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(54) **CONTROL MATERIAL, AND METHOD FOR PRODUCING THE SAME**

STEUERUNGSMATERIAL UND VERFAHREN ZUR HERSTELLUNG DAVON

MATÉRIAU DE CONTRÔLE ET SON PROCÉDÉ DE PRODUCTION

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(56) References cited:
**EP-A1- 0 292 205 EP-A1- 1 887 090
JP-A- 2014 015 644**

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Description

Technical Field

[0001] The present invention relates generally to ductile cast iron production, and more particularly to a control material that is filled, with a magnesium alloy, in a wire used with a wire injection process for graphite spheroidization and a method for producing that control material.

Background Art of the Invention

[0002] For conventional ductile cast iron production, a wire injection process is used as one of processes for carrying out graphite spheroidization.

[0003] In the wire injection process, a wire having a magnesium alloy filled as a graphite spheroidizing agent in it is cast in a molten metal with the aid of an exclusive feeder. With the wire injection process, the wire having the magnesium alloy filled in it may be cast deep into the molten metal.

[0004] Further, even when the surface of a molten metal is covered with slag, the wire injection process may be used to inject the wire filled up with the magnesium alloy into the molten metal through such slag.

[0005] The wire injection process makes sure of an improvement in the production yield of ductile cast iron because the magnesium component required for graphite spheroidization is added to the molten metal in a stabilized manner.

[0006] In addition, the wire injection process is well compatible with ductile cast iron's quality control and quantitative fluctuations of molten metal, and lends itself to automated addition of magnesium or the like because the wire's addition rate can freely be adjusted with the aid of the dedicated feeder.

[0007] Patent Publication 1 discloses an apparatus capable of injecting a wire into a molten metal by such a wire injection process. Upon contact with a high-temperature molten metal, magnesium contained in the wire reacts to it explosively because of its low boiling point. For the purpose of controlling such an explosive reaction of magnesium, a reaction control material is filled up in the wire together with the magnesium alloy.

[Prior Art]

[Patent Publication(s)]

[0008] [Patent Publication 1] Patent Publication 1: Japanese Patent Application Publication No. 2016-16415

Summary of the Invention

[Problems to be solved by the invention]

[0009] As the control material is filled up in the wire together with the magnesium alloy, however, it gives rise

to a problem that the wire gets heavy, which in turn leads to an increased load on wire delivery work and an increased load on the injection of the wire using the dedicated feeder.

[0010] The situations being like this, an object of the present invention is to provide a wire capable of controlling the reaction of magnesium and achieving weight reductions in the wire injection process for graphite spheroidization upon ductile cast iron production.

[Means for solving the problems]

[0011] According to claim 1, the abovementioned object is achieved by the provision of a control material used in a wire injection process for graphite spheroidization and filled together with a magnesium alloy within a wire, characterized in that the control material is fired and is a porous, volcanic silicate mineral containing 70 to 75% by weight of SiO_2 .

[0012] The control material of claim 1 is so filled in the wire together with the magnesium alloy that the concentration of magnesium in the wire can be kept low, enabling to control the reaction of magnesium upon injection in a molten metal in the wire injection process for graphite spheroidization.

[0013] Also, the control material of claim 1, because of being a porous, volcanic silicate mineral containing 70 to 75% by weight of SiO_2 , is lighter than a conventional control material that is filled together a magnesium alloy in a wire; it works in favor of wire weight reductions. Further, the control material comprising a porous, volcanic silicate mineral containing SiO_2 remains stabilized in terms of the amount of foaming, by being fired.

[0014] According to the control material of claim 2, the control material of claim 1 has a porosity of 60 to 80%.

[0015] In ductile cast iron, there is dross occurring in a molten metal. As casting takes place while dross remains in the molten metal, it causes casting defects in the ductile cast iron. This dross floats on the surface of the molten metal in the form of slag that may then be removed.

[0016] However, an increased amount of slag leads to an increased load on slag removal work. Removal of slag from the surface of the high-temperature molten metal is very dangerous; so the load on slag removal work is preferably reduced as much as possible.

[0017] The control material comprising the porous, volcanic silicate mineral containing much SiO_2 is foamed in the molten metal, turning to dross. The dross produced out of the porous, volcanic silicate mineral containing SiO_2 floats on the surface of the molten metal, turning to slag.

[0018] Working in much the same manner as the control material of claim 1, the control material of claim 2 has a porosity of as high as 60 to 80% or its density gets low for that portion. Thus, even as the control material of claim 2 is foamed, the resulting dross decreases in volume; so the slag resulting from the floating of dross decreases in

amount too. With the control material of claim 2, it is therefore possible to ease off loads on slag removal work.

[0019] According to the control material of claim 3, the control material of claim 1 or 2 has an lg. loss of 0.5% or less.

[0020] The smaller the lg. loss is, the more the control material comprising the porous, volcanic silicate mineral containing SiO_2 remains stabilized in terms of the amount of foaming in the molten metal.

[0021] Working in much the same manner as the control material of claim 1 or 2, the control material claim 3 has an lg. loss of as small as 0.5% or less; so it is stabilized in terms of the volume of foaming. With the control material of claim 3, it is therefore possible to gain fine control of the amounts of dross and slag formed.

[0022] The control material of claim 3 is so stabilized in terms of the amount of foaming that the amount of the control material foamed in the molten metal can finely be controlled. As the amount of the control material foamed in the molten metal is adjusted within a proper range, it permits for adjustment of buoyant force generated in the foamed control material. It is thus possible to adjust the time of the control material remaining in the molten metal and, hence, to gain efficient control of the reaction of magnesium.

[0023] On the other hand, the component(s) added by way of the magnesium-containing wire also turns into dross in the molten metal. When a molten metal-receiving ladle of large size is used, there is some time taken for such dross to float on the surface of the molten metal, during which some problems arise such as a lowering of the molten metal temperature and disappearance of the graphite spheroidization effect.

[0024] For instance by adjusting the amount of the control material foamed in the molten metal in such a way as to come within a proper range, it is possible to adjust buoyant force occurring in the foamed control material. The control material of claim 3 is thus foamed in the molten metal and floats on the molten metal together with dross of the component(s) added by the magnesium-containing wire; so the time during which the dross floats on the surface of the molten metal can be adjusted.

[0025] As the amount of the control material foamed becomes excessive, it may cause the control material to come in contact with and be deposited onto the inner surface of the ladle. Such deposition of the foamed control material may possibly have an adverse influence on the quality of ductile cast iron, doing damage to the ladle.

[0026] For instance, if the control material of claim 3 is adjusted such that the amount of the control material foamed in the molten metal comes within a proper range, it is then possible to easily eliminate the foamed control material before coming in contact with and being deposited onto the inner surface of the ladle.

[0027] According to the control material of claim 4, the control material of any one of claims 1 to 3 has a specific gravity of 0.5 to 1.0 g/cm^3 .

[0028] The control material of claim 4 does just only

work in much the same manner as that of any one of claims 1 to 3 but also has a specific gravity of 0.5 to 1.0 g/cm^3 that is much lower than that of a conventional control material. For this reason, the control material of claim 4 helps reduce the weight of the wire in which it is filled together with the magnesium alloy.

[0029] According to the control material of claim 5, the control material of any one of claims 1 to 4 comprises a fired spherical member having a diameter of less than 5 mm or a fired rod member having a length of less than 5 mm.

[0030] If the control material comprising a porous, volcanic silicate mineral containing SiO_2 is fired, it is then more stabilized in terms of the amount of foaming.

[0031] Working in much the same way as is the case with the control material of any one of claims 1 to 4, the control material of claim 5 remains more stabilized in terms of the amount of foaming because of taking the form of a fired spherical member having a diameter of less than 5 mm or a fired rod member having a length of less than 5 mm. It is thus possible to finely control the amount of foaming of the control material of claim 5 in the molten metal because of the stabilized amount of foaming. In other words, this control material works like that of claim 3.

[0032] Recited in claim 6 is a method for producing a control material used with a wire injection process for graphite spheroidization wherein the control material comprises a porous, volcanic silicate mineral containing 70 to 75% by weight of SiO_2 , and the control material is produced by processing a porous, volcanic silicate mineral having a particle diameter of 3 mm or less into a spherical member having a diameter of less than 5 mm or a rod member having a length of less than 5 mm while using a powdery, volcanic silicate mineral having a particle diameter of 0.1 mm or less and a water content of 15 to 35% by weight.

[0033] The control material produced by the control material production method of claim 6 is so filled in the wire together with the magnesium alloy that the concentration of magnesium in the wire can be kept low, enabling to control the reaction of magnesium upon injection in a molten metal in the wire injection process for graphite spheroidization.

[0034] Also, the control material produced by the control material production method of claim 6, because of being a porous, volcanic silicate mineral containing 70 to 75% by weight of SiO_2 , is lighter than a conventional control material that is filled together a magnesium alloy in a wire; it works in favor of wire weight reductions.

[0035] Further, the control material produced by the production method of claim 6 ensures that depending on the amount of a molten metal and conditions such as temperature, the control material is properly molten and the proper reaction time for graphite spheroidization by magnesium is achieved as well.

[0036] According to the control material production method of claim 7, the control material is fired at 900 to

1000°C.

[0037] With the control material produced by the control material production method of claim 7, the proper reaction time for graphite spheroidization by magnesium is achievable depending on the amount of a molten metal and conditions such as temperature and the amount of foaming is adjustable by being fired. Therefore, the control material produced by the control material production method of claim 7 works in much the same way as is the case with that of claim 3.

[Advantages of the Invention]

[0038] With the control material of any one of claims 1 to 5 as well as the control material produced by the control material production method of any one of claims 6 or 7, it is possible to control the reaction of magnesium and achieve weight reductions of the wire in the wire injection process for graphite spheroidization by magnesium on ductile cast iron production.

Modes for Carrying out the Invention

[0039] A wire used with the wire injection process has a diameter of 6 to 16 mm, and is obtained by covering a magnesium alloy, a control material and additives with a metallic thin sheet.

[0040] The control material production method that is one embodiment of the invention is now explained.

[0041] In the first step, a porous, volcanic silicate mineral containing SiO_2 is sieved into a powdery, volcanic silicate mineral having a particle diameter of 0.1 mm or less and a water content of 15 to 35% weight and a porous, volcanic silicate mineral having a particle diameter of 3 mm or less.

[0042] The process then goes to the second step in which the powdery, volcanic silicate mineral having a particle diameter of 0.1 mm or less is used as a binder and mixed with the porous, volcanic silicate mineral having a particle diameter of 3 mm or less, and the mixture is granulated with a diameter of less than 5 mm.

[0043] The process then goes to the third step in which the granulated spheres having a diameter of less than 5 mm are dried.

[0044] The process then goes to the fourth step in which the granulated spheres having a diameter of less than 5 mm are fired at 900 to 1000°C.

[0045] Through the steps as mentioned above, the control material that is one embodiment of the invention is produced.

[0046] By analysis, the thus produced control material is found to have the following features.

[0047] The control material is a porous, volcanic silicate mineral containing 73.0% by weight of SiO_2 , and has a porosity of 60 to 80%, an Ig. loss of 0.33% and a specific gravity of 0.5 to 1.0 g/cm³. The spherical control material has a diameter of less than 5 mm.

[0048] To ascertain the water absorption of the control

material according to the embodiment here, the following experimentation is done. Fifty (50) grams of the control material were placed in an aluminum dish having a diameter of 120 mm and a depth of 30 mm, and dried in a drying furnace having a temperature of 105°C for a time period of 24 hours. The mass (mass upon drying) of the dried control material was measured.

[0049] The dried control material was then placed in an environmental tank having a temperature of 20°C and a humidity of 90% RH in which the mass of the control material (mass upon water feeding) was measured while water was periodically absorbed in the control material for 120 hours.

[0050] As calculated in accordance with water absorption (%) = (mass upon water feeding - mass upon drying/mass upon drying) × 100, the control material according to this embodiment was found to have a water absorption of less than 1% from the start of water feeding up to the lapse of 120 hours.

[0051] In other words, the control material according to the embodiment here is less likely to absorb water from the atmosphere over time so much so that its storage over an extended period is facilitated. In addition, the control material after storage over an extended period remains stabilized in terms of the amount of foaming in a molten metal as is the case with a control material not subject to storage over an extended period.

[0052] In the aforesaid embodiment of the control material production method, a mixture of the binder powdery, volcanic silicate mineral having a particle diameter of 0.1 mm or less with the porous, volcanic silicate mineral having a particle diameter of 3 mm or less is spherically granulated with a diameter of less than 5 mm; however, the present invention is in no sense limited to it. For instance, a mixture of the binder powdery, volcanic silicate mineral having a particle diameter of 0.1 mm or less with the porous, volcanic silicate mineral having a particle diameter of 3 mm or less may be formed into a rod member having a length of less than 5 mm.

[0053] In the aforesaid control material embodiment, the control material is a porous, volcanic silicate mineral containing 73.0% by weight of SiO_2 ; however, the present invention is by no means limited to it. For instance, depending on the casting conditions used, the control material may comprise a porous, volcanic silicate mineral containing 70 to 75% by weight of SiO_2 .

[0054] In the aforesaid control material embodiment, the control material has an Ig. loss of 0.33%; however, the present invention is not limited to it whatsoever. For instance, depending on the casting conditions used, the control material may have an Ig. loss of 0.5% or less.

Claims

1. A control material that is filled together with a magnesium alloy in a wire in a wire injection process for graphite spheroidization, **characterized in that** the

control material is fired and is a porous, volcanic silicate mineral containing 70 to 75% by weight of SiO_2 .

2. The control material according to claim 1, **characterized by** having a porosity of 60 to 80%.
3. The control material according to claim 1 or 2, **characterized by** having an lg. loss of 0.5% or less.
4. The control material according to any one of claims 1 to 3, **characterized by** having a specific gravity of 0.5 to 1.0 g/cm^3 .
5. The control material according to any one of claims 1 to 4, **characterized by** being a fired spherical member having a diameter of less than 5 mm or a fired rod member having a length of less than 5 mm.
6. A method for producing a control material that is used with a wire injection process for graphite spheroidization, **characterized in that** said control material comprises a porous, volcanic silicate mineral containing 70 to 75% by weight of SiO_2 and the control material is produced by processing a porous, volcanic silicate mineral having a particle diameter of 3 mm or less into a spherical member having a diameter of less than 5 mm or a rod member having a length of less than 5 mm while using a powdery, volcanic silicate mineral having a particle diameter of 0.1 mm or less and a water content of 15 to 35% by weight.
7. The method for producing a control material according to claim 6, **characterized in that** the control material is fired at 900 to 1000°C.

dadurch gekennzeichnet,

dass es ein spezifisches Gewicht von 0,5 bis 1,0 g/cm^3 aufweist.

- 5 5. Steuerungsmaterial nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet,** **dass** es ein gebranntes sphärisches Element mit einem Durchmesser von weniger als 5 mm oder ein gebranntes stabförmiges Element mit einer Länge von weniger als 5 mm ist.
- 10 6. Verfahren zum Herstellen eines Steuerungsmaterials welches sich in einem Drahtinjektionsverfahren zur Graphiteinformung verwenden lässt, **dadurch gekennzeichnet,** **dass** das Steuerungsmaterial ein poröses, vulkanisches Silikatmineral enthält, welches 70 bis 75 Gew.-% SiO_2 umfasst und das Steuerungsmaterial hergestellt wird, indem ein poröses, vulkanisches Silikatmineral mit einem Partikel-durchmesser von 3 mm oder weniger zu einem sphärischen Element mit einem Durchmesser von weniger als 5 mm oder einem stabförmigen Element mit einer Länge von weniger als 5 mm verarbeitet wird, wobei ein pulvriges, vulkanisches Silikatmineral mit einem Partikeldurchmesser von 0,1 mm oder weniger und einem Wassergehalt von 15 bis 35 Gew.-% verwendet wird.
- 15 7. Verfahren zum Herstellen eines Steuerungsmaterials nach Anspruch 6, **dadurch gekennzeichnet,** **dass** das Steuerungsmaterial bei 900 bis 1000 °C gebrannt wird.
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Patentansprüche

1. Steuerungsmaterial, welches sich zusammen mit einer Magnesiumlegierung in einem Drahtinjektionsverfahren zur Graphiteinformung in einen Draht füllen lässt, **dadurch gekennzeichnet,** **dass** das Steuerungsmaterial gebrannt ist und es sich um ein poröses, vulkanisches Silikatmineral handelt, welches 70 bis 75 Gew.-% SiO_2 enthält.
2. Steuerungsmaterial nach Anspruch 1, **dadurch gekennzeichnet,** **dass** es eine Porösität von 60 bis 80% aufweist.
3. Steuerungsmaterial nach Anspruch 1 oder 2, **dadurch gekennzeichnet,** **dass** es einen Verlust bei Zündung (LOI) von 0,5 % oder weniger aufweist.
4. Steuerungsmaterial nach einem der Ansprüche 1 bis 3,

Revendications

1. Matériau de contrôle qui est introduit conjointement avec un alliage de magnésium dans un fil dans un procédé d'injection de fils pour la sphéroïdisation de graphite, **caractérisé par le fait que** le matériau de contrôle est cuit et est un minéral silicate volcanique, poreux, contenant 70 à 75 % en poids de SiO_2 .
2. Matériau de contrôle selon la revendication 1, **caractérisé par le fait qu'il** a une porosité de 60 à 80 %.
3. Matériau de contrôle selon l'une des revendications 1 ou 2, **caractérisé par le fait qu'il** a une perte au feu de 0,5 % ou moins.
4. Matériau de contrôle selon l'une quelconque des revendications 1 à 3, **caractérisé par le fait qu'il** a une masse volumique de 0,5 à 1,0 g/cm^3 .

5. Matériau de contrôle selon l'une quelconque des revendications 1 à 4, **caractérisé par le fait qu'il** est un élément sphérique cuit ayant un diamètre de moins de 5 mm ou un élément bâton cuit ayant une longueur de moins de 5 mm. 5
6. Procédé de production d'un matériau de contrôle qui est utilisé avec un procédé d'injection de fils pour la sphéroïdisation de graphite, **caractérisé par le fait que** ledit matériau de contrôle comprend un minéral silicate volcanique, poreux, contenant 70 à 75 % en poids de SiO_2 , et 10
le matériau de contrôle est produit par traitement d'un minéral silicate volcanique, poreux, ayant un diamètre de particule de 3 mm ou moins en un élément sphérique ayant un diamètre de moins de 5 mm ou un élément bâton ayant une longueur de moins de 5 mm tout en utilisant un minéral silicate volcanique, pulvérulent, ayant un diamètre de particule de 0,1 mm ou moins et une teneur en eau de 15 à 35 % en poids. 15
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7. Procédé de production d'un matériau de contrôle selon la revendication 6, **caractérisé par le fait que** le matériau de contrôle est cuit à 900 à 1000°C. 25

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2016016415 A [0008]