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material was maintained at 500°C for three hours (after the second aging treatment) is defined by B.

[0095] In addition, as shown in Table 2, it is confirmed that the invention examples had precipitates in a needle shape or precipitates in a plate shape containing Cr. In addition, it is confirmed that the invention examples had the Vickers hardness and the electrical conductivity which were significantly enhanced by the second aging thermal treatment compared with those in the comparative examples.

[0096] In addition, as a result of the structural observation, in Comparative Example 2, as illustrated in FIG. 2, no precipitates in a needle shape or precipitates in a plate shape containing Cr were observed in the test specimen which had been slowly cooled after the thermal spraying treatment, and granular precipitates were observed.

[0097] In contrast, in Invention Example 4, as illustrated in FIG. 2, precipitates in a needle shape or precipitates in a plate shape containing Cr were observed in the test specimen which had been slowly cooled after the thermal spraying treatment.

[0098] Meanwhile, as a result of enlarging and observing the precipitates in the test specimen which has been subjected to the second aging thermal treatment in Invention Example 4, Cr was detected from the precipitates in a needle shape or the precipitates in a plate shape, and Cr and Zr were detected from the granular precipitates as illustrated in FIGS. 3(a) to 3(c).

Industrial Applicability

[0099] It is possible to provide a casting mold material which is capable of sufficiently improving the strength (hardness) and the electrical conductivity of the casting mold material even in a case where an aging treatment is carried out after a thermal spraying treatment on the casting mold material made of a Cu-Cr-Zr-Al alloy material and has superior durability in severe environments.

Claims

1. A casting mold material used in casting a metal material, the casting mold material having a composition including:

0.3 mass% or more and less than 0.5 mass% of Cr;

0.01 mass% or more and 0.15 mass% or less of Zr;

0.1 mass% or more and less than 2.0 mass% of Al; and

a Cu balance including inevitable impurities,

wherein the casting mold material comprises precipitates in a needle shape or precipitates in a plate shape.

2. The casting mold material according to Claim 1,

wherein sizes of the precipitates in a needle shape or the precipitates in a plate shape are 100 μm or less.

3. The casting mold material according to Claim 1 or 2, wherein the composition of the casting mold material further comprises:

0.01 mass% or more and 0.15 mass% or less of one or more elements selected from Fe, Si, Co, and P as a total.

4. A Cu-Cr-Zr-Al alloy material having a composition including:

0.3 mass% or more and less than 0.5 mass% of Cr;

0.01 mass% or more and 0.15 mass% or less of Zr;

0.1 mass% or more and less than 2.0 mass% of Al; and

a Cu balance including inevitable impurities,

wherein the Cu-Cr-Zr-Al alloy material satisfies a relationship of $B/A > 1.1$ where an electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is maintained at 1,000°C for one hour and is then cooled from 1,000°C to 600°C at a cooling rate of 10°C/min is defined by A and an electrical conductivity (%IACS) after the Cu-Cr-Zr-Al alloy material is further maintained at 500°C for three hours is defined by B.

5. The Cu-Cr-Zr-Al alloy material according to Claim 4, wherein the composition of the Cu-Cr-Zr-Al alloy material further comprises, 0.01 mass% or more and 0.15 mass% or less of one or more elements selected from Fe, Si, Co, and P as a total.

FIG. 1

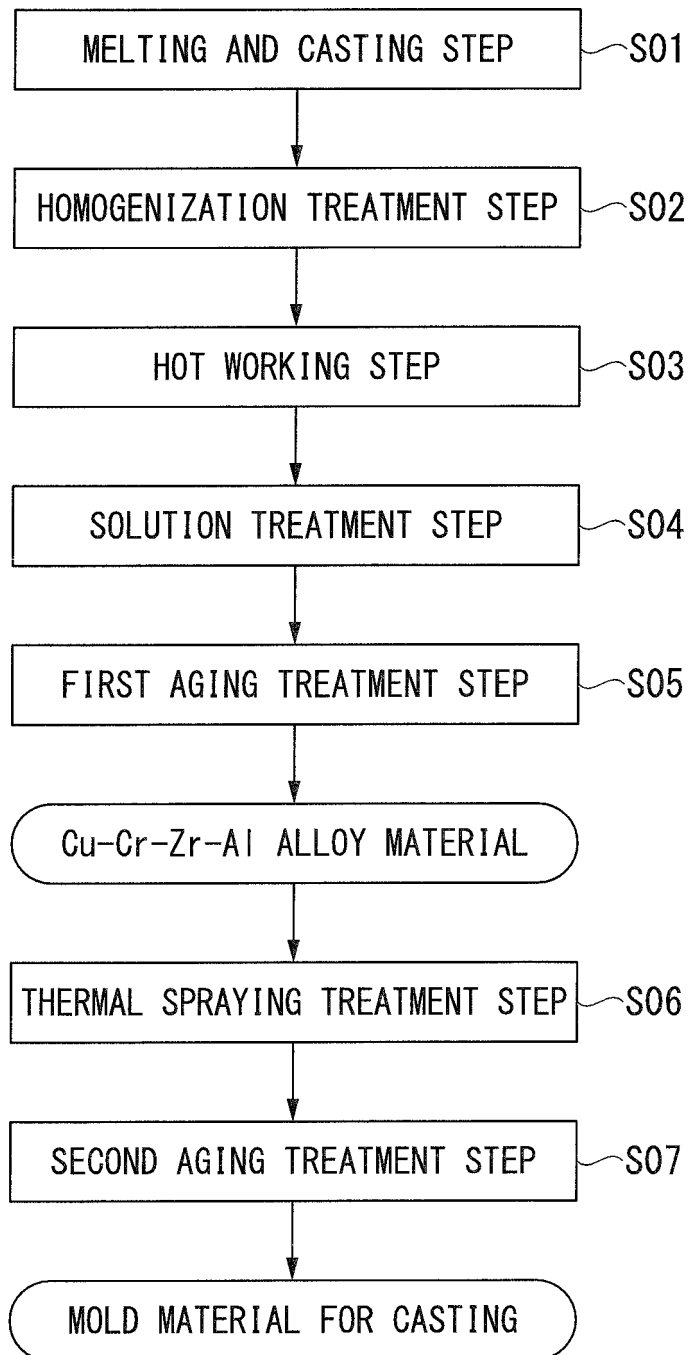


FIG. 2

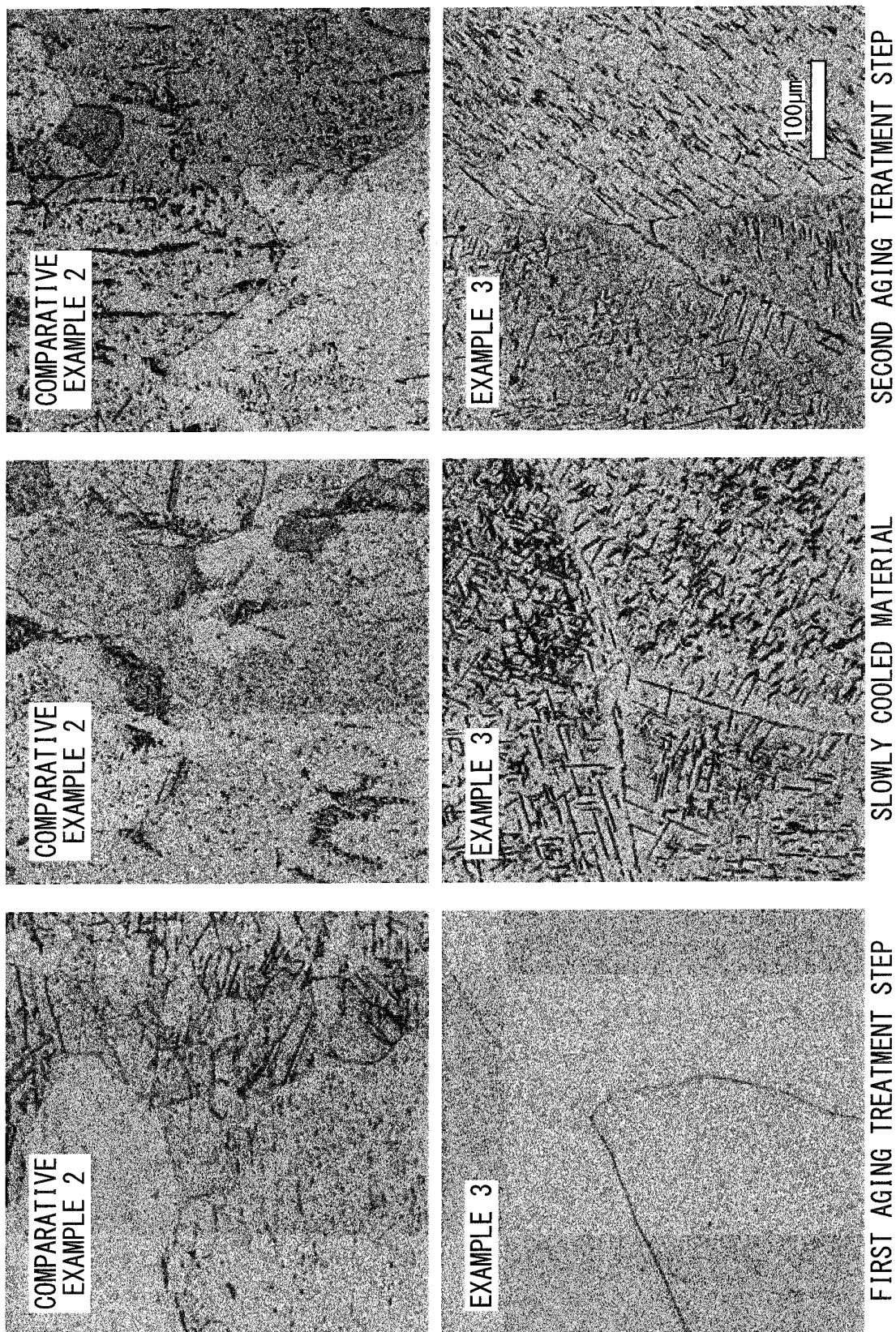
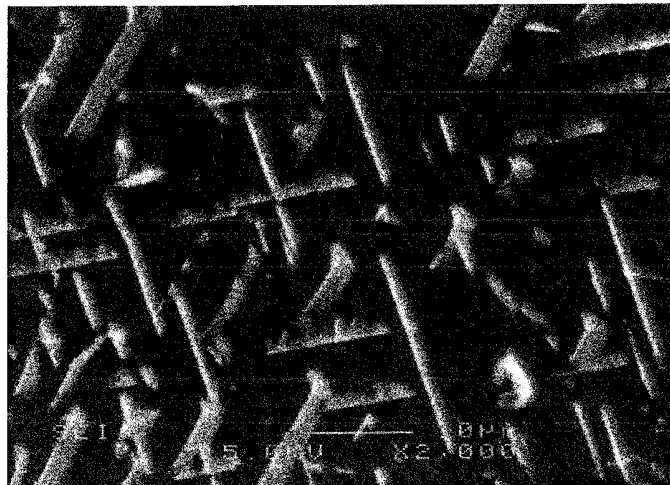
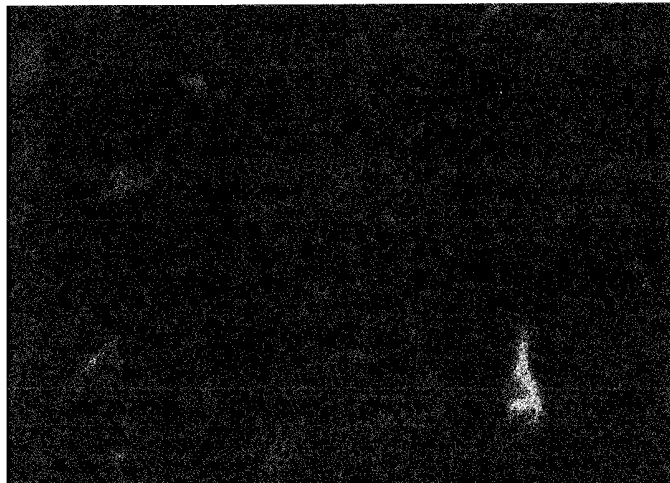


FIG. 3A



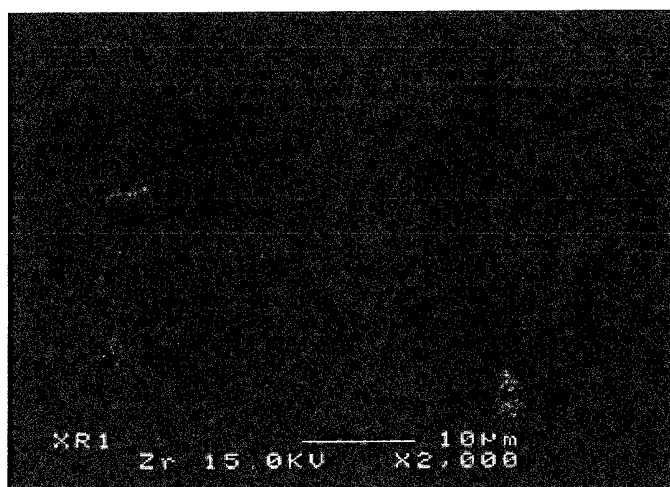
SEM IMAGE

FIG. 3B



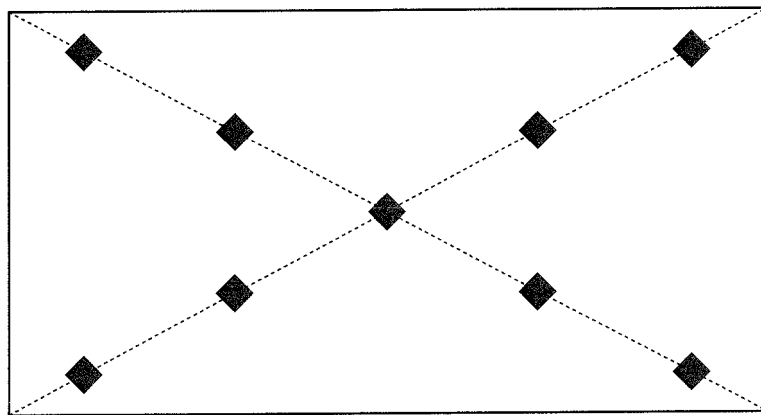
Cr

FIG. 3C



Zr

FIG. 4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/079641

A. CLASSIFICATION OF SUBJECT MATTER

C22C9/01(2006.01)i, B22C9/06(2006.01)i, B22D11/059(2006.01)i, C22C9/00(2006.01)i, C22F1/00(2006.01)n, C22F1/08(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)
C22C9/00-9/10

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 A	JP 58-212839 A (Mitsubishi Metal Corp.), 10 December 1983 (10.12.1983), claims; examples; Cu alloy sheet material 1 according to the present invention in table 1 (Family: none)	4-5 1-3
X A	JP 2005-96678 A (Mitsubishi Materials Corp.), 14 April 2005 (14.04.2005), claims; examples; table 1, inventive article 9 (Family: none)	4-5 1-3
X A	JP 2000-282156 A (Nippon Mining & Metals Co., Ltd.), 10 October 2000 (10.10.2000), claims; examples; fig. 2, no.8 (Family: none)	4-5 1-3

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

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
02 December 2016 (02.12.16)Date of mailing of the international search report
13 December 2016 (13.12.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/079641

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 58-107459 A (Chuetsu Metal Works Co., Ltd.), 27 June 1983 (27.06.1983), (Family: none)	1-5
A	JP 58-107462 A (Chuetsu Metal Works Co., Ltd.), 27 June 1983 (27.06.1983), (Family: none)	1-5
A	JP 58-84641 A (NKK Corp.), 20 May 1983 (20.05.1983), (Family: none)	1-5

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

REFERENCES CITED IN THE DESCRIPTION

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- JP S62041302 B [0010]
- JP H05339688 B [0010]