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• **National University Corporation Kumamoto University**
Kumamoto-shi, Kumamoto 860-8555 (JP)

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(72) Inventors:
• **ISHIMOTO Kazuhiro**
Tokyo 103-8306 (JP)
• **KAWAMURA Yoshihito**
Kumamoto-shi, Kumamoto 860-8555 (JP)

(71) Applicants:
• **Tokyo Rope Manufacturing Co., Ltd.**
Tokyo 103-8306 (JP)

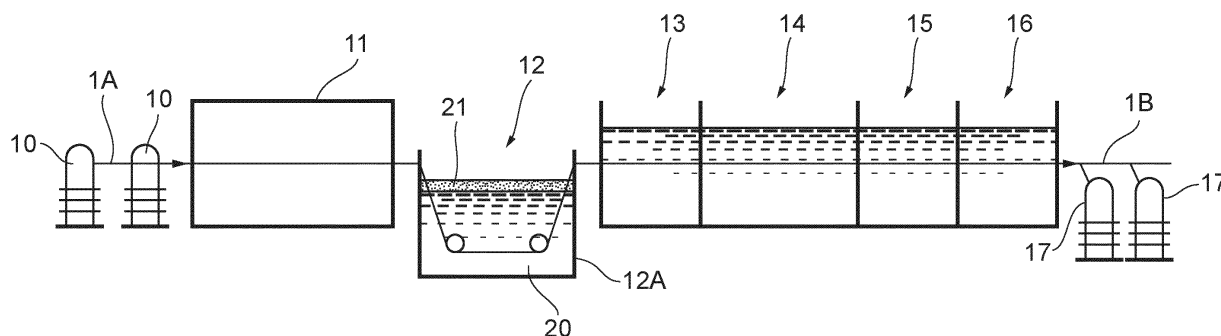
(74) Representative: **Knöner, Gregor et al**
Kahler Käck Mollekopf
Partnerschaft von Patentanwälten mbB
Vorderer Anger 239
86899 Landsberg am Lech (DE)

(54) **HEAT EXCHANGE METHOD, HEAT EXCHANGE MEDIUM, HEAT EXCHANGE DEVICE, PATENTING METHOD, AND CARBON STEEL WIRE**

(57) The present invention provides a novel heat exchange medium to replace lead. A carbon-steel wire 1A heated in a heating furnace 11 is passed through a bath 12A filled with a liquid-phase Mg-Al-Ca alloy 20 obtained by melting a Mg-Al-Ca alloy in which the main constituent elements are Mg (magnesium), Al (aluminum) and Ca

(calcium). When it passes through the bath 12A, the carbon-steel wire 1A, which has been heated for example to about 950°C in the heating furnace 11, is cooled to about 550°C. The Mg-Al-Ca alloy is non-toxic and has no environmental impact as well.

Fig. 1



Description

Technical Field

[0001] This invention relates to a heat exchange method, a heat exchange medium and a heat exchange apparatus. The invention further relates to a patenting treatment and carbon-steel wire.

Background Art

[0002] By drawing a carbon-steel wire on which a uniform and fine pearlite structure has been caused to precipitate, the drawn carbon-steel wire can be imparted with high strength and toughness. The uniform and fine pearlite structure is caused precipitated by heating the carbon-steel wire in a heating furnace and cooling it in a cooling tank (cooling furnace) (this is so-called "patenting"). As one example, a carbon-steel wire is heated to about 900 to 1000°C in a heating furnace and then cooled to about 500 to 600°C in a cooling tank, although this will differ depending upon the constituents.

[0003] Lead (molten lead), a fluidized bed, water or the like are employed as the media for cooling the carbon-steel wire (see Patent Document 1 with regard to patenting using a fluidized bed and Patent Document 2 with regard to patenting using water). However, these have drawbacks in that a fluidized bed has a low cooling capacity and water has the drawback of causing supercooling. On the other hand, lead, which has a boiling point of 1749°C and a melting point of 327.5°C, is still presently in wide use because it is in a stable liquid-phase state in the temperature range necessary for patenting (a temperature range for suitably cooling the heated carbon-steel wire and precipitating the pearlite structure).

[0004] Although lead (Pb) is suitable as the cooling medium in the patenting of carbon-steel wire, as mentioned above, there are instances where its use is restricted on account of its toxicity. For example, according to the RoHS (Restriction on Hazardous Substances) directive which is in force in EU member states, the marketing in EU member states of electronic and electrical equipment containing lead in excess of 1,000 ppm is restricted.

Prior Art Documents

[0005]

Patent Document 1: Japanese Patent Publication No. 2002-507662

Patent Document 2: Japanese Patent Publication No. 2005-529235

Disclosure of the Invention

[0006] An object of the present invention is to provide a novel heat exchange medium to replace lead, as well as a heat exchange method which utilizes this medium.

[0007] A heat exchange method according to the present invention is characterized by: bringing an object into contact with or in close proximity to a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are main constituent elements; and exchanging (transferring) thermal energy between the object and the liquid-phase Mg-Al-Ca alloy.

[0008] A heat exchange medium according to the present invention is characterized by including a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are main constituent elements. It goes without saying that so-called unavoidable impurities, namely those which exist in the raw materials or which inevitably become mixed in during the manufacturing process and are inherently unwanted but are allowed because they are in trace amounts and have no influence upon the characteristics of the product, are contained in the Mg-Al-Ca alloy or in the liquid-phase Mg-Al-Ca obtained by melting the alloy.

[0009] The present invention also provides a heat exchange apparatus. The heat exchange apparatus according to the present invention includes a bath filled with a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are main constituent elements.

[0010] The present invention also provides a patenting treatment for cooling heated carbon steel, an example of which is carbon-steel wire. The patenting treatment according to the present invention comprises: passing heated carbon steel through a bath filled with a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are main constituent elements; and cooling the heated carbon steel when it passes through the bath.

[0011] According to the present invention, a liquid-phase Mg-Al-Ca alloy put in the liquid phase by heating and melting an Mg-Al-Ca alloy that is a solid at room temperature is used as a heat exchange medium (heating medium or cooling medium) for applying heat to (heating) an object or removing heat from (cooling) an object. The object may be heated or cooled by bringing it into direct contact with the liquid-phase Mg-Al-Ca alloy, or the object can also be heated or cooled in contactless fashion by bringing the liquid-phase Mg-Al-Ca alloy into close proximity with the object without contacting it directly. For example, causing the liquid-phase Mg-Al-Ca alloy to flow through a pipe will heat or cool the pipe surroundings. In a case where the liquid-phase Mg-Al-Ca alloy is used as a heating medium, it may be utilized in a bluing treatment, degreasing treatment or carbon spheroidizing treatment, for example. In a case where the liquid-phase Mg-Al-Ca alloy is used as a cooling medium, it may be utilized in patenting (annealing of steel), cooling of a fuel rod and stepwise cooling of steel material.

[0012] The Mg-Al-Ca alloy is a ternary alloy the main constituent elements of which are Mg (magnesium), Al (aluminum) and Ca (calcium). Among these elements, magnesium (pure magnesium) has an ignition point

(about 470°C) lower than its boiling point (about 1090°C), but by being fused with Ca and furthermore with Al, it will not combust or will not combust easily at room temperature, as a matter of course, or even in a comparatively high temperature environment. In order to improve in-combustibility (raise the ignition temperature to the high-temperature region), rare earth elements such as, for example, Mn (manganese), Zr (zirconium), Ag (silver), Y (yttrium) or Nd (neodymium) may be added.

[0013] Further, the Mg-Al-Ca alloy enables the liquidus temperature thereof to be lowered below the melting point (650°C) of magnesium, the melting point (660°C) of aluminum and the melting point (842°C) of calcium. Furthermore, it has been found that the liquid-phase Mg-Al-Ca alloy can transfer heat faster than molten lead. The liquid-phase Mg-Al-Ca alloy can be used suitably as a heating medium or cooling medium in place of molten lead. The main constituent elements Mg, Al and Ca of the liquid-phase Mg-Al-Ca alloy are all harmless metal elements and have no environmental impact.

[0014] In a case where a heat exchange (heat transfer) is performed between an object and the liquid-phase Mg-Al-Ca alloy by bringing the object directly into contact with the liquid-phase Mg-Al-Ca alloy, the object may simply be immersed in the liquid-phase Mg-Al-Ca alloy or may be passed through the liquid-phase Mg-Al-Ca alloy while the object is being moved.

[0015] When the bath is filled with the liquid-phase Mg-Al-Ca alloy, a thin film forms on the surface (liquid surface layer) of the liquid-phase Mg-Al-Ca alloy. Owing to the film that forms on the surface of the liquid-phase Mg-Al-Ca alloy collected in the bath, the liquid-phase Mg-Al-Ca alloy in the bath can be prevented from direct exposure to air (oxygen) or such exposure can be made unlikely to occur. This makes it difficult for the liquid-phase Mg-Al-Ca alloy filling the bath to combust. However, since the Mg-Al-Ca alloy used in the present invention is in the liquid-phase state, it is employed in a state in which it is less combustible in comparison with use in the solid phase (inclusive of use in powder form).

[0016] WO2015/060459 discloses a magnesium alloy obtained by adding other elements (such as Mn, Zn, Zr, Ag, Y, Nd) to an alloy (Mg, Al)₂Ca, which is the result of adding calcium and aluminum to magnesium. The magnesium alloy disclosed in WO2015/060459 can, in molten form, be used suitably as the liquid-phase Mg-Al-Ca alloy used in the heat exchange medium in the present invention. However, since the Mg-Al-Ca alloy is used in the liquid phase and not in the solid phase in the present invention, the mechanical strength and toughness required in the solid phase are unnecessary and there is also no need to take corrosion resistance into consideration.

[0017] If the liquid-phase Mg-Al-Ca alloy is used as a cooling medium in the patenting of carbon-steel wire, the temperature of the carbon-steel wire when it is immersed in the liquid-phase Mg-Al-Ca alloy will be about 900 to 1000°C. The liquid-phase Mg-Al-Ca alloy used in the

present invention, therefore, preferably should have an ignition temperature of 900°C or higher, and 1000°C or higher for safety reasons. A magnesium alloy having an ignition temperature of 1000°C or higher is disclosed in WO2015/060459 cited above.

[0018] As set for above, the Mg-Al-Ca alloy in the present invention is used in the liquid phase, not the solid phase, and can be used without coming into direct contact with air. That is, it is used in a state in which it is positively less likely to combust in comparison with an Mg-Al-Ca alloy in the solid phase (powder form). Consequently, for example, even if the ignition temperature of a Mg-Al-Ca alloy in the solid phase (powder form) is less than 1000°C and a carbon-steel wire heated to 1000°C is immersed in liquid-phase Mg-Al-Ca alloy obtained by melting the solid-phase alloy, the liquid-phase Mg-Al-Ca alloy is unlikely to ignite immediately. Still, for safety reasons, it is preferred that the liquid-phase Mg-Al-Ca alloy used in the present invention have an ignition temperature of 1000°C or higher even when it is in the solid phase.

[0019] When prototypes of Mg-Al-Ca alloy having various Mg, Al, Ca composition ratios were fabricated, it was confirmed that the ignition temperature nears 1000°C if the Ca content of the Mg-Al-Ca alloy is too small. Further, when the Al content of the Mg-Al-Ca alloy is increased, ignition becomes difficult even if the amount of Ca is small. If safety is taken into consideration, it is preferred that the amount of Ca be $x \times 0.015$ (at%) or higher, where x (at%) is the amount of Mg.

[0020] With regard to the Mg-Al-Ca alloy, if a liquidus temperature lower than the above-mentioned melting points of magnesium (650°C), aluminum (660°C) and calcium (842°C) is achieved, then it will suffice if the amount of Ca is made less than $x \times 0.1 + 10$ (at%), where x (at%) is the amount of Mg. The upper limit of the liquidus temperature of the Mg-Al-Ca alloy can be made 640°C. It should be noted that the liquidus temperature of the Mg-Al-Ca alloy can be lowered down to below 550°C (460°C according to calculation) by adjusting the composition ratio of the Mg, Al and Ca occupying the Mg-Al-Ca alloy, thus enabling the alloy to be suitable for use in patenting in place of molten lead. In any case, the liquid-phase Mg-Al-Ca alloy used as the heat exchange medium in the present invention can be put into a liquid-phase state which is stable in a temperature range of from about 1000°C to about 460°C.

[0021] When carbon-steel wire was actually produced by carrying out patenting using the liquid-phase Mg-Al-Ca alloy instead of molten lead as the cooling medium followed by drawing, it was confirmed that tensile strength was higher in comparison with carbon-steel wire that was subjected to patenting using molten lead as the cooling medium. Further, when the diameter was reduced by performing drawing repeatedly, it was confirmed that occurrence of delamination (brittle fracture) of the carbon-steel wire produced using the liquid-phase Mg-Al-Ca alloy as the cooling medium was suppressed more as compared with a carbon-steel wire produced

using molten lead as the cooling medium. When the metallic structure immediately after patenting was observed under an electron microscope, almost no bainite was observed with use of molten lead as the cooling medium, whereas a slight amount of bainite was observed with use of the liquid-phase Mg-Al-Ca alloy as the cooling medium. This suggests that these results may be ascribed to the fact that the liquid-phase Mg-Al-Ca alloy exhibits a higher cooling rate in comparison with molten lead.

[0022] In any case, when a carbon-steel wire produced using the liquid-phase Mg-Al-Ca alloy as the cooling medium is processed into fine wire, it is less prone to delamination or experiences no delamination, i.e., its processing limit (marginal workability) is improved, in comparison with a carbon-steel wire produced using molten lead as the cooling medium. Further, as mentioned above, a carbon-steel wire obtained by carrying out patenting using the liquid-phase Mg-Al-Ca alloy as the cooling medium followed by drawing exhibits a tensile strength higher than that of a carbon-steel wire produced using molten lead as the cooling medium.

[0023] Lead does not adhere to carbon-steel wire produced using the liquid-phase Mg-Al-Ca alloy as the cooling medium in a patenting treatment. Carbon-steel wire having little environmental impact is provided.

Brief Description of the Drawings

[0024]

Fig. 1 is a block diagram illustrating patenting treatment of carbon-steel wire;

Fig. 2 is a cross-sectional view illustrating a drawing process of carbon-steel wire;

Fig. 3 illustrates a liquid-phase diagram of an Mg-Al-Ca alloy, in which the constituent elements are Mg, Al and Ca, in a rectangular coordinate system where the horizontal axis is a plot of the weight ratios of Mg and Al and the vertical axis a plot of the weight ratio of Ca;

Fig. 4 illustrates the weight ratios and element ratios of each of Mg, Al and Ca included in prepared Samples I to V, as well as the phase states at 550°C and combustion states at 1000°C;

Fig. 5 is a plot of the composition ratios of the prepared Samples I to V, which are shown in Fig. 4, in the liquid-phase diagram illustrated in Fig. 3;

Fig. 6 is a plot of the composition ratios of Mg, Al and Ca for each of the prepared Samples I to V and for eutectic alloys, which correspond to the eutectic points E1 to E3 and U4 to U6 shown in Fig. 3, in a rectangular coordinate system in which the horizontal axis is a plot of the element ratios of Mg and Al and the vertical axis a plot of the element ratio of Ca;

Fig. 7 illustrates the results of a tensile test and torsion test applied to carbon-steel wire; and

Fig. 8 illustrates the results of a tensile test and tor-

sion test applied to another carbon-steel wire.

Best Mode for Carrying Out the Invention

[0025] Fig. 1, which illustrates an embodiment of the present invention, is a block diagram schematically showing patenting treatment of carbon-steel wire. Fig. 2 is a cross-sectional view schematically showing a drawing process of carbon-steel wire. A wire rope, steel cord or the like is produced by bundling and twisting together multiple carbon-steel wires obtained by a patenting treatment and drawing process.

[0026] A carbon-steel wire (starting-wire material) 1A with a circular cross-section manufactured by hot rolling is wound on each of a plurality of delivery reels 10. The carbon-steel wire 1A delivered from each of the delivery reels 10 proceeds to a heating furnace 11 where it is heated to a predetermined temperature of, for example, 950°C.

[0027] Next, the heated carbon-steel wire 1A proceeds to a cooling tank (cooling furnace) 12. The cooling tank 12 contains a bath 12A filled with a liquid-phase Mg-Al-Ca alloy 20. The bath 12A is heated. The Mg-Al-Ca alloy, which is a solid at room temperature, is melted and placed in the liquid phase by being heated in the bath 12A. It goes without saying that the bath 12A is heated to a temperature above the temperature (liquidus temperature) necessary to place the Mg-Al-Ca alloy in the liquid phase. The liquidus temperature of the Mg-Al-Ca alloy used in the present invention is on the order of 460 to 640°C, as described below. The liquidus temperature of the Mg-Al-Ca alloy varies depending on the weight ratios or element ratios (composition ratios) of respective ones of Mg, Al, Ca included in the Mg-Al-Ca alloy.

[0028] For example, the liquid-phase Mg-Al-Ca alloy 20 in the bath 12A is maintained at a temperature of about 550°C. When it passes through the bath 12A, the carbon-steel wire 1A that was heated in the heating furnace 11 is cooled from about 950°C to about 550°C.

[0029] A thin film (such as an oxide film) 21 forms on the surface of the liquid-phase Mg-Al-Ca alloy 20 in the bath 12A owing to exposure to air. As a consequence, the liquid-phase Mg-Al-Ca alloy 20 collected in the bath 12A (the liquid-phase portion covered by the film 21 inside the bath 12A) is hardly exposed to air.

[0030] The carbon-steel wire 1A cooled by the liquid-phase Mg-Al-Ca alloy 20 is then cooled further in a bath 13 filled with water, after which it proceeds to a bath 14 filled with hydrochloric acid, where scale (an iron oxide film) is removed from the surface of the carbon-steel wire 1A. The carbon-steel wire 1A from which the scale has been removed is washed in a bath 15 filled with water and finally proceeds to a bath 16 filled with zinc phosphate, where the surface is coated with zinc phosphate for purposes of rust prevention and lubrication. The resultant carbon-steel wire 1B coated with the zinc phosphate is wound onto multiple take-up reels 17.

[0031] The carbon-steel wire 1B wound by the take-up

reel 17 then proceeds to a wire drawing process. With reference to Fig. 2, the carbon-steel wire 1B is drawn to a predetermined diameter by a wire drawing machine equipped with a carbide alloy die 31 (the carbon-steel wire after being drawn is indicated by reference character 1C). In a case where carbon-steel wire 1C of small diameter is manufactured, carbon-steel wire having an intermediate diameter is manufactured and the above-described drawing process is repeated using this wire as a starting-wire material.

[0032] Fig. 3 is a liquid-phase diagram created using phase diagram calculation software for the Mg-Al-Ca alloy (ternary alloy) used as the cooling medium in the above-mentioned patenting treatment.

[0033] Fig. 3 shows the liquid-phase diagram of a ternary alloy, in which the main constituent components are Mg (magnesium), Al (aluminum) and Ca (calcium), in a rectangular coordinate system where the horizontal axis is a plot of the weight ratios of Mg and Al and the vertical axis is a plot of the weight ratio of Ca. In Fig. 3, the horizontal axis shows the weight percent concentration (wt%) of Al that occupies the Mg-Al-Ca alloy, indicating that the weight ratio of Mg occupying the Mg-Al-Ca alloy is larger toward the left side and that the weight ratio of Al occupying the Mg-Al-Ca alloy is larger toward the right side. The vertical axis shows the weight percent concentration of Ca that occupies the Mg-Al-Ca alloy. In Fig. 3, the remainder of the weight percent concentration of Al (horizontal axis) and of the weight percent concentration of Ca (vertical axis) represents the weight percent concentration of Mg.

[0034] Further, in the liquid-phase diagram shown in Fig. 3, multiple isothermal lines in 20°C increments, in which numerical values representing temperature (liquidus temperature) are indicated by three-digit numerals, are illustrated by fine lines. Furthermore, the names of primary crystals (C14, C36, C15, (Mg), Al4Ca (Al), β and γ) that crystallize out are shown in the liquid-phase diagram illustrated in Fig. 3, as well as boundary lines, indicated by the bold lines, that demarcate the different primary crystals.

[0035] Six eutectic points E1, E2, E3, U4, U5 and U6 are illustrated in the liquid-phase diagram shown in Fig. 3. The liquidus temperatures of Mg-Al-Ca alloys having the composition ratios of these six eutectic points, as well as the weight ratios (element ratios) of Mg, Al and Ca, are as follows:

Eutectic point E1: liquidus temperature 515°C,
76.1wt%Mg, 9.4wt%Al, 14.5wt%Ca
(81.51at%Mg, 9.07at%Al, 9.42at%Ca)

Eutectic point E2: liquidus temperature 446°C,
32.5wt%Mg, 66.2wt%Al, 1.3wt%Ca
(34.98at%Mg, 64.18at%Al, 0.85at%Ca)

Eutectic point E3: liquidus temperature 445°C,
37.7wt%Mg, 60.9wt%Al, 1.4wt%Ca

(40.36at%Mg, 58.73at%Al, 0.91at%Ca)

Eutectic point U4: liquidus temperature 468°C,
49.6wt%Mg, 46.9wt%Al, 3.5wt%Ca
(52.78at%Mg, 44.96at%Al, 2.26at%Ca)

Eutectic point U5: liquidus temperature 477°C,
48.7wt%Mg, 47.9wt%Al, 3.4wt%Ca
(51.86at%Mg, 45.95at%Al, 2.20at%Ca)

Eutectic point U6: liquidus temperature 458°C,
66.5wt%Mg, 30.2wt%Al, 3.3wt%Ca
(69.48at%Mg, 28.42at%Al, 2.09at%Ca)

[0036] Among the six eutectic points, eutectic point E1 has the highest liquidus temperature (melting point), which is 515°C. In an ideal Mg-Al-Ca alloy (the Mg-Al-Ca alloy having the composition ratio indicated by the eutectic point), it has been confirmed by calculations that, by heating the Mg-Al-Ca alloy to a temperature above 515°C, the Mg-Al-Ca alloy will melt and take on the liquid phase.

[0037] The Inventors actually prepared five samples of Mg-Al-Ca alloy having different composition ratios of Mg, Al and Ca and, for each alloy sample, the inventors analyzed the weight ratio (element ratio) of every constituent element using an ICP (Inductively Coupled Plasma) (high-frequency inductively coupled plasma) analyzer and checked whether the alloy sample was in the liquid phase at 550°C and whether it combusted at 1000°C. Further, one sample (Sample I described below) of the five alloy samples was melted for conversion to the liquid phase and was used in the above-described patenting treatment (namely the liquid-phase Mg-Al-Ca alloy 20 collected in the bath 12A in order to cool the heated carbon-steel wire 1A) and was subjected to drawing, thereby manufacturing a carbon-steel wire, and the manufactured carbon-steel wire was subjected to a tensile test and torsion test. The results of analysis, confirmation and testing are described below.

[0038] Fig. 4 illustrates, for each of the five prepared Samples I to V of Mg-Al-Ca alloy, the composition ratios (both wt% and at%) of every constituent element analyzed using the ICP analyzer, as well as the results of confirming the phase state at heating to 550°C and the combustion state at heating to 1000°C. Fig. 5 is a plot (indicated by mark Δ) of the composition ratios of Mg, Al and Ca for each of Samples I to V in a form superimposed on the liquid-phase diagram shown in Fig. 3.

[0039] With reference to Fig. 5, although Samples I to V are all Mg-Al-Ca alloys having composition ratios outside the eutectic points, it is confirmed by reference to Fig. 4 that all Samples I to V are completely in the liquid phase at 550°C and non-combustible at 1000°C, from which it will be understood that there is no problem in using them as cooling media in the patenting treatment. For example, in accordance with Fig. 5, according to calculations Sample I has a liquidus temperature near

580°C and it might be thought that the solid phase (a state in which the liquid and solid phases are mixed) would be found at 550°C. However, the solid phase could not be confirmed.

[0040] For Samples I to IV, absolutely no combustion could be confirmed, but with regard to Sample V, combustion was observed when the above-mentioned film formed on the surface was torn. It can be inferred that, in Sample V, the element ratio or weight ratio of Ca that endows the liquid-phase Mg-Al-Ca alloy with incombustibility at 1000°C is near the limit value.

[0041] Sample V is an Mg-Al-Ca alloy in which the element ratio of Mg is comparatively large and the element ratio of Ca comparatively small. The ease with which the Mg-Al-Ca alloy combusts is related to the element ratio of Mg occupying the Mg-Al-Ca alloy; it is thought that the larger the element ratio of Mg, the higher the element ratio of Ca should be made in order to make the alloy less prone to combust. Conversely, if the element ratio of Al occupying the Mg-Al-Ca alloy is increased, the element ratio of Ca can be reduced to make the alloy less prone to combust.

[0042] Fig. 6 is a plot of the composition ratios of Mg, Al and Ca for each of the prepared Samples I to V and for the eutectic alloys, which correspond to the eutectic points E1 to E3 and U4 to U6 shown in Fig. 3, in a rectangular coordinate system in which the horizontal axis is a plot of the element ratios of Mg and Al and the vertical axis a plot of the element ratio of Ca (in units of at%). In Fig. 6, Samples I to V are indicated by mark ■ and the eutectic points E1 to E3 and U4 to U6 by mark x, and sample identification symbols (I) to (V) and eutectic point identification symbols (points E1 to E3 and U4 to U6) are shown near the respective plots. If we assume that Sample V is near the limit value (lower-limit value) of Ca that should be added to make 1000°C the ignition temperature, and that the element ratio of Ca for making the Mg-Al-Ca alloy less prone to combust can be reduced if the element ratio of Al occupying the Mg-Al-Ca alloy is increased, then it can be inferred that the single-dot chain line shown in Fig. 6 will be the approximate lower-limit value of Ca to make the ignition temperature of the liquid-phase Mg-Al-Ca alloy 20 greater than 1000°C. The single-dot chain line shown in Fig. 6 is represented by " $\text{Mg} \times 0.015$ " with Mg (the element ratio thereof) (at%) that occupies the liquid-phase Mg-Al-Ca alloy 20 serving as the reference.

[0043] With reference to Fig. 6, the solid line shown in Fig. 6 indicates a straight line represented by " $\text{Mg} \times 0.1 + 10$ ", this indicating the upper-limit value of Ca for making the liquidus temperature of the Mg-Al-Ca alloy less than about 620 to 640°C. If, calculated based on the liquidus diagram, the element ratio (at%) of Ca occupying the liquid-phase Mg-Al-Ca alloy 20 is made less than " $\text{Mg} \times 0.1 + 10$ ", then the liquidus temperature of the liquid-phase Mg-Al-Ca alloy 20 will not exceed 620 to 640°C and it is thought that the liquidus temperature of the liquid-phase Mg-Al-Ca alloy 20 can be made lower than the

melting point (650°C) of magnesium, the melting point (660°C) of aluminum and the melting point (842°C) of calcium.

[0044] Fig. 7 illustrates the results of a tensile strength test and torsion test and results of a fracture test of carbon-steel wire manufactured by using the Mg-Al-Ca alloy of Sample I in the above-described patenting treatment upon melting the alloy to convert it to the liquid phase. For purposes of comparison, carbon-steel wire manufactured using molten lead in the patenting treatment was subjected to similar tests.

[0045] Carbon-steel wire (SWRH72A) having a diameter of 5.500 mm was heated to about 950°C and then immersed for 1 min in the liquid-phase Mg-Al-Ca alloy 20 (550°C) obtained by melting the Mg-Al-Ca alloy of Sample I, after which the wire underwent water cooling. After scale was removed by hydrochloric acid and followed by washing with water, the wire was coated with zinc phosphate.

[0046] Wire diameter of the carbon-steel wire was gradually reduced by a drawing process multiple times to obtain wires with wire diameters of 1.748 mm, 1.553 mm, 1.408 mm and 1.248 mm, and each of these was subjected to the tensile test and torsion test.

[0047] Similarly, carbon-steel wires immersed for 1 min in molten lead, which was heated to 550°C, instead of the liquid-phase Mg-Al-Ca alloy 20 were also prepared, and wires with wire diameters of 1.748 mm, 1.553 mm, 1.408 mm and 1.248 mm were subjected to the tensile test and torsion test.

[0048] In the tensile test, the carbon-steel wire was gradually pulled until it broke, and stress at the time of breakage was measured. The tensile strength (in units of Mpa) column in Fig. 7 shows the tensile strength of carbon-steel wires of diameters 1.748 mm, 1.553 mm, 1.408 mm and 1.248 mm using the liquid-phase Mg-Al-Ca alloy 20 and molten lead as the cooling media for each wire.

[0049] In the torsion test, the carbon-steel wire was set in a torsion testing machine, both ends of the wire were gripped at a gripping spacing 100 times the diameter of the carbon-steel wire, and one end was rotated in one direction at a predetermined rotational speed. Fig. 7 shows twist values (numbers of times twisted at time of breakage) and results of observing fracture (breakage surface) for the carbon-steel wires having diameters of 1.748 mm, 1.553 mm, 1.408 mm and 1.248 mm using the liquid-phase Mg-Al-Ca alloy 20 as the cooling medium, as well as twist values and results of observing fracture for the carbon-steel wires having diameters of 1.748 mm, 1.553 mm, 1.408 mm and 1.248 mm using molten lead as the cooling medium.

[0050] With reference to the tensile strength in Fig. 7, it is confirmed that for the carbon-steel wires of any of the diameters of 1.748 mm to 1.248 mm, the carbon-steel wires prepared using the liquid-phase Mg-Al-Ca alloy 20 as the cooling medium exhibit a tensile strength higher in comparison with the carbon-steel wires prepared using

molten lead as the cooling medium. When the metallic structure before drawing (immediately after patenting) was observed under an electron microscope, almost no bainite was observed for the carbon-steel wire where molten lead was used as the cooling medium, whereas a slight amount of bainite was observed for the carbon-steel wire where the liquid-phase Mg-Al-Ca alloy 20 was used as the cooling medium. This suggests that when the liquid-phase Mg-Al-Ca alloy 20 is used as the cooling medium, the cooling rate is higher in comparison with use of molten lead as the cooling medium, and it is thought that this affected the tensile strength.

[0051] With reference to the "Fracture" column in Fig. 7 and with regard to the carbon-steel wire having the smallest wire diameter of 1.248 mm, it was confirmed that the carbon-steel wire prepared using the liquid-phase Mg-Al-Ca alloy 20 as the cooling medium exhibited fracture that was normal, whereas delamination occurred with regard to the carbon-steel wire prepared using molten lead as the cooling medium. It can be seen that processing limit (marginal workability) is improved by using the liquid-phase Mg-Al-Ca alloy 20 as the cooling medium as compared with use of molten lead as the cooling medium. It is inferred that the rise in processing limit also is ascribable to the fact that the liquid-phase Mg-Al-Ca alloy has a higher cooling rate than molten lead.

[0052] The twist values were substantially the same regardless of whether the liquid-phase Mg-Al-Ca alloy or molten lead was used as the cooling medium.

[0053] Fig. 8 illustrates the results of other tests conducted under different test conditions. Fig. 8 shows the results of a tensile strength test and torsion test applied to carbon-steel wire of smaller diameter manufactured using in the patenting treatment a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy different from Sample I. For purposes of comparison, test results are also shown for carbon-steel wire manufactured using molten lead instead of liquid-phase Mg-Al-Ca alloy in the patenting treatment.

[0054] Carbon-steel wire (SWRH62A) having a diameter of 1.060 mm was prepared and heated to about 950°C. Subsequently the carbon-steel wire was immersed for 1 min in the liquid-phase Mg-Al-Ca alloy 20 (about 600°C) obtained by melting an Mg-Al-Ca alloy having a composition ratio of Mg = 76.1 wt% (81.51 at%), Al = 9.40 wt% (9.07 at%) and Ca = 14.5 wt% (9.42 at%). The carbon-steel wire was then water-cooled, descaled with hydrochloric acid and washed with water, after which the wire was coated with zinc phosphate. The wire diameter of the carbon-steel wire was gradually reduced by a drawing process multiple times, and carbon-steel wire of diameter reduced down to about 0.360 mm was subjected to the tensile test and torsion test and to observation of fracture. The Mg-Al-Ca alloy having the above-described composition ratio took on a stable liquid phase by being heated at about 600°C and did not combust.

[0055] It can be seen that a carbon-steel wire fabricated using the liquid-phase Mg-Al-Ca alloy 20 as the cool-

ing medium exhibits a higher tensile strength than a carbon-steel wire fabricated using molten lead as the cooling medium, even with regard to carbon-steel wire having a smaller diameter manufactured from starting wire material having a smaller diameter.

[0056] In the embodiment set forth above, an example is described in which the liquid-phase Mg-Al-Ca alloy 20 is used as the cooling medium for cooling the heated carbon-steel wire 1A. However, it goes without saying that the liquid-phase Mg-Al-Ca alloy 20 can also be used as a heating medium for heating an object.

[0057] Further, in the embodiment set forth above, the heated carbon-steel wire 1A is brought into direct contact with (immersed in) the liquid-phase Mg-Al-Ca alloy 20. However, the liquid-phase Mg-Al-Ca alloy 20 can, for example, be brought into close proximity with the object without directly contacting it, and the object can be heated or cooled in contactless fashion. For example, by causing the liquid-phase Mg-Al-Ca alloy 20 to flow through a pipe, the pipe surroundings can be heated or cooled.

[0058] Description of Symbols

1A, 1B, 1C	carbon-steel wire
11	heating furnace
12	cooling tank (cooling furnace)
12A	bath
20	liquid-phase Mg-Al-Ca alloy
21	film
31	carbide alloy die

Claims

1. A heat exchange method comprising:

bringing an object into contact with or in close proximity to a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are main constituent elements; and exchanging thermal energy between said object and said liquid-phase Mg-Al-Ca alloy.

2. A heat exchange method according to claim 1, wherein said liquid-phase Mg-Al-Ca alloy is a cooling medium for cooling said object.

3. A heat exchange method according to claim 1, wherein said liquid-phase Mg-Al-Ca alloy is a heating medium for heating said object.

4. A heat exchange method according to any one of claims 1 to 3, wherein said liquid-phase Mg-Al-Ca alloy has an ignition temperature of 1000°C or higher.

5. A heat exchange method according to any one of claims 1 to 4, wherein said liquid-phase Mg-Al-Ca alloy has a liquidus temperature lower than 640°C.

6. A heat exchange method according to any one of claims 1 to 4, wherein said liquid-phase Mg-Al-Ca alloy has a liquidus temperature lower than 550°C.
7. A heat exchange method according to any one of claims 1 to 6, wherein the element ratio of Ca is $x \times 0.015$ (at%) or higher, where x (at%) is the element ratio of Mg in said liquid-phase Mg-Al-Ca alloy. 5
8. A heat exchange method according to any one of claims 1 to 7, wherein the element ratio of Ca is less than $x \times 0.1 + 10$ (at%), where x (at%) is the element ratio of Mg in said liquid-phase Mg-Al-Ca alloy. 10
9. A heat exchange method according to any one of claims 1 to 8, wherein said object is carbon steel. 15
10. A heat exchange medium including a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are the main constituent elements. 20
11. A heat exchange apparatus having a bath filled with a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are main constituent elements. 25
12. A heat exchange apparatus according to claim 11, wherein a thin film forms on the surface of the liquid-phase Mg-Al-Ca alloy with which said bath is filled. 30
13. A patenting treatment comprising:

passing heated carbon steel through a bath filled with a liquid-phase Mg-Al-Ca alloy obtained by melting an Mg-Al-Ca alloy in which Mg, Al and Ca are main constituent elements; and cooling the heated carbon steel when it passes through the bath. 35

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- 14. A carbon-steel wire obtained by being subjected to a patenting treatment using a liquid-phase Mg-Al-Ca alloy, and to a drawing process.
- 15. A carbon-steel wire according to claim 14, having a tensile strength higher than that of a carbon-steel wire that has been subjected to a patenting treatment using molten lead. 45
- 16. A carbon-steel wire according to claim 14 or 15, having a processing limit higher than that of a carbon-steel wire that has been subjected to a patenting treatment using molten lead. 50
- 17. A carbon-steel wire according to any one of claims 14 to 16, wherein no lead adheres to the surface thereof. 55

Fig. 1

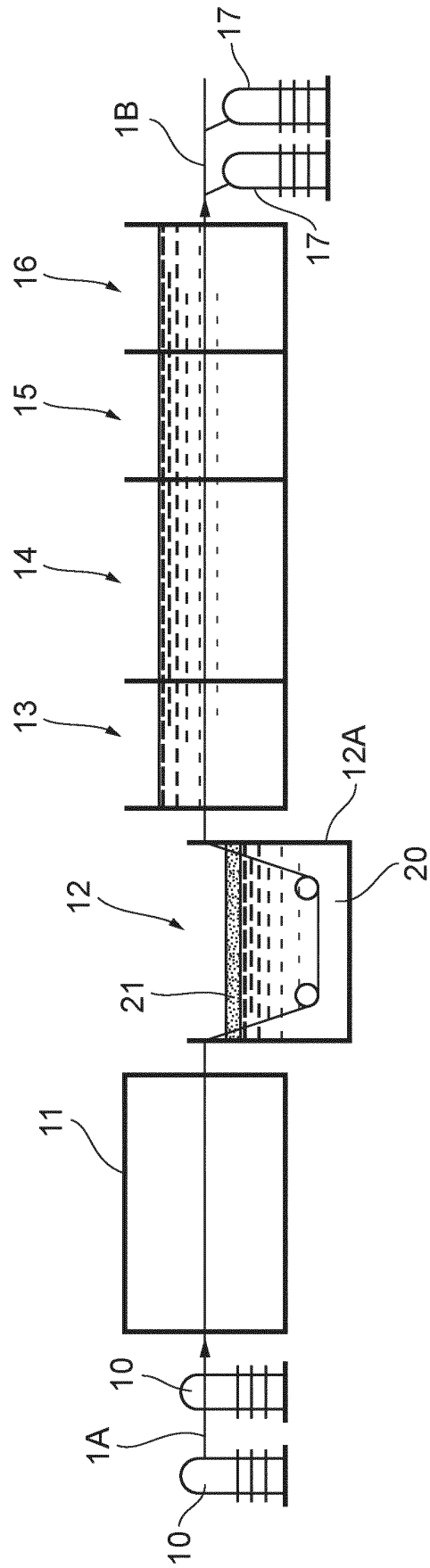


Fig. 2

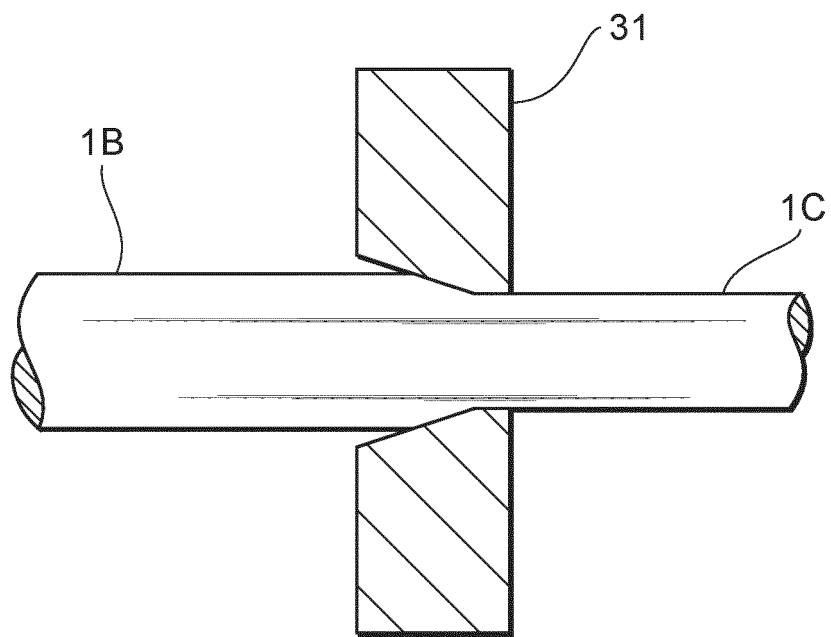


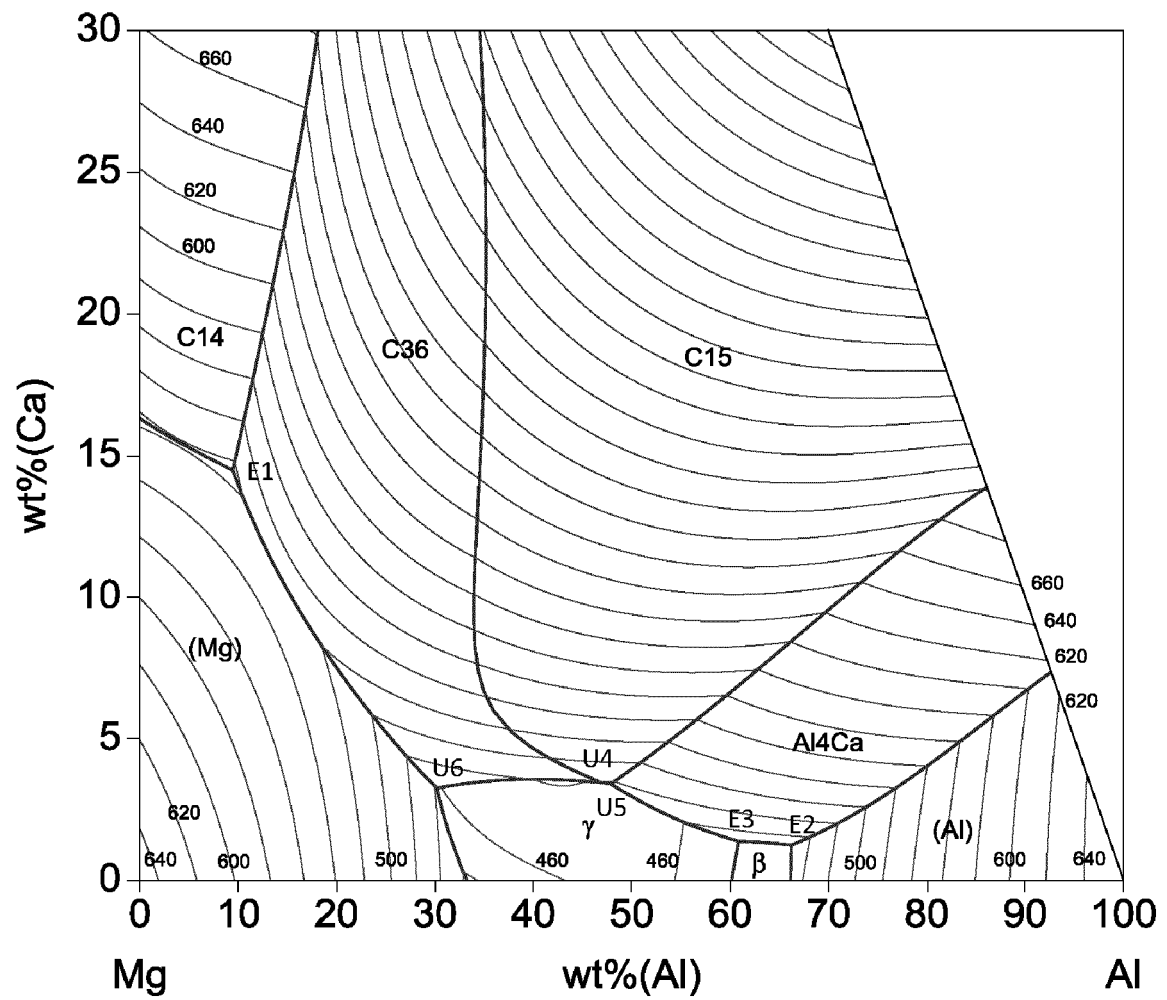
Fig. 3

Fig. 4

	Mg	Al	Ca	PHASE STATE AT 550°C	STATE AT 1000°C
SAMPLE I	68.9wt%	9.45wt%	21.65wt%	LIQUID PHASE	NO COMBUSTION
	76.1at%	9.4at%	14.5at%	LIQUID PHASE	NO COMBUSTION
SAMPLE II	79.0wt%	8.3wt%	12.7wt%	LIQUID PHASE	NO COMBUSTION
	83.9at%	7.9at%	8.2at%	LIQUID PHASE	NO COMBUSTION
SAMPLE III	82.5wt%	10.4wt%	7.1wt%	LIQUID PHASE	NO COMBUSTION
	85.8at%	9.7at%	4.5at%	LIQUID PHASE	NO COMBUSTION
SAMPLE IV	46.3wt%	43.7wt%	10.0wt%	LIQUID PHASE	NO COMBUSTION
	50.5at%	42.9at%	6.6at%	LIQUID PHASE	NO COMBUSTION
SAMPLE V	69.1wt%	26.5wt%	4.4wt%	LIQUID PHASE	NO COMBUSTION
	72.3at%	24.9at%	2.8at%	LIQUID PHASE	NO COMBUSTION

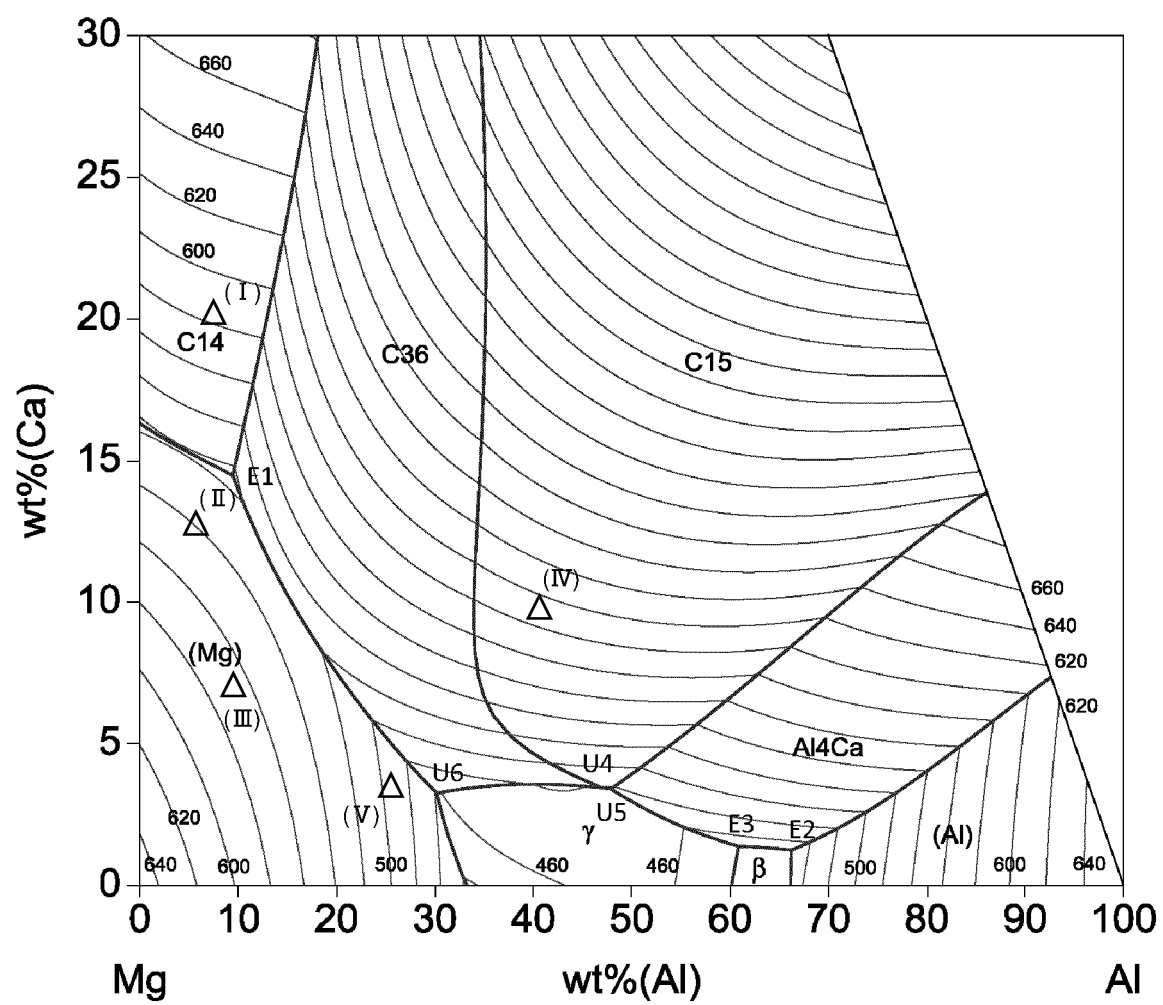
Fig. 5

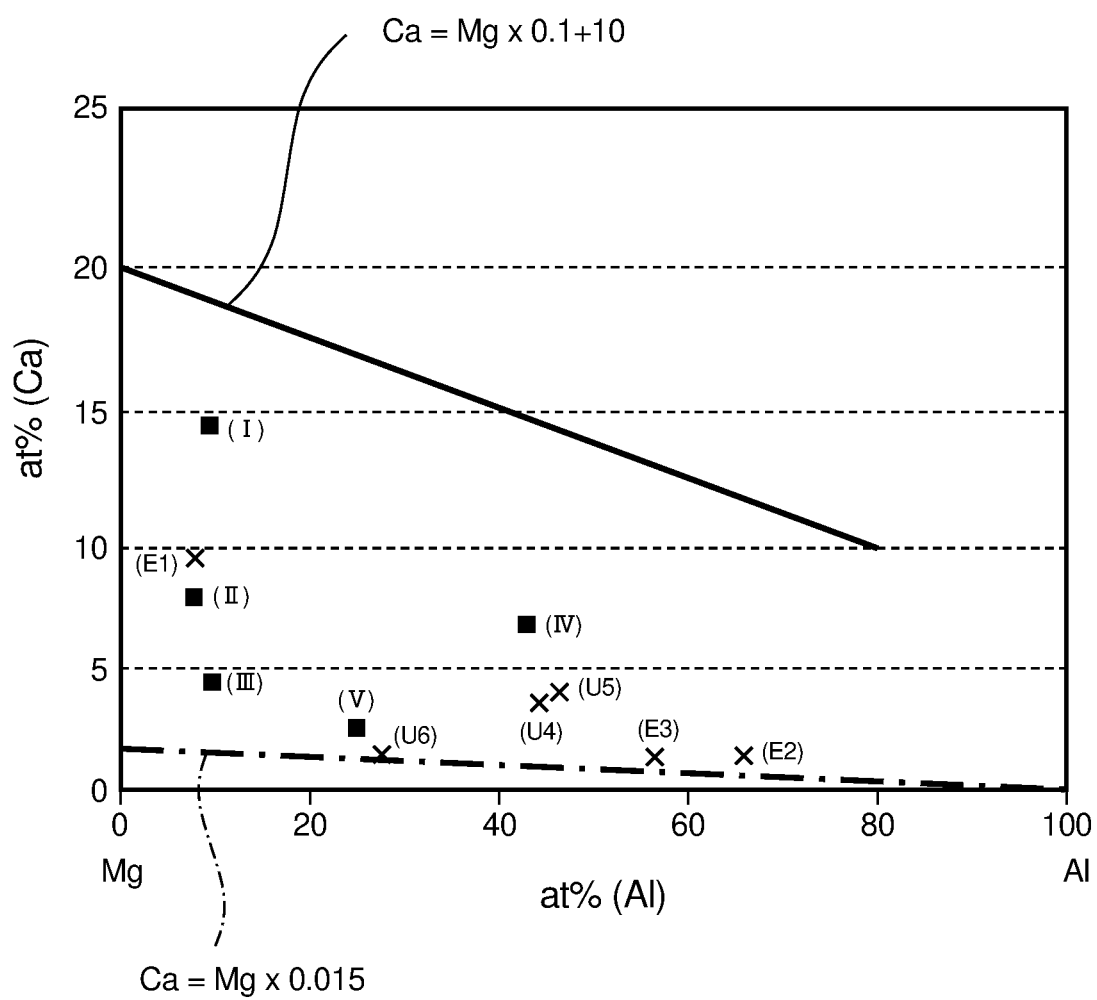
Fig. 6

Fig. 7

STARTING WIRE DIAMETER : 5.500(mm), TYPE OF STEEL WIRE : SWRH72A

COOLING MEDIUM	DIAMETER AFTER DRAWING (mm)	TENSILE STRENGTH (MPa)	TWIST VALUE (TIMES / 100D)	FRACTURE
LIQUID-PHASE Mg-Al-Ca ALLOY	1.748	2,160	36	NORMAL
MOLTEN LEAD	1.748	2,094	37	NORMAL
LIQUID-PHASE Mg-Al-Ca ALLOY	1.553	2,327	37	NORMAL
MOLTEN LEAD	1.553	2,235	38	NORMAL
LIQUID-PHASE Mg-Al-Ca ALLOY	1.408	2,495	40	NORMAL
MOLTEN LEAD	1.408	2,419	42	NORMAL
LIQUID-PHASE Mg-Al-Ca ALLOY	1.248	2,681	38	NORMAL
MOLTEN LEAD	1.248	2,654	37	DELAMINATION OCCURRED

Fig. 8

STARTING WIRE DIAMETER : 1.060(mm), TYPE OF STEEL WIRE : SWRH62A

COOLING MEDIUM	DIAMETER AFTER DRAWING (mm)	TENSILE STRENGTH (MPa)	TWIST VALUE (TIMES / 100D)	FRACTURE
LIQUID-PHASE Mg-Al-Ca ALLOY	0.362	1,891	44	NORMAL
MOLTEN LEAD	0.363	1,836	48	NORMAL

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/002904

A. CLASSIFICATION OF SUBJECT MATTER

C21D 1/48(2006.01)i; C21D 9/64(2006.01)i; C22C 23/02(2006.01)i; C22C 30/00(2006.01)i

FI: C21D1/48; C22C23/02; C22C30/00; C21D9/64

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)

C21D1/48; C21D9/64; C22C23/02; C22C30/00

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

Published examined utility model applications of Japan 1922-1996

Published unexamined utility model applications of Japan 1971-2020

Registered utility model specifications of Japan 1996-2020

Published registered utility model applications of Japan 1994-2020

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.
Y A	CN 108467927 A (GUANGZHOU YUZHONG TECHNOLOGY CO., LTD.) 31.08.2018 (2018-08-31) claims 1-3, paragraphs [0002], [0008], [0011]-[0014]	1-2, 4-17 3
Y	JP 2016-023334 A (TOBATA SEISAKUSHO CO., LTD.) 08.02.2016 (2016-02-08) claims, paragraphs [0025], [0056]-[0080], [0134], fig. 3, 7	1-17
Y A	JP 164161 C1 (HITACHI KOKUKI KK) 02.08.1944 (1944-08-02) claims, page 1	1, 3-12 2, 13-17
A	JP 2011-522113 A (N.V. BEKAERT S.A.) 28.07.2011 (2011-07-28)	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
13 April 2020 (13.04.2020)Date of mailing of the international search report
21 April 2020 (21.04.2020)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2020/002904

5	Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
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	JP 2016-023334 A	08 Feb. 2016	(Family: none)	
10	JP 164161 C1	02 Aug. 1944	(Family: none)	
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			SI 2271779 T1	
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REFERENCES CITED IN THE DESCRIPTION

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- JP 2005529235 A [0005]
- WO 2015060459 A [0016] [0017]