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(54) A METHOD OF MODIFYING LIQUID STEEL WITH BORON BY USING SCRAP FERRO-NEODYMIUM-BORON MAGNETS

(57) The subject of the invention is a method for modifying liquid steel with boron, characterized in that neodymium Fe-Nd-B magnets scrap is used for modifying liquid steel with boron, wherein said method comprises melting a feedstock of steel and/or cast steel scrap into a metal bath with a temperature of at least 1450°C, and wherein after prior completing of the chemical composition and deoxidizing of the metal bath, the neodymium Fe-Nd-B magnets scrap is introduced and boron-modified steel for castings is obtained.

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Description

Field of the invention

[0001] The subject of the invention is a method of modifying liquid steel with boron by using neodymium magnets scrap. Specifically, the subject of the invention is the use of neodymium magnets scrap to modify liquid steel so that the modification results in a presumed boron content.

[0002] The invention belongs to the field covering the foundry and metallurgy industries and waste management - scrap magnets.

Background of the invention

[0003] The metallurgy industry manufactures unalloyed, low-alloyed and alloyed steels and cast steels for components that are required to have good hardenability, as well as steels and cast steels for use at elevated temperatures. In general, cast steel is steel cast into casting moulds that give the final shape to the products. Steel and cast steel are used to produce components for the engineering industry, power industry (e.g. turbine components), thermal power industry (e.g. coal mill components), and the wide-ranging application of castings in the offshore area.

[0004] At present, neodymium magnets are used in almost all industries: electronics, electrical, construction, clothing, furniture, household appliances, etc. The increasing amount of electro-scrap (including cell phones and electric motors) creates the need to manage such electro-waste. In addition to Nd, neodymium magnets contain such elements as B and Fe. In neodymium magnets, boron (B) is present in the form of Nd2Fe14B, and its content does not exceed 1%. However, the chemical composition of magnets is modified by manufacturers, and depending on the grade, the proportion of individual components may vary (they may contain more B, for example, or may be doped with other elements). Boron is the only element added to structural and tool steels usually in thousandths of a percentage (0.001 - 0.003%). It is the element that mainly influences hardenability, but also increases creep strength, stabilizes M23C6 carbides and retards their growth, especially in steels designed for operation at elevated temperatures (steels and cast steels used in the power industry). Its strongest effect on steel hardenability is achieved at 0.003%. Boron can be used as a modifier in alloys with carbon content of up to 0.7%, but its effect is the stronger, the less carbon there is, so in most structural alloys.

Description of the state of the art

[0005] The known patent PL216,943 B1 describes a method of modifying chromium cast iron, containing by weight: 2.5-3.5% C; 0.5-3.5% Si; 8.0-25.0% Cr; 0.2-1.0% Mn; 0.5-2.0% Mo; and 0.0-8.0% Ni, by first introducing into the metal bath of the starting cast iron shredded scrap of chromium steel and/or chromium cast iron and/or ferrochrome, and then boron carbide in granular form. Another way of modification is that boron carbide in granular form is introduced into the metal bath of the starting cast iron along with the shredded scrap of chromium steel and/or chromium cast iron and/or ferrochrome.

[0006] In the well-known state of the art, the reuse of neodymium magnets scrap in metallurgical processes to improve the quality of smelted steel is not known, and the reuse of neodymium magnets scrap to modify liquid steel with boron is not known either.

The purpose of the invention

[0007] The purpose of the invention is a method of using neodymium magnets scrap as one of the compounds in the processes of modification and refinement of steels for castings that can be quenched (structural steels, tool steels) and can operate at elevated temperatures. Our research shows that 1kg of magnets scrap (used as a modifier) per 1000 kg of liquid steel is sufficient to obtain 0.001 % by weight of B in the steel.

[0008] The purpose of the invention is to obtain low-carbon (up to 2 % by weight of C) Fe-C alloys with other elements, in which the addition of boron will primarily ensure their high hardenability.

[0009] According to the invention, the Fe-B ferroalloy currently used (containing about 18 % by weight of B, sometimes as much as 25 % by weight of B), which is an expensive modifier, will be replaced by neodymium magnets scrap during the modification and refinement processes of liquid steel.

[0010] By adding neodymium magnets scrap to liquid steel, we simultaneously introduce boron with neodymium, which belongs to the rare earth elements (REEs). The aforementioned REEs belong to the group of expensive modifiers for good deoxidation and desulfurization of the metal bath.

[0011] The present invention uses the recycling of electro-scrap, which raises an important environmental aspect.

[0012] Boron-modified cast steel requires the use of Fe-B ferroalloy, which is one of the most expensive modifiers. The use of neodymium Fe-Nd-B magnets scrap with high B yields may be cheaper and more efficient, especially since

the introduction of boron in the presence of Nd is not known.

[0013] The addition of 0.003% B can replace up to 2.5% of alloying additives (Ni, Cr, Mo, Mn, V) in the steel, thus reducing the cost and use of alloying additives introduced into the steel.

[0014] The addition of boron even in low-carbon steels for casting increases the hardenability, so that steel with boron can be hardened in air, resulting in savings during heat treatment and absence of any negative impact on the environment (no hardening in oil and no need to dispose of used oil, no additional equipment - tubs, coolers, pumps). Boron in tool alloys promotes fragmentation and uniform distribution of carbides in the alloy matrix (breaks up the carbide eutectic), which improves the strength properties of castings and reduces the risk of damage during heat treatment and cooling in the mould, resulting in savings from the reduced number of casting defects (fewer defective castings).

Disclosure of the invention

[0015] The subject of the present invention is a new solution comprising a method for modifying liquid steel with boron, characterized in that for modifying liquid steel with boron, neodymium Fe-Nd-B magnets is used, wherein said method comprises melting a feedstock of steel and/or cast steel scrap into a metal bath with a temperature of at least 1450°C, and wherein after prior completing of the chemical composition and deoxidizing of the metal bath, the neodymium Fe-Nd-B magnets scrap is introduced and boron-modified steel for castings is obtained.

[0016] Preferably, in the method according to the invention, the neodymium magnets scrap is used relative to liquid steel selected depending on the composition of the magnets scrap.

[0017] Preferably, in the method according to the invention, the neodymium Fe-Nd-B magnets scrap in any available form is used, including waste magnets from production, cracked magnets, crushed magnets and/or powders thereof.

[0018] Preferably, in the method according to the invention, a single-stage or a two-stage deoxidation, more preferably a two-stage deoxidation, is used after melting of the steel and/or cast steel scrap feedstock.

[0019] Preferably, in the method according to the invention, the two-stage deoxidation comprising the deoxidation with Fe-Ca-Si followed by deoxidation with aluminium is used.

[0020] Preferably, in the method according to the invention, the liquid metal is held in a furnace to equalize the chemical composition and to achieve a temperature of at least 1500°C, more preferably from 1560°C to 1580°C, for the mould pouring or metal draining into the bath.

[0021] Preferably, the method according to the invention is carried out in the furnace or during draining of the metal into the bath, including either on the bottom of the bath or gradually on the metal stream during the draining operation.

[0022] Preferably, in the method according to the invention, the neodymium Fe-Nd-B magnets scrap is introduced at least once to obtain the assumed boron content in the steel for castings.

Detailed description of the invention

[0023] In the following section, the subject of the present invention is described in detail, which is not limited to the detailed embodiments of the invention described here.

[0024] According to the embodiments of the invention, the method of obtaining steel modified with neodymium Fe-Nd-B magnets scrap is carried out in an induction furnace with a crucible of 10 kg capacity. Modification according to the invention in a bath is also possible.

[0025] The neodymium Fe-Nd-B magnets scrap is a currently available product and can, for example, be purchased commercially as shredded electro-scrap, which may be contaminated with other elements not mentioned above. According to the invention, any available scrap in any form, such, as waste from magnet production, cracked magnets, crushed magnets, and others, can be used.

[0026] According to the invention, any grade of steel and cast steel can be modified with neodymium Fe-Nd-B magnets scrap.

Example 1.

[0027] Table 1 shows a summary of the feedstock materials for melting the sample steel for castings modified with neodymium magnets scrap.

Table 1. Summary of chemical composition and weight of feedstock materials, where Fe, C, Mn, Si, Nd, B, Cr, Ni, Al are shown as weight percentages.

	Fe	C	Mn	Si	Nd	B	Cr	Ni	Al	Weight [g]
Fe-Nd-B scrap					26,00	1,0000				50,00

(continued)

	Fe	C	Mn	Si	Nd	B	Cr	Ni	Al	Weight [g]
G70CrMnSiNiMo8 steel scrap	95,000	0,70	0,80	0,60			2,0000	0,80		9300,00
Al									100,00	2,50
Calculated chemical composition	94,47	0,70	0,80	0,60	0,1390	0,0053	1,9888	0,80	0,03	9352,50

[0028] A batch of 9300 g of cast G70CrMnSiNiMo8 steel scrap of known chemical composition shown in Table 2, residual Fe, other additives and unavoidable impurities were used as feedstock and loaded to the bottom of the crucible before the furnace was turned on. After melting the feedstock, the metal was heated to about 1550-1600°C, stirred and temperature-equilibrated. The metal was deoxidized in two stages with Fe-Ca-Si in an amount of about 10 g and aluminium in an amount of 2.5 g, and then 50 g of neodymium Fe-Nd-B magnets scrap was introduced to the metal surface. The liquid metal was held in the furnace for about 2 minutes to equalize the chemical composition and obtain the mould pouring temperature (1560 1580°C). The metal thus prepared was poured into a "Y" type sand mould. This produced a test ingot with the chemical composition shown in Table 2, containing residual Fe, other additives and unavoidable impurities.

Table 2. Chemical composition of the obtained cast steel according to the invention.

Content of elements in % by weight									
C	Mn	Si	P	S	Cr	Ni	Mo	Al	B
0,7	0,8	0,6	0,02	0,02	2,0	0,8	0,03	0,02	**0,006**

[0029] The boron content obtained by the method according to the invention shown in Table 2 above is higher than the calculated one (see Table 1), so its content in scrap magnets must indeed be higher than 1 % by weight of B. The boron content (shown in Table 2) in the test ingot was determined by the optical emission spectroscopy method.

Example 2.

[0030] Table 3 shows a summary of the feedstock materials for melting the cast steel modified with neodymium magnets scrap.

Table 3. Summary of chemical composition and weight of feedstock materials, where C, Mn, Si, Nd, B, Cr, Ni, Al are shown as weight percentages.

	C	Mn	Si	Nd	B	Cr	Ni	Al	Weight [g]
Fe-Nd-B scrap				26,00	2,0000				50,00
The ingot from Example 1	0,70	0,80	0,60		0,0060	2,0000	0,80		9300,00
Al								100,00	2,50
G70CrMnSiNiMo8 steel scrap	0,70	0,80	0,60			2,0000	0,80		500,00
Calculated chemical composition	0,70	0,80	0,60	0,1319	0,0158	1,9893	0,80	0,03	9852,50

[0031] Since boron content in the magnet scrap was not known, the boron content of 2 % by weight was assumed in Example 2.

[0032] A batch of 9300 g of cast G70CrMnSiNiMo8 steel scrap after modification from Example 1, and 500 g of cast G70CrMnSiNiMo8 steel scrap of known chemical composition shown in Table 2, residual Fe, other additives and unavoidable impurities were used as feedstock, which was loaded to the bottom of the crucible before the furnace was turned on. After melting the feedstock, heating the metal to about 1550-1600°C, stirring and equilibrating the temperature, the metal was deoxidized in two stages with Fe-Ca-Si in an amount of about 10 g and aluminium in an amount of 2.5 g, and then 50 g of neodymium magnets scrap was introduced to the metal surface. The liquid metal was held in the furnace for about 2 minutes to equalize the chemical composition and obtain the mould pouring temperature (1560-1580°C). Approximately 5 kg of the metal thus prepared was poured into the first "Y" type sand mould. To the remainder of the liquid metal (weighing about 5 kg), 25 g of neodymium magnets scrap was introduced to the metal surface. The liquid metal was held in the furnace for about 2 minutes to equalize the chemical composition and obtain the mould pouring temperature. The metal thus prepared was poured into a second "Y" type sand mould.

[0033] Thus, two test ingots with the chemical composition shown in Table 4, containing the residual Fe, other additives, and unavoidable impurities, and characterized by two different boron contents were obtained.

Table 4. Chemical composition of the resulting cast steel.

Mould number	Content of elements in % by weight									
	C	Mn	Si	P	S	Cr	Ni	Mo	Al	**B**
Mould 1	0,7	0,8	0,6	0,02	0,02	2,0	0,8	0,03	0,02	**0,011**
Mould 2	0,7	0,8	0,6	0,02	0,02	2,0	0,8	0,03	0,02	**0,014**

[0034] The boron content in the test ingot was determined by the optical emission spectroscopy method.

[0035] According to the invention, the addition of neodymium magnets scrap (Fe-Nd-B) provides an increase in the boron content in the alloy, and the experiments presented (Example 1 and Example 2 above) are intended to confirm that the addition of neodymium magnets scrap to molten steel results in an increase in its content in the alloy, where:

According to Example 1 above:

[0036]

The addition of 50 g of the magnets scrap to about 10 kg of steel yields	0.006% B
According to Example 2 above:	
The addition of 50 g of the magnets scrap to the melt composed of process scrap (i.e. of known chemical composition) from Example 1 yields	0.011% B
The addition of 25 g to the rest of the melt (5 kg) further 0.003% yields	0.014% B

Claims

1. A method for modifying liquid steel with boron, **characterized in that** neodymium Fe-Nd-B magnets scrap is used for modifying liquid steel with boron, wherein said method comprises melting a feedstock of steel and/or cast steel scrap into a metal bath with a temperature of at least 1450°C, and wherein after prior completing of the chemical composition and deoxidizing of the metal bath, the neodymium magnets scrap of Fe-Nd-B is introduced and boron-modified steel for castings is obtained.

2. The method according to claim 1, **characterized in that** the neodymium magnets scrap is used relative to liquid steel selected depending on the composition of the magnets scrap.

3. The method according to claim 1 or 2, **characterized in that** the neodymium Fe-Nd-B magnets scrap in any available form is used, including waste magnets from production, cracked magnets, crushed magnets and/or powders thereof.

4. The method according to any of the claims 1-3, **characterized in that** a single-stage or a two-stage deoxidation, more preferably a two-stage deoxidation is used after melting of the steel and/or cast steel scrap feedstock.

5. The method according to claim 4, **characterized in that** the two-stage deoxidation comprising the deoxidation with Fe-Ca-Si followed by deoxidation with aluminium is used.

6. The method according to any of the claims 1-5, **characterized in that** the liquid metal is held in a furnace to equalize the chemical composition and to achieve a temperature of at least 1500°C, more preferably 1560°C to 1580°C, for the mould pouring or metal draining into the bath.

7. The method according to any of the claims. 1-6, **characterized in that** it is carried out in the furnace or during draining of the metal into the bath, including either on the bottom of the bath or gradually on the metal stream during the draining operation.

8. The method according to any of the claims 1-7, **characterized in that** the neodymium Fe-Nd-B magnets scrap is introduced at least once to obtain the assumed boron content in the steel for castings.

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EUROPEAN SEARCH REPORT

Application Number
EP 23 17 2987

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	YANG YONGXIANG ET AL: "REE Recovery from End-of-Life NdFeB Permanent Magnet Scrap: A Critical Review", JOURNAL OF SUSTAINABLE METALLURGY, vol. 3, no. 1, 20 September 2016 (2016-09-20), pages 122-149, XP093086208, DE ISSN: 2199-3823, DOI: 10.1007/s40831-016-0090-4 Retrieved from the Internet: URL:http://link.springer.com/article/10.1007/s40831-016-0090-4/fulltext.html> [retrieved on 2023-09-27] * abstract * * page 128, column 2, paragraph 3 * * figure 7 *	1-8	INV. C21C5/52 C21C7/00 H01F1/057
			TECHNICAL FIELDS SEARCHED (IPC)
			C21C H01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	29 September 2023	Vermeulen, Yves

CATEGORY OF CITED DOCUMENTS

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- PL 216943 B1 **[0005]**