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	Designated Validation States: MA MD	(74)	Representative: van Dam, Vincent Octrooibureau Vriesendorp & Gaade B.V. Koninginnegracht 19 2514 AB Den Haag (NL)	

# (54) DE-LEADING TREATMENT METHOD FOR LEAD-CONTAINING COPPER ALLOY AND DE-LEADING CORED WIRE USED IN SAID METHOD

(57) A copper alloy such as brass and bronze centered on rod products in which machinability is mainly required contains a certain amount of lead. The scrap of these products has been recycled at a high rate. A lead-removing step is indispensable for recycling the scrap of these products for low-lead products, and development of lead-removal techniques is urgently necessary. It is known that a material containing metal element calcium exhibits an effect in removing lead in a copper alloy, and since there are differences in the specific gravity and the melting point between a de-leading agent and a copper alloy, a de-leading method at a practical mass production level is required. In order to solve this problem, for the purpose of de-leading treatment of a copper alloy molten metal, there is provided a cored wire for lead removal characterized in that a metal band which does not affect the components of a copper alloy molten metal is used as a sheath material; a single de-leading agent and/or a de-leading coagent such as an aggregation/floatation agent for a Pb-Ca compound required for a step is used as contents; and physical properties that endure mechanical and continuous feed by a cored wire feeding device are provided.



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#### Description

#### **TECHNICAL FIELD**

<sup>5</sup> **[0001]** The present invention relates to a cored wire for lead removal used for the de-leading treatment of molten metal of a lead-containing copper alloy and to a de-leading treatment method using the same.

#### **BACKGROUND ART**

- 10 [0002] Since a copper alloy, mainly a brass rod, is required for workability (machinability), it has conventionally been effective to incorporate about 2 to 4 wt% of lead into a copper alloy. Examples of the objects in which a brass rod is used include faucets utilized in a water supply system, worked parts of various optical equipment, and automobile parts. In recent years, the control in the direction of reducing or eliminating lead contained in a brass rod has been strengthened from the point of view of environmental control.
- 15 [0003] It is a known fact that the workability (machinability) similar to that of a conventional lead-containing brass rod can be imparted technically by incorporating a metal such as bismuth as a substitute of lead. However, a product using expensive bismuth, which is generally called a leadless product, cannot satisfy all of the conventional objects to be used also in terms of performance. Further, with respect to a brass rod already used mainly for the faucets utilized in a water supply system, a product in which the content of lead is reduced in consideration of an influence given to a human body,
- which is generally called a low-lead product, has also been developed and used.
  [0004] However, the percentage of these new products in the market is low, and a large percentage is composed of conventional products. Meanwhile, a large number of products of a copper alloy including brass are produced by the remelting of scrap, and it is extremely difficult to control the scrap based on the origin of the products. Therefore, there is a high possibility that most of the scrap originated from leadless or low-lead products may also be mixed with con-
- <sup>25</sup> ventional raw materials.

**[0005]** As a measure to cope with these problems, there is proposed a method of removing lead as a compound with calcium by adding metal element calcium and/or a copper-calcium alloy to brass molten metal containing lead (Patent Literature 1). Further, there is proposed a method comprising adding a de-leading material to a copper alloy molten metal followed by mixing to produce a lead compound, adding a desiliconizing agent to liberate the lead compound, and

- 30 separating and floating the lead compound to eliminate the same (Patent Literature 2). Further, there is proposed a method of adding a tin blocking agent to a copper alloy molten metal followed by mixing and then adding a de-leading agent thereto followed by mixing, thereby similarly separating and floating the lead compound to eliminate the same (Patent Literature 3). With respect to the use of a cored wire, there is proposed, for example, a method of charging a cored wire, in which a desulfurizing agent is covered with an iron-based band material or a sheath material, into molten
- <sup>35</sup> iron or molten steel to allow the desulfurizing agent to react with the molten iron or molten steel to thereby exert a desulfurization effect (Patent Literature 4).

#### **CITATION LIST**

40 Patent Literature

#### [0006]

Patent Literature 1: Japanese Patent Laid-Open No. Heisei 10-140254
 Patent Literature 2: Japanese Patent Laid-Open No. 2005-8970
 Patent Literature 3: Japanese Patent Laid-Open No. 2006-161136
 Patent Literature 4: Japanese Patent Laid-Open No. 2008-95136

#### SUMMARY OF INVENTION

#### 50

**Technical Problem** 

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**[0007]** The method of Patent Literature 1 is a method in which 300 kg of a raw material has been subjected to deleading and removal in a small crucible, wherein a de-leading agent has been added at a time and allowed to stand to perform component analysis. Further, the method of Patent Literature 2 is a method of using, as an example, 4 kg of bronze, 320 g of a de-leading agent, and 150 g of a desiliconizing agent and feeding nitrogen gas by ejecting it into molten metal. At the same time, Patent Literature 3 is an experiment in which 5 kg of bronze and 400 g of a deblocking material are used. All of these methods are small-scale experimental methods. For example, the addition, stirring, and mixing of additives can be manually performed.

**[0008]** Metal calcium is most effective for the purpose of lead removal. However, it is a water-reactive combustible substances which generates hydrogen in contact with water particularly when it is in a granular or powdery form. Therefore, it is necessary to keep a water-prohibitive state particularly in a mass production stage, to store in a dry, cool, dark place,

<sup>5</sup> and to take care also of the reactivity when charged into molten metal. Thus, the handling of metal calcium requires high attention. Also with respect to calcium silicon, the same hazard increases when it takes a granular or powdery form. Therefore, this is a problem in the handling in practical mass production.

[0009] Further, these de-leading agents (density of Ca: 1.55), coagents, and the like have small specific gravity and float in molten metal of brass or bronze having a specific gravity of more than 8. Therefore, sufficient de-leading effect cannot be obtained only by adding these de-leading agents and coagents to the molten metal. A method of using a stirrer or the like may technically contribute to improve the de-leading effect. However, it will probably be required to install equipment and add treatment steps and time. Therefore, the method has not been established in practical mass production.

[0010] As described in Patent Literature 4, a cored wire, known as an existing technique, has been used in steel and casting industry as a material to be charged into molten iron or molten steel to be treated, the material being prepared by covering an additive raw material required for deoxidation, desulfurization, or graphite spheroidization, singly or in combination, with an iron outer metal band (sheath material).

**[0011]** The contents used for conventional cored wires are composed of a combination of various raw materials such as a deoxidizer, a desulfurizing agent, and a graphite spheroidizing agent depending on the purpose of use. The sheath

- 20 material may be changed depending on the purpose and the object of treatment, but the outer metal band used for products actually circulating in the market is only a thin plate of iron. Metal (for example, aluminum) thin plates other than the iron thin plate which can be theoretically supplied and used have been hardly selected from the point of view of operation technique, cost, and difficulty in supply.
- [0012] Moreover, an object of the present invention is the de-leading of a copper alloy, and conventionally used iron, aluminum, and the like cannot be used because they affect the quality of a copper alloy to be subjected to de-leading. Not only the components but also physical properties such as strength (tensile strength), flexibility, and workability are required for the sheath material to be selected in this case. These physical properties are required in order that the contents are reliably fixed after the shape working to form a cored wire and that the sheath material does not cause fracture, rupture, opening, and the like during the feed, so that the core wire is suitably fed to molten metal by a cored
- 30 wire feeding device. Particularly when the cored wire is fed by a cored wire feeding device, a balance between the strength and the flexibility of a cored wire is required.
  100121 The main component of a de leading count in the present invention is metal colorium end/or colorium eilier.

**[0013]** The main component of a de-leading agent in the present invention is metal calcium and/or calcium silicon, and a de-leading coagent also has a small specific gravity compared with that of the copper alloy molten metal to be subjected to de-leading treatment. Therefore, if the de-leading agent and the de-leading coagent are simply charged into molten metal, they will float on the surface of the molten metal, and reaction will occur only on the surface. Conse-

quently, an expected de-leading effect cannot be obtained.
[0014] In order to obtain an effective de-leading method, it is required to apply, to the de-leading agent, the gravity corresponding to the buoyancy thereof to allow the de-leading agent to sink in the molten metal. Generally, the buoyancy in fluid is determined by the following formula 1.

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(Formula 1)  
F = 
$$\rho$$
Vg

(wherein F = buoyancy,  $\rho$  = fluid density, V = volume of object, g = gravitational acceleration) **[0015]** The strength required when 10 kgs of metal calcium having a density of 1.55 is intended to sink in brass molten metal having a density (specific gravity) of 8.2 is determined from the resultant force obtained by subtracting own weight of the object from the buoyancy. Therefore, the following formula is obtained.

55

(Formula 2)  
F' = 
$$(\rho_1 - \rho_2)$$
Vg

(wherein  $\rho_1$  = density of brass,  $\rho_2$  = density of metal calcium) Therefore, the following formula is obtained.

 $F' = [8.2 (g/cm^3) - 1.55 (g/cm^3)] \times [10,000 (g)/1.55 (g/cm^3)] \times 9.8 (m/s^2) = 420,452 (g \cdot m/s^2) \approx 43 \text{ kgf}$ 

**[0016]** By simple calculation, it is required to perpendicularly attach a weight of 43 kgs from right above molten metal having a temperature of about 1000°C, or a pushing operation into molten metal by mechanical force is required. Of course, in practical mass production, this value probably significantly increases depending on the amount of molten metal to be treated and the target amount of lead removal, which cannot be coped with by human power but requires a

<sup>5</sup> large-scale apparatus. Further, a jig required to push de-leading agent into molten metal needs to be infusible at a temperature of molten metal and in the components thereof, or it is required to prepare each time a jig or the similar that does not adversely affect the quality of molten metal even when it is fused into the molten metal. Therefore, the pushing is not suitable for practical mass production in terms of cost and an increase in operation steps.

#### 10 SOLUTION TO PROBLEM

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**[0017]** The present invention provides means and a method of solving the above problems in order to perform deleading in the mass production of a copper alloy. The present invention has minimized contact with water in the air to reduce a hazard by covering metal calcium or/and calcium silicon with a metal sheath material and mitigated and solved

- <sup>15</sup> safety problems and handling problems in the de-leading treatment in practical mass production by having enabled continuous automatic charge of integrated form of a cored wire by a machine. Here, a copper alloy refers to an alloy comprising copper as main component, and the chief object is brass or bronze, but not particularly limited thereto. [0018] In the present invention, by continuously feeding a cored wire containing a de-leading agent to molten metal,
- the collective charge of the de-leading agent is first avoided; the resistance per unit time against the buoyancy of the molten metal is suppressed to a minimum level; the de-leading agent is dispersed over the whole molten metal to effectively perform de-leading; the performance of the cored wire that can be mechanically and continuously fed by a cored wire feeding device is achieved; and dangerous work by human power or right above the molten metal is eliminated. Thereby, the above problems are solved.

[0019] Thus, the present invention proposes a de-leading treatment method of a lead-containing copper alloy, comprising: successively feeding a cored wire for lead removal to molten metal of a copper alloy containing lead and allowing the cored wire to sink in the molten metal to subject the molten metal to de-leading treatment, the cored wire for lead removal comprising a de-leading agent and/or a de-leading coagent covered, singly or in combination, with a sheath material comprising copper or a copper alloy, wherein the de-leading agent is a granular or powdery de-leading agent agentations metal element aclaim and the de leading concent is a granular or powdery de-leading agent

containing metal element calcium, and the de-leading coagent is a granular or powdery de-leading coagent containing
 at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin.

**[0020]** Further, the present invention proposes a de-leading treatment method, wherein a cored wire for lead removal comprising the de-leading agent covered with the sheath material and a cored wire for lead removal comprising the de-leading coagent covered with the sheath material are fed and allowed to sink in the molten metal to treat the molten metal for lead removal.

**[0021]** Further, the present invention proposes a de-leading treatment method, wherein a cored wire for lead removal comprising at least one of the de-leading agent and the de-leading coagent covered with the sheath material is fed and allowed to sink in the molten metal once or multiple times to subject the molten metal to de-leading treatment.

[0022] Further, the present invention proposes a cored wire for lead removal comprising a sheath material comprising copper or a copper alloy having a tensile strength of 150 to 600 N/mm<sup>2</sup> and a ductility of 15 to 60% and a granular or powdery de-leading agent containing metal calcium or/and calcium silicon, wherein the de-leading agent is covered with the sheath material.

[0023] Further, the present invention proposes a cored wire for lead removal comprising a sheath material comprising copper or a copper alloy having a tensile strength of 150 to 600 N/mm<sup>2</sup> and a ductility of 15 to 60% and a granular or

<sup>45</sup> powdery de-leading coagent containing at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin, wherein the de-leading coagent is covered with the sheath material.

**[0024]** Further, the present invention proposes a cored wire for lead removal comprising a sheath material comprising copper or a copper alloy having a tensile strength of 150 to 600 N/mm<sup>2</sup> and a ductility of 15 to 60%, a granular or powdery

<sup>50</sup> de-leading agent containing metal calcium or/and calcium silicon, and a granular or powdery de-leading coagent containing at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin, wherein the de-leading agent and the de-leading coagent are covered with the sheath material.

[0025] Further, the present invention proposes a cored wire for lead removal, wherein the diameter of the cored wire for lead removal is 4 to 30 mm.

**[0026]** Further, the present invention proposes a cored wire for lead removal, wherein the thickness of the sheath material of the cored wire for lead removal is 0.1 to 3 mm.

[0027] Further, the present invention proposes a method for producing a cored wire for lead removal, comprising:

subjecting a sheath material comprising copper or a copper alloy to shape working to thereby closely fix a granular or powdery de-leading agent containing metal calcium or/and calcium silicon and/or a granular or powdery de-leading coagent containing at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin, to the sheath material to secure the de-leading agent

<sup>5</sup> and/or the de-leading coagent so that the de-leading agent and/or the de-leading coagent may not move relative to the sheath material.

#### ADVANTAGEOUS EFFECTS OF INVENTION

- <sup>10</sup> **[0028]** According to the present invention, the fracture, rupture, and opening of a cored wire can be prevented by a structure having suitable strength and flexibility after taking the work hardening of a sheath material into consideration; thereby, continuous feeding of a proper amount of a cored wire to molten metal can be automatically performed; deleading treatment of a copper alloy molten metal in practical mass production is achieved; the difficulty of mixing treatment of a de-leading agent having a small specific gravity with a large amount of molten metal having a large specific gravity
- <sup>15</sup> is mitigated; and it has been possible to reduce hazards due to use of a large amount of a highly reactive de-leading agent and operation at a location above molten metal.

#### **BRIEF DESCRIPTION OF DRAWINGS**

#### 20 [0029]

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[Figure 1] Figure 1 is a schematic explanatory diagram of a cored wire feeding device for carrying out the present invention.

[Figure 2] Figure 2 is an explanatory diagram of a cross section of a cored wire for lead removal showing an example of the present invention.

[Figure 3] Figure 3 is an explanatory diagram of a cross section of a cored wire for lead removal showing an example of the present invention.

[Figure 4] Figure 4 is an explanatory diagram of a cross section of a cored wire for lead removal showing an example of the present invention.

[Figure 5] Figure 5 is an explanatory diagram of a cross section of a cored wire for lead removal showing an example of the present invention.

#### **DESCRIPTION OF EMBODIMENTS**

- <sup>35</sup> **[0030]** The cored wire feeding device used in the present invention will be described using Figure 1 showing an example. A cored wire feeding device 10 is a device for feeding a cored wire for lead removal 1 to a treatment container 11 such as a melting furnace for treating a lead-containing copper alloy molten metal which is an object of the present invention. The cored wire for lead removal 1 is pulled out of a coil 12 wound in a coiled form and fed to the treatment container 11 by a feeder 13.
- 40 [0031] The feeder 13 is installed on a mount 14 and is configured to pull the cored wire for lead removal 1 out of the coil 12 and charge it into the molten metal 17 received in the treatment container 11. Various types of mechanisms can be employed in this feeder 13, but in a general mechanism, the cored wire for lead removal 1 is sandwiched by plural rolls rotated by a motor and a plurality of carrying rolls to continuously perform the pulling out and the charge.
- [0032] A plurality of guides 15 for the cored wire for lead removal 1 are provided at suitable places on the mount 14 to smoothly pull out the cored wire for lead removal 1 pulled out of the coil 12 and send it to the feeder 13. A guide pipe 16 is provided between the feeder 13 and the treatment container 11 and bears the sending of the cored wire for lead removal 1 and the continuous charge thereof in the vertical direction into the molten metal 17. Further, the guide pipe 16 can be movably supported by a support arm 141 projecting from the mount 14.
- **[0033]** The lower end of the guide pipe 16 may project into the treatment container 11 provided that it does not contact molten metal. The cored wire for lead removal 1 is preferably fed near the bottom of the treatment container 11, and it is preferred to adjust the feeding rate in consideration of the material and the thickness of the sheath material 4 so that it melts near the bottom of the treatment container 11. In the cored wire for lead removal 1 used in the present invention, metal calcium and calcium silicon are used singly or in combination as a de-leading agent 2. A granular or powdery deleading agent 2 may be used.
- <sup>55</sup> **[0034]** Further, as shown in Figures 2 to 5 which are the cross section diagrams of the cored wire for lead removal, the de-leading agent 2 may be used in combination with the de-leading coagent 3 as the contents, that is, the components, of the cored wire for lead removal (Figures 2 and 3), but only one of the de-leading agent 2 and the de-leading coagent 3 may also be used as the content to form an independent separate cored wire for lead removal 1 (Figures 4 and 5).

This suggests that various matrices of de-leading treatment occurring in practical mass production can be flexibly responded to by using a plurality of cored wires for lead removal 1. Therefore, the cored wire for lead removal 1 used for lead removal in the present invention includes those in which the de-leading agent 2 and/or the de-leading coagent 3 is used singly or in combination.

<sup>5</sup> **[0035]** The present invention is characterized by using a metal such as copper, brass or bronze, or a copper alloy containing zinc, tin, or the like that does not have compositional influence on the copper alloy, as the sheath material 4 for covering the de-leading agent 2 and/or the de-leading coagent 3.

**[0036]** Unlike an iron cored wire produced using an existing technique, the sheath material of copper or a copper alloy used in the present invention shows high work hardening when it is worked. This is a phenomenon that when stress is

given to a metal, hardness of the metal is increased by plastic deformation, and the characteristics are shown by the size of a work hardening factor. A common carbon steel (0.6C steel) has a work hardening factor of 0.15, while 65/35 brass which is one of the sheath materials 4 used in the present invention has a work hardening factor of 0.53, which is a numerical value 3 times or more larger than that of the common carbon steel. This means that when the copper alloy is worked as the sheath material 4, the function such as flexibility that is expected from the cored wire for lead removal 1 will be lost.

**[0037]** Since tensile strength and ductility are generally significantly different depending on material, a cored wire for lead removal 1 that endures practical use must be prepared by changing production conditions of the cored wire taking the type and physical properties of the sheath material 4 into account. In order to solve this problem, the metal to be used for the sheath material 4 has been tested in the present invention, and it has been elucidated that, with respect to

- the physical properties required for the cored wire for lead removal, tensile strength is desirably in the range of 150 to 600N/mm<sup>2</sup>, and ductility is desirably from 15 to 60%. When tensile strength is less than 150 N/mm<sup>2</sup>, risk of cutting is high, and the metal does not endure use; and when tensile strength is larger than 600 N/mm<sup>2</sup>, the metal is too strong and adversely affects the production of the cored wire for lead removal, and the use of winding into and pulling out of a coil has been difficult. Further, when ductility is less than 15%, there is no room for deformation, and the production,
- <sup>25</sup> working, and feed of the cored wire for lead removal is difficult; and when ductility is larger than 60%, an inconvenience occurs in the dimension of the cored wire for lead removal and in keeping the shape thereof during feed.
  [0038] Further, the diameter of the cored wire for lead removal is preferably 4 to 30 mm for the purpose of facilitating production and working of the cored wire for lead removal and keeping the shape thereof during feed. Furthermore, from the same purpose, the thickness of the sheath material 4 used in the present invention is desirably in the range of 0.1
- <sup>30</sup> mm to 3.0 mm. This is because when the thickness is less than 0.1 mm, strength is low, which may cause tearing and cutting, and when the thickness is more than 3.0 mm, it is difficult to bend a cored wire for lead removal 1, which makes it difficult to produce and feed the cored wire.

[0039] Further, the best material and thickness of the sheath 41 used in the present invention can be selected in the range proposed above in consideration of the matrix of physical properties and the de-leading effect also taking the

- <sup>35</sup> result of calculation of the position and time to melt into account so that the contents may act more efficiently in the molten metal to be de-leaded. Furthermore, with respect to the material of the sheath material 4, those having the quality described in JIS material symbols C1020-1441 and C2100-4640 correspond to the material used in the present invention, and it is practically convenient to use these materials.
- [0040] With respect to the contents of the cored wire for lead removal, the following various additives can be provided as the de-leading coagent 3 for increasing the de-leading effect. A granular or powdery coagent can be used as the deleading coagent 3. Examples include a Ca compound 31 such as CaF2, CaCO3, and CaO which contributes to the fixing of the de-leading agent in the cored wire for lead removal and is used for the flux after the reaction, an aggregation/floatation agent for a Pb-Ca compound 32, a mineral containing sodium fluoride and alumina silica glass or the like 33, which is generally called a tin blocking agent, a metal such as copper, zinc, and tin, or a compound thereof 34, which is a
- <sup>45</sup> component constituting the copper alloy itself to be de-leaded and which contributes to the fixing of the de-leading agent in the cored wire for lead removal and the adjustment of components of the molten metal after de-leading. These can be contained in the cored wire for lead removal by selecting desired additives. Further, as an alternative in the present invention, it is possible to produce a cored wire for lead removal containing only one of these additives, for example, only a Ca compound 31 (Figure 5), only an aggregation floatation agent, only a tin blocking agent, or only a metal such
- <sup>50</sup> as copper or a compound thereof. The cored wire containing only the de-leading coagent may also be referred to as an auxiliary cored wire for lead removal. As described above, the cored wire for lead removal 1 include those in which one or more de-leading agents and one or more de-leading coagents are covered with a sheath material, those in which one or more de-leading agents are covered with a sheath material, and those in which one or more de-leading coagents are covered with a sheath material. Further, the cored wire for lead removal 1 include those in which one or more de-leading coagents are
- <sup>55</sup> agents and one de-leading coagent are covered with a sheath material and those in which one de-leading agent and one or more de-leading coagents are covered with a sheath material.

**[0041]** For integrating and fixing the de-leading agent 2 and/or the de-leading coagent 3 to the cored wire 1, the ductility of the sheath material 4 is exhibited during the working of the cored wire for lead removal 1, and the cored wire for lead

removal 1 is compressed while closely contacting the de-leading agent 2 and the de-leading coagent 3 as the contents with the cored wire for lead removal 1. As a method for performing the above, both ends of the sheath material 4 are preferably secured, for example, by caulking 5 to cover the contents.

#### 5 **EXAMPLES**

[0042] In order to verify the effectiveness of the present invention, the tests shown in Table 1 were performed utilizing the cored wire feeding device 10 shown in Figure 1.

10	[lable 1]					
			Example 1	Example 2		
	Wire contents	Metal calcium (mass%)	90	90		
45		Specific gravity (g/cm <sup>3</sup> )	1.55	1.55		
15		Fluorite (mass%)	10	10		
		Specific gravity (g/cm <sup>3</sup> )	3.18	3.18		
	Sheath material	Material	Brass	Brass		
20		Wire diameter (mm)	13	13		
		Sheath material thickness (mm)	0.35	0.4		
	Wire average specific gravity (g/cm <sup>3</sup> )		4.6	5.0		
25	Copper alloy molten metal	Material	Brass	Brass		
20		Specific gravity (g/cm <sup>3</sup> )	8.3	8.2		
		Molten metal weight (kg)	4000	4500		
		Molten metal temperature (°C)	950	950		
30	Number of wires		1	1		
	Wire feed length (m)		350	450		
	Wire feed time (min)		10	15		
35	Amount of removed lead (kg)		40	70		

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[0043] In the above Examples 1 and 2, the cored wire for lead removal 1 was continuously fed into the brass molten metal 17. A predetermined amount (length) of the cored wire for lead removal 1 of the present invention was able to be charged into the molten metal without causing problems such as fracture, rupture, and opening, and the de-leading described in Table 1 was accomplished. From Examples, it is determined that the best cored wire for lead removal can be produced, and the conditions of feeding the same can be set, in accordance with the weight and temperature of molten metal and the shape of a furnace. The results of Examples above proved that it was possible to perform deleading in tens of kilogram unit in the mass production scale using a real machine which was not able to be achieved in prior art examples. Further, since problems such as fracture, rupture, and opening did not occur irrespective of using a

45 sheath material which did not belong to a prior art material, it is determined that the characteristics required for the sheath material specified in the present invention satisfy the conditions that can endure the production of a cored wire for lead removal and the feed thereof by a machine.

[0044] Note that although the tests using brass were performed in the Examples, it is apparent that the tests are not limited to brass but can be similarly applied to a copper alloy such as bronze.

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### INDUSTRIAL APPLICABILITY

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[0045] In view of the present circumstances in which many products of a copper alloy including brass are produced by remelting the scrap thereof, it is extremely important to remake scrap into a raw material to produce a good quality copper alloy. The present invention extremely efficiently removes lead contained in a copper alloy, allows mass remaking of a copper alloy in a good condition, and can achieve quality improvement of copper alloy products and cost reduction of the products produced therefrom. Thus, the present invention has a large in-use effect.

#### Claims

- A de-leading treatment method of a lead-containing copper alloy, comprising: successively feeding a cored wire for lead removal to molten metal of a copper alloy containing lead and allowing the cored wire to sink in the molten metal to subject the molten metal to de-leading treatment, the cored wire for lead removal comprising a de-leading agent and/or a de-leading coagent covered, singly or in combination, with a sheath material comprising copper or a copper alloy, wherein the de-leading agent is a granular or powdery de-leading agent containing metal element calcium, and the de-leading coagent is a granular or powdery de-leading coagent containing at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin.
  - 2. The de-leading treatment method according to claim 1, wherein a cored wire for lead removal comprising the deleading agent covered with the sheath material and a cored wire for lead removal comprising the de-leading coagent covered with the sheath material are fed and allowed to sink in the molten metal to subject the molten metal to deleading treatment.
    - **3.** The de-leading treatment method according to claim 1 or 2, wherein a cored wire for lead removal comprising at least one of the de-leading agent and the de-leading coagent covered with the sheath material is fed and allowed to sink in the molten metal once or multiple times to subject the molten metal to de-leading treatment.
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- **4.** A cored wire for lead removal comprising a sheath material comprising copper or a copper alloy having a tensile strength of 150 to 600 N/mm<sup>2</sup> and a ductility of 15 to 60% and a granular or powdery de-leading agent containing metal calcium or/and calcium silicon, wherein the de-leading agent is covered with the sheath material.
- 5. A cored wire for lead removal comprising a sheath material comprising copper or a copper alloy having a tensile strength of 150 to 600 N/mm<sup>2</sup> and a ductility of 15 to 60% and a granular or powdery de-leading coagent containing at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin, wherein the de-leading coagent is covered with the sheath material.
  - 6. A cored wire for lead removal comprising a sheath material comprising copper or a copper alloy having a tensile strength of 150 to 600 N/mm<sup>2</sup> and a ductility of 15 to 60%, a granular or powdery de-leading agent containing metal calcium or/and calcium silicon, and a granular or powdery de-leading coagent containing at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin, wherein the de-leading agent and the de-leading coagent are covered with the sheath material.
    - 7. The cored wire for lead removal according to any one of claims 4 to 6, wherein the diameter of the cored wire for lead removal is 4 to 30 mm.
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- **8.** The cored wire for lead removal according to any one of claims 4 to 7, wherein the thickness of the sheath material of the cored wire for lead removal is 0.1 to 3 mm.
- 9. A method for producing a cored wire for lead removal, comprising: subjecting a sheath material comprising copper or a copper alloy to shape working to thereby closely fix a granular or powdery de-leading agent containing metal calcium or/and calcium silicon and/or a granular or powdery de-leading coagent containing at least one of a Ca compound, an aggregation/floatation agent for a Pb-Ca compound, a tin blocking material, copper, zinc, tin, and a compound of copper, zinc, or tin, to the sheath material to secure the de-leading agent and/or the de-leading coagent so that the de-leading agent and/or the de-leading coagent may not move relative to the sheath material.

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[Fig.1]



[Fig.2]







[Fig.4]





		INTERNATIONAL SEARCH REPORT	International app	lication No.			
			PCT/JP	2015/082039			
5	A. CLASSIFIC C22B15/14	CLASSIFICATION OF SUBJECT MATTER 22B15/14(2006.01)i, C22B9/10(2006.01)i					
	According to Int	ernational Patent Classification (IPC) or to both nationa	ll classification and IPC				
	B. FIELDS SE	ARCHED					
10	Minimum documentation searched (classification system followed by classification symbols) C22B15/14, C22B9/10						
5	Documentation : Jitsuyo Kokai J	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searchedJitsuyo Shinan Koho1922–1996Jitsuyo Shinan Toroku Koho1996–2015Kokai Jitsuyo Shinan Koho1971–2015Toroku Jitsuyo Shinan Koho1994–2015					
0	Electronic data b	base consulted during the international search (name of	data base and, where practicable, search	h terms used)			
-	C. DOCUMEN	NTS CONSIDERED TO BE RELEVANT		1			
	Category*	Citation of document, with indication, where ap	propriate, of the relevant passages	Relevant to claim No.			
5	A	JP 2006-161136 A (Kabushiki Tabuchi), 22 June 2006 (22.06.2006), (Family: none)	Kaisha Kyushu	1-9			
	A	JP 10-140254 A (Kobe Steel, 26 May 1998 (26.05.1998), (Family: none)	Ltd.),	1-9			
)	Further do	cuments are listed in the continuation of Box C.	See patent family annex.				
	<ul> <li>* Special cates</li> <li>"A" document de be of particu</li> <li>"E" earlier applie date</li> </ul>	gories of cited documents: fining the general state of the art which is not considered to lar relevance cation or patent but published on or after the international filing	<ul> <li>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</li> <li>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive</li> </ul>				
	<ul> <li>"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)</li> <li>"O" document referring to an oral disclosure, use, exhibition or other means</li> <li>"P" document published prior to the international filing date but later than the</li> </ul>		<ul> <li>step when the document is taken alone</li> <li>'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</li> <li>'e" document members of the semi pattert formily.</li> </ul>				
)	Date of the actua 27 Nov	carmed al completion of the international search ember 2015 (27.11.15)	Date of mailing of the international search report 08 December 2015 (08.12.15)				
5	Name and mailin Japan 3-4-3, K	ng address of the ISA/ Patent Office asumigaseki,Chiyoda-ku, 00-8815 Japan	Authorized officer				
	Form PCT/ISA/21	10 (second sheet) (July 2009)					

#### **REFERENCES CITED IN THE DESCRIPTION**

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#### Patent documents cited in the description

- JP HEISEI10140254 B [0006]
- JP 2005008970 A [0006]

- JP 2006161136 A [0006]
- JP 2008095136 A [0006]