



(51) International Patent Classification:

C21C 7/06 (2006.01) C21C 7/076 (2006.01)
C21C 7/064 (2006.01)

(21) International Application Number:

PCT/IB2015/001754

(22) International Filing Date:

15 July 2015 (15.07.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/031,568 31 July 2014 (31.07.2014) US

(71) Applicant: SABIC GLOBAL TECHNOLOGIES B.V.
[NL/NL]; Plasticslaan 1, NL-4612 PX Bergen Op Zoom
(NL).

(72) Inventor: PINHEIRO, Carlos, Albertos, Martins; c/o
Sabic Global Technologies B.V., Plasticslaan 1, NL-4612
PX Bergen Op Zoom (NL).

(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,
DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG,
MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM,
PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC,
SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ,
TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,
TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE,
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU,
LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK,
SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ,
GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))

(54) Title: METHODS AND COMPOSITIONS FOR DEOXIDIZED STEEL

(57) Abstract: The present disclosure relates to compositions and method for producing deoxidized steel comprising: combining molten steel and at least one deoxidizing agent under conditions effective to provide deoxidized steel, wherein the at least one deoxidizing agent comprises an alloy of Fe-Mn-Si-Ca.



METHODS AND COMPOSITIONS FOR DEOXIDIZED STEEL

BACKGROUND

[0001] Killed and semi-killed steels are traditionally deoxidized with an alloy of iron-silicon (Fe-Si) or iron-silicon-manganese (Fe-Si-Mn) with some addition of aluminum (Al) during tapping. However, the residual oxygen levels in the steel can vary between 20-30 ppm. Consequently, when oxygen levels in the steel are above 23 ppm, there is a higher probability of forming more surface defects in cast billets. To avoid these surface and sub-surface defects, most steel making plants inject an alloy of calcium-silicon (CaSi) wire to decrease the residual oxygen levels to below 18 ppm. However, in many situations, CaSi is too light to be added during tapping, and injection of CaSi at the ladle furnace cannot be done in large quantities at many steel making plants due to space constraints.

[0002] Accordingly, there exists a growing need for deoxidizing materials for use in the steel making process, and which can also provide good yields.

SUMMARY

[0003] In accordance with the purpose(s) of the invention, as embodied and broadly described herein, the invention, in one aspect, relates to a method for producing deoxidized steel.

[0004] In an exemplary aspect, disclosed is a method, comprising combining molten steel and at least one deoxidizing agent under conditions effective to provide deoxidized steel, wherein the at least one deoxidizing agent comprises an alloy of iron-manganese-silicon-calcium (Fe-Mn-Si-Ca).

[0005] In another exemplary aspect, disclosed are steel compositions produced by the disclosed methods.

[0006] In another exemplary aspect, disclosed are steel compositions comprising at least one oxide of the alloy of Fe-Mn-Si-Ca.

[0007] In another exemplary aspect, disclosed are articles of manufacture comprising the disclosed compositions.

[0008] Additional advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or can be learned by practice of the invention. The advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims. It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

DESCRIPTION

[0009] The present invention can be understood more readily by reference to the following detailed description of the invention and the Examples included therein.

[0010] Before the present compounds, compositions, articles, systems, devices, and/or methods are disclosed and described, it is to be understood that they are not limited to specific synthetic methods unless otherwise specified, or to particular reagents unless otherwise specified, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular aspects only and is not intended to be limiting. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, example methods and materials are now described.

[0011] All publications mentioned herein are incorporated herein by reference to disclose and describe the methods and/or materials in connection with which the publications are cited. The publications discussed herein are provided solely for their disclosure prior to the filing date of the present application. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided herein can be different from the actual publication dates, which can require independent confirmation.

A. DEFINITIONS

[0012] As used herein, nomenclature for compounds, including organic compounds, can be given using common names, IUPAC, IUBMB, or CAS recommendations for nomenclature.

[0013] As used in the specification and the appended claims, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “an oxidation product,” includes mixtures of two or more such oxidation products, and the like.

[0014] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, a further aspect includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms a further aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint. It is also understood that there are a number of values disclosed herein, and that each value is also herein disclosed as “about” that particular value in addition to the value itself. For example, if the value “10” is disclosed, then “about 10” is also disclosed. It is also understood that each unit between two particular units are also disclosed. For example, if 10 and 15 are disclosed, then 11, 12, 13, and 14 are also disclosed.

[0015] References in the specification and concluding claims to parts by weight of a particular element or component in a composition denotes the weight relationship between the element or component and any other elements or components in the composition or article for which a part by weight is expressed. Thus, in a compound containing 2 parts by weight of component X and 5 parts by weight component Y, X and Y are present at a weight ratio of 2:5, and are present in such ratio regardless of whether additional components are contained in the compound.

[0016] A weight percent (wt. %) of a component, unless specifically stated to the contrary, is based on the total weight of the formulation or composition in which the component is included.

[0017] As used herein, the terms “optional” or “optionally” means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0018] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to

be limited to a specific order, it is no way intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps or operational flow; plain meaning derived from grammatical organization or punctuation; and the number or type of embodiments described in the specification.

[0019] Disclosed are the components to be used to prepare the compositions of the invention as well as the compositions themselves to be used within the methods disclosed herein. These and other materials are disclosed herein, and it is understood that when combinations, subsets, interactions, groups, etc. of these materials are disclosed that while specific reference of each various individual and collective combinations and permutation of these compounds cannot be explicitly disclosed, each is specifically contemplated and described herein. For example, if a particular compound is disclosed and discussed and a number of modifications that can be made to a number of molecules including the compounds are discussed, specifically contemplated is each and every combination and permutation of the compound and the modifications that are possible unless specifically indicated to the contrary. Thus, if a class of molecules A, B, and C are disclosed as well as a class of molecules D, E, and F and an example of a combination molecule, A-D is disclosed, then even if each is not individually recited each is individually and collectively contemplated meaning combinations, A-E, A-F, B-D, B-E, B-F, C-D, C-E, and C-F are considered disclosed. Likewise, any subset or combination of these is also disclosed. Thus, for example, the sub-group of A-E, B-F, and C-E would be considered disclosed. This concept applies to all aspects of this application including, but not limited to, steps in methods of making and using the compositions of the invention. Thus, if there are a variety of additional steps that can be performed it is understood that each of these additional steps can be performed with any specific embodiment or combination of embodiments of the methods of the invention.

[0020] As used herein, the term “slag” refers to a by-product of the steelmaking process, which separates the desired metal fraction from the unwanted fraction.

[0021] As used herein, the terms “steel ladle furnace slag,” and “deoxidized slag” are used interchangeably and refers to the slag produced by the deoxidized steel making process.

[0022] As used herein, the term “killed steel” refers to steel that has been treated to substantially or fully deoxidize the steel during the steel making process.

[0023] As used herein, the term “semi-killed steel” refers to steel that has been treated to partially deoxidize the steel during the steel making process.

[0024] It is understood that the compositions disclosed herein have certain functions. Disclosed herein are certain structural requirements for performing the disclosed functions, and it is understood that there are a variety of structures that can perform the same function that are related to the disclosed structures, and that these structures will typically achieve the same result.

B. METHOD

[0025] In various aspects, disclosed herein are methods for producing deoxidized steel.

[0026] In one aspect, disclosed herein is a method, comprising: combining molten steel and at least one deoxidizing agent under conditions effective to provide deoxidized steel, wherein the at least one deoxidizing agent comprises an alloy of Fe-Mn-Si-Ca.

[0027] In a further aspect, the underlying steel making process comprises the same or substantially same steps as in the steel making process utilizing a conventional electric arc furnace (EAF). According to various aspects of the present invention, the electric arc furnace is used for melting materials that has been fed into the furnace. In one aspect, and as one of ordinary skill in the art would appreciate, the energy required for melting in the electric arc furnace, is introduced by means of an electric current via one or more electrodes, and the heat is transferred to the metallic charge via an electric arc. In further aspects of the invention, the materials fed into the electric arc furnace have to avoid contact with the electrodes and damage the same when charging the furnace.

[0028] In various aspects, the steps can comprise a melting step, a refining step, and a tapping step. In a further aspect, the steel making process comprises liquefying the steel, tapping in the ladle, and transferring to the ladle processing station. In a still further aspect, the steel making process can comprise any desired process parameters, for example, and without limitation, the parameters used in the conventional electric arc furnace (EAF), such as temperature, residence time, reactors, and pressure.

[0029] The steel making process can follow any number of process routes or steps before proceeding to the final casting step. Generally, the process can start with the raw material, then proceed to the direct reduction, then proceed to the steelmaking, and then to the ladle treatment.

[0030] In one aspect, the molten steel is tapped into a ladle furnace prior to combining the molten steel and at least one deoxidizing agent. In a further aspect, the step of combining the molten steel and at least one deoxidizing agent is performed at the tapping stage of the steel making process.

[0031] In various aspects, the deoxidizing agent is typically added at a tapping stage to deoxidize steel in order to reduce the oxygen content and form a slag. In one aspect, the steel making process involves removing the slag. In a further aspect, the slag can have a lower density than the liquid steel. As such, the slag can float on top of the liquid steel. In a still further aspect, the slag floats in the steel ladle and remains in the ladle. In a yet further aspect, the slag can be removed prior to the casting from the ladle. In various aspects, the conditions effective to provide deoxidized steel can comprise forming a slag layer over the molten steel. In a further aspect, the slag layer comprises at least one oxidation product of the Fe-Mn-Si-Ca alloy.

[0032] In various aspects, molten steels can contain residual dissolved oxygen after their conversion from molten iron. Therefore, several strategies have been developed for deoxidation based on the final product requirement. According to the degree of deoxidation, carbon steels may be subdivided into three groups: (1) killed steel, (2) semi-killed and (3) rimming steel. Killed steel is free from oxygen, semi-killed steel is incompletely deoxidized steels containing some amount of oxygen, and rimming steel is non-deoxidized or partly deoxidized steel.

[0033] In one aspect, the deoxidized steel can comprise killed or semi-killed steel. In some aspects, the deoxidized steel is killed steel. In other aspects, the deoxidized steel is semi-killed steel.

[0034] In one aspect, the deoxidized steel has an oxygen content of less than about 23 ppm. In a further aspect, the deoxidized steel has an oxygen content of less than about 20 ppm. In a still further aspect, the deoxidized steel has an oxygen content of less than about 18 ppm. In a yet further aspect, the deoxidized steel has an oxygen content of less about 15 ppm.

[0035] In one aspect, the deoxidized steel has an oxygen content ranging from about 1 ppm to 20 ppm, including exemplary values 2 ppm, 3 ppm, 4 ppm, 5 ppm, 6 ppm, 7 ppm, 8 ppm, 9 ppm, 10 ppm, 11 ppm, 12 ppm, 13 ppm, 14 ppm, 15 ppm, 16 ppm, 17 ppm, 18 ppm, and 19 ppm. In another aspect, the range can be derived from any two exemplary values. In

another aspect, the range can be derived from any two exemplary values. For example, the oxygen content can range from 1 ppm to 18 ppm.

[0036] According to aspects of the disclosure, a deoxidizing agent is added at a ladle step in the steel making process. In another aspect, the ladle step can comprises heating, desulfurization, alloying, or rinsing, or combinations thereof. In a further aspect, the ladle treatment step can be used for desulfurization, homogenization of temperature, or to adjust the chemical composition for casting, or combinations thereof.

[0037] In a further aspect, a ladle step in the steel making process serves to refine the steel. For example, unwanted impurities in the steel can be removed and the steel can be homogenized. A ladle step can comprise heating molten steel by the use of electrodes, which are operated by electricity. Homogenization of the steel temperature and chemistry can be achieved by use of inert gas which is stirred with the molten steel. The production of alloys can also be achieved through bulk or trim chemical control. The ladle step can also be used for desulfurization of the steel. The ladle step acts as a buffer for downstream steelmaking equipment. As such, the addition of a deoxidizing agent to the steel process during the ladle step promotes the refinement of the final product, deoxidized steel. The composition of the deoxidizing agent has beneficial properties for the deoxidized steel process.

[0038] In one aspect, the deoxidizing agent comprises an alloy of Fe-Mn-Si-Ca. In a further aspect, the alloy comprises calcium in an amount ranging from 1 wt % to 30 wt %, including exemplary values of 2 wt %, 3 wt %, 4 wt %, 5 wt %, 6 wt %, 7 wt %, 8 wt %, 9 wt %, 10 wt %, 11 wt %, 12 wt %, 13 wt %, 14 wt %, 15 wt %, 16 wt %, 17 wt %, 18 wt %, 19 wt %, 20 wt %, 21 wt %, 22 wt %, 23 wt %, 24 wt %, 25 wt %, 26 wt %, 27 wt %, 28 wt %, or 29 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise calcium in an amount ranging from 1 wt % to 29 wt %, based on the total weight percentage of the alloy.

[0039] In a further aspect, the alloy comprises manganese in an amount ranging from 1 wt % to 20 wt %, including exemplary values of 2 wt %, 3 wt %, 4 wt %, 5 wt %, 6 wt %, 7 wt %, 8 wt %, 9 wt %, 10 wt %, 11 wt %, 12 wt %, 13 wt %, 14 wt %, 15 wt %, 16 wt %, 17 wt %, 18 wt %, or 19 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise manganese in an amount ranging from 1 wt % to 19 wt %, based on the total weight percentage of the alloy.

[0040] In a further aspect, the alloy comprises silicon in an amount ranging from 40 wt % to 60 wt %, including exemplary values of 41 wt %, 42 wt %, 43 wt %, 44 wt %, 45 wt %, 46 wt %, 47 wt %, 48 wt %, 49 wt %, 50 wt %, 51 wt %, 52 wt %, 53 wt %, 54 wt %, 55 wt %, 56 wt %, 57 wt %, 58 wt %, or 59 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise silicon in an amount ranging from 41 wt % to 59 wt %, based on the total weight percentage of the alloy.

[0041] In a further aspect, the alloy comprises iron in an amount ranging from greater than 0 wt % to 10 wt %, including exemplary values of 2 wt %, 3 wt %, 4 wt %, 5 wt %, 6 wt %, 7 wt %, 8 wt %, or 9 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise iron in an amount ranging from 1 wt % to 9 wt %, based on the total weight percentage of the alloy.

[0042] In a further aspect, the alloy comprises: calcium in an amount ranging from 1 wt % to 30 wt %; manganese in an amount ranging from 1 wt % to 20 wt %; silicon in an amount ranging from 40 wt % to 60 wt %; and wt % balance of Fe.

[0043] In some aspects, the alloy is an alloy consisting essentially of Fe-Mn-Si-Ca. In other aspects, the alloy is an alloy consisting of Fe-Mn-Si-Ca. In further aspects, the alloy does not comprise a substantial amount of aluminum, barium, or strontium. In still further aspects, the alloy is substantially free of any amount of aluminum, barium, or strontium.

[0044] In one aspect, the deoxidizing agent is added before the molten steel to the ladle furnace. In another aspect, the deoxidizing agent is added at the same time as the molten steel to the ladle furnace. In a further aspect, the deoxidizing agent is added after 20 wt % to 25 wt % of the total amount of the molten steel has been added to the ladle, including exemplary values of 21 wt %, 22 wt %, 23 wt %, and 24 wt %. In another aspect, the range can be derived from any two exemplary values. For example, the deoxidizing agent is added after 21 wt % to 25 wt % of the total amount of the molten steel has been added to the ladle.

[0045] In a further aspect, the ladle step can have any desired residence time. In a still further aspect, the ladle step has a residence time in an amount ranging from 25 min to 50 min after the tapping step, including exemplary values of 26 min, 27 min, 28 min, 29 min, 30 min, 31 min, 32 min, 33 min, 34 min, 35 min, 36 min, 37 min, 38 min, 39 min, 40 min, 41 min, 42 min, 43 min, 44 min, 45 min, 46 min, 47 min, 48 min, and 49 min. In another aspect, the range can be derived from any two exemplary values. For example, the ladle step can

have a residence time in an amount ranging from 30 minutes to 45 minutes after the tapping step.

[0046] After the ladle step, the process continues to the billet caster step.

[0047] In a further aspect, method comprises adding the deoxidizing agent to a ladle under conditions effective to provide deoxidized steel, wherein the conditions effective comprises adjusting the ladle to a temperature ranging from about 1500 °C to about 1700 °C, including exemplary values 1510 °C, 1520 °C, 1530 °C, 1540 °C, 1550 °C, 1560 °C, 1570 °C, 1580 °C, 1590 °C, 1600 °C, 1610 °C, 1620 °C, 1630 °C, 1640 °C, 1650 °C, 1660 °C, 1670 °C, 1680 °C, and 1690 °C. In another aspect, the range can be derived from any two exemplary values. For example, the temperature ranges from 1510 °C to 1690 °C.

[0048] In one aspect, the method comprises a tapping step. In a further aspect, the deoxidizing agent can be added at the time of tapping. In a still further aspect, the molten steel is tapped prior to combining the molten steel and at least one deoxidizing agent.

[0049] The tapping step occurs once the desired steel composition and temperature are achieved in the electric arc furnace, then the tap-hole is opened, the furnace is tilted, and the steel pours into a ladle for transfer to the next batch operation (usually a ladle furnace or ladle station).

[0050] In one aspect, the method comprises a casting or forming step. In a further aspect, the deoxidized molten steel is casted into an article of manufacture. In a still further aspect, the casting steel is a billet caster step.

[0051] In a further aspect, the billet caster step can produce the steel as a long product. In one aspect, the long product comprises a bar, rod, wire, and/or beam. In another aspect, the size of the billet cross section produced by the billet caster can vary from 100x100mm to 250x250 mm.

[0052] In various aspects, the disclosed methods can be used to make the disclosed steel compositions.

C. STEEL COMPOSITIONS

[0053] In various aspect, the invention relates to a steel composition. In a further aspect, the steel composition is produced by a disclosed method.

[0054] In one aspect, disclosed herein is a steel composition comprising at least one oxide of the alloy of Fe-Mn-Si-Ca.

[0055] In another aspect, disclosed herein is a steel composition produced by the step of combining molten steel and at least one deoxidizing agent under conditions effective to provide deoxidized steel, wherein the at least one deoxidizing agent comprises an alloy of Fe-Mn-Si-Ca.

[0056] In one aspect, the steel composition comprises at least one oxide of the alloy of Fe-Mn-Si-Ca. In a further aspect, the at least one oxide is present in the steel is SiO₂, MnO, CaO, FeO, or a combination thereof. In a still further aspect, the steel composition comprises SiO₂, MnO, CaO, and FeO.

[0057] In one aspect, the steel composition can comprise killed or semi-killed steel. In some aspects, the steel composition is killed steel. In other aspects, the deoxidized steel is semi-killed steel.

[0058] In a one aspect, the steel composition has an oxygen content of less than about 23 ppm. In a further aspect, the steel composition has an oxygen content of less than about 20 ppm. In a still further aspect, the steel composition has an oxygen content of less than about 18 ppm. In a yet further aspect, the steel composition has an oxygen content of less about 15 ppm.

[0059] In one aspect, the steel composition has an oxygen content ranging from about 1 ppm to 20 ppm, including exemplary values 2 ppm, 3 ppm, 4 ppm, 5 ppm, 6 ppm, 7 ppm, 8 ppm, 9 ppm, 10 ppm, 11 ppm, 12 ppm, 13 ppm, 14 ppm, 15 ppm, 16 ppm, 17 ppm, 18 ppm, and 19 ppm. In another aspect, the range can be derived from any two exemplary values. In another aspect, the range can be derived from any two exemplary values. For example, the oxygen content can range from 1 ppm to 18 ppm.

[0060] In one aspect, the deoxidizing agent comprises an alloy of Fe-Mn-Si-Ca. In a further aspect, the alloy comprises calcium in an amount ranging from 1 wt % to 30 wt %, including exemplary values of 2 wt %, 3 wt %, 4 wt %, 5 wt %, 6 wt %, 7 wt %, 8 wt %, 9 wt %, 10 wt %, 11 wt %, 12 wt %, 13 wt %, 14 wt %, 15 wt %, 16 wt %, 17 wt %, 18 wt %, 19 wt %, 20 wt %, 21 wt %, 22 wt %, 23 wt %, 24 wt %, 25 wt %, 26 wt %, 27 wt %, 28 wt %, or 29 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise calcium in an amount ranging from 1 wt % to 29 wt %, based on the total weight percentage of the alloy.

[0061] In a further aspect, the alloy comprises manganese in an amount ranging from 1 wt % to 20 wt %, including exemplary values of 2 wt %, 3 wt %, 4 wt %, 5 wt %, 6 wt %, 7 wt %, 8 wt %, 9 wt %, 10 wt %, 11 wt %, 12 wt %, 13 wt %, 14 wt %, 15 wt %, 16 wt %, 17 wt %, 18 wt %, or 19 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise manganese in an amount ranging from 1 wt % to 19 wt %, based on the total weight percentage of the alloy.

[0062] In a further aspect, the alloy comprises silicon in an amount ranging from 40 wt % to 60 wt %, including exemplary values of 41 wt %, 42 wt %, 43 wt %, 44 wt %, 45 wt %, 46 wt %, 47 wt %, 48 wt %, 49 wt %, 50 wt %, 51 wt %, 52 wt %, 53 wt %, 54 wt %, 55 wt %, 56 wt %, 57 wt %, 58 wt %, or 59 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise silicon in an amount ranging from 41 wt % to 59 wt %, based on the total weight percentage of the alloy.

[0063] In a further aspect, the alloy comprises iron in an amount ranging from greater than 0 wt % to 10 wt %, including exemplary values of 2 wt %, 3 wt %, 4 wt %, 5 wt %, 6 wt %, 7 wt %, 8 wt %, or 9 wt %. In another aspect, the range can be derived from any two of the foregoing exemplary values. For example, the alloy can comprise iron in an amount ranging from 1 wt % to 9 wt %, based on the total weight percentage of the alloy.

[0064] In a further aspect, the alloy comprises: calcium in an amount ranging from 1 wt % to 30 wt %; manganese in an amount ranging from 1 wt % to 20 wt %; silicon in an amount ranging from 40 wt % to 60 wt %; and wt % balance of Fe.

[0065] In some aspects, the alloy is an alloy consisting essentially of Fe-Mn-Si-Ca. In other aspects, the alloy is an alloy consisting of Fe-Mn-Si-Ca. In further aspects, the alloy does not comprise a substantial amount of aluminum, barium, or strontium. In still further aspects, the alloy is substantially free of any amount of aluminum, barium, or strontium.

[0066] In various aspects, the disclosed methods and steel compositions can be used to make the disclosed articles of manufacture.

D. ARTICLE OF MANUFACTURE

[0067] In one aspect, the invention relates to an article of manufacture comprising deoxidized steel produced using the disclosed methods. In a further aspect, the article is a long product.

[0068] In one aspect, the long product comprises a bar, a rod, a wire, or a beam. Such articles can be used in construction and structural applications.

[0069] It is also understood that the disclosed methods can be employed to make the articles of manufacture.

E. ASPECTS

[0070] The disclosed methods and articles include at least the following aspects.

[0071] Aspect 1: A method, comprising:

combining molten steel and at least one deoxidizing agent under conditions effective to provide deoxidized steel, wherein the at least one deoxidizing agent comprises an alloy of Fe-Mn-Si-Ca.

[0072] Aspect 2: The method of claim 1, wherein the molten steel is tapped into a ladle furnace prior to combining the molten steel and at least one deoxidizing agent.

[0073] Aspect 3: The method of claim 1 or 2, wherein step of combining the molten steel and at least one deoxidizing agent is performed at the tapping stage of the steel making process.

[0074] Aspect 4: The method of claims 1-3, wherein the conditions effective to provide deoxidized steel comprises forming a slag layer over the molten steel.

[0075] Aspect 5: The method of claim 4, wherein the slag layer comprises at least one oxidation product of the FeMnSiCa alloy.

[0076] Aspect 6: The method of claim 5, wherein the oxidization product comprises at least one of CaO, MnO, SiO₂, FeO, or a combination thereof.

[0077] Aspect 7: The method of claims 1-6, wherein the deoxidized steel is semi-killed or killed steel.

[0078] Aspect 8: The method of claims 1-7, wherein the deoxidized steel has a oxygen content of less than about 23 ppm.

[0079] Aspect 9: The method of claims 1-8, wherein the deoxidized steel has a oxygen content of less than about 20 ppm.

[0080] Aspect 10: The method of claimss 1-9, wherein the deoxidized steel has a oxygen content of less than about 18 ppm.

[0081] Aspect 11: The method of claims 1-10, wherein deoxidized steel has a oxygen content of less about 15 ppm.

[0082] Aspect 12: The method of claims 1-11, wherein the alloy comprises calcium in an amount ranging from 1 wt % to 30 wt %.

[0083] Aspect 13: The method of claims 1-12, wherein the alloy comprises manganese in an amount ranging from 1 wt % to 20 wt %.

[0084] Aspect 14: The method of claims 1-13, wherein the alloy comprises silicon in an amount ranging from 40 wt % to 60 wt %.

[0085] Aspect 15: The method of claims 1-14, wherein the alloy comprises iron in an amount ranging from greater than 0 wt % to 10 wt %.

[0086] Aspect 16: The method of claims 1-15, wherein the alloy comprises

- a. calcium in an amount ranging from 1 wt % to 30 wt %;
- b. manganese in an amount ranging from 1 wt % to 20 wt %;
- c. silicon in an amount ranging from 40 wt % to 60 wt %; and
- d. wt % balance of Fe.

[0087] Aspect 17: The method of claims 1-15, wherein the alloy is an alloy consisting essentially of Fe-Mn-Si-Ca.

[0088] Aspect 18: The method of claims 1-15, wherein the alloy is an alloy consisting of Fe-Mn-Si-Ca.

[0089] Aspect 19: The method of claims 1-18, wherein the alloy does not comprise a substantial amount of aluminum, barium, or strontium.

[0090] Aspect 20: The method of claims 1-19, wherein the oxygen content of the deoxidized molten steel is less than the oxygen content of the molten steel prior to combining with the at least one deoxidizing agent.

[0091] Aspect 21: The method of claims 1-20, wherein the deoxidized molten steel is casted into an article of manufacture.

[0092] Aspect 22: The method of claim 21, wherein the article is a long product.

[0093] Aspect 23: The method of claim 21, wherein the long product comprises a bar, a rod, a wire, or a beam.

[0094] Aspect 24: A steel composition produced by the method of any preceding claim.

[0095] Aspect 25: The composition of claim 21, where the steel composition comprises at least one oxide of the alloy of Fe-Mn-Si-Ca.

[0096] Aspect 26: The composition of claim 25, wherein the at least one oxide is present in the steel is SiO₂, MnO, CaO, FeO, or a combination thereof.

[0097] Aspect 27: The composition of claim 25, wherein the steel composition comprises SiO₂, MnO, CaO, and FeO.

[0098] Aspect 28: The composition of claims 21-27, wherein the steel composition has a oxygen content of less than about 23 ppm.

[0099] Aspect 29: The composition of claim 21-27, wherein steel composition has a oxygen content less than about 20 ppm.

[00100] Aspect 30: The composition of of claims 21-27, wherein steel composition has a oxygen content less than about 18 ppm.

[00101] Aspect 31: A steel composition comprising at least one oxide of the alloy of Fe-Mn-Si-Ca.

[00102] Aspect 32: The composition of claim 31, wherein the alloy is an alloy consisting essentially of Fe-Mn-Si-Ca.

[00103] Aspect 33: The composition of claim 31, wherein the steel composition comprises SiO₂, MnO, CaO, and FeO.

[00104] Aspect 34: The composition of claims 31-33, wherein the the steel composition has a oxygen content of less than about 23 ppm.

[00105] Aspect 35: The composition of claims 31-33, wherein the the steel composition has a oxygen content of less than about 20 ppm.

[00106] Aspect 36: The composition of claims 31-33, wherein the the steel composition has a oxygen content of less than about 18 ppm.

[00107] Aspect 37: An article of manufacture comprising the composition of any preceding claim.

[00108] Aspect 38: The article of manufacture of claim 37, wherein the article is a long product.

[00109] Aspect 39: The article of manufacture of any preceding claim, wherein the long product comprises a bar, a rod, a wire, or a beam.

F. EXPERIMENTAL

[00110] While aspects of the present invention can be described and claimed in a particular statutory class, such as the system statutory class, this is for convenience only and one of skill in the art will understand that each aspect of the present invention can be described and claimed in any statutory class. Unless otherwise expressly stated, it is in no way intended that any method or aspect set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not specifically state in the claims or descriptions that the steps are to be limited to a specific order, it is no way. Appreciably intended that an order be inferred, in any respect. This holds for any possible non-express basis for interpretation, including matters of logic with respect to arrangement of steps or operational flow, plain meaning derived from grammatical organization or punctuation, or the number or type of aspects described in the specification.

[00111] Throughout this application, various publications are referenced. The disclosures of these publications in their entirety are hereby incorporated by reference into this application in order to more fully describe the state of the art to which this pertains. The references disclosed are also individually and specifically incorporated by reference herein for the material contained in them that is discussed in the sentence in which the reference is relied upon. Nothing herein is to be construed as an admission that the present invention is not entitled to antedate such publication by virtue of prior invention. Further, the dates of publication provided herein can be different from the actual publication dates, which can require independent confirmation.

CLAIMS

What is claimed is:

1. A method, comprising:

combining molten steel and at least one deoxidizing agent under conditions effective to provide deoxidized steel, wherein the at least one deoxidizing agent comprises an alloy of Fe-Mn-Si-Ca.
2. The method of claim 1, wherein the molten steel is tapped into a ladle furnace prior to combining the molten steel and at least one deoxidizing agent.
3. The method of claim 1 or 2, wherein step of combining the molten steel and at least one deoxidizing agent is performed at the tapping stage of the steel making process.
4. The method of claims 1-3, wherein the conditions effective to provide deoxidized steel comprises forming a slag layer over the molten steel.
5. The method of claim 4, wherein the slag layer comprises at least one oxidation product of the FeMnSiCa alloy.
6. The method of claim 5, wherein the oxidization product comprises at least one of CaO, MnO, SiO₂, FeO, or a combination thereof.
7. The method of claims 1-6, wherein the deoxidized steel is semi-killed or killed steel.
8. The method of claims 1-7, wherein the deoxidized steel has a oxygen content of less than about 23 ppm.
9. The method of claims 1-8, wherein the deoxidized steel has a oxygen content of less than about 20 ppm.
10. The method of claimss 1-9, wherein the deoxidized steel has a oxygen content of less than about 18 ppm.
11. The method of claims 1-10, wherein deoxidized steel has a oxygen content of less about 15 ppm.
12. The method of claims 1-11, wherein the alloy comprises calcium in an amount ranging from 1 wt % to 30 wt %.
13. The method of claims 1-12, wherein the alloy comprises manganese in an amount ranging from 1 wt % to 20 wt %.
14. The method of claims 1-13, wherein the alloy comprises silicon in an amount ranging from 40 wt % to 60 wt %.

15. The method of claims 1-14, wherein the alloy comprises iron in an amount ranging from greater than 0 wt % to 10 wt %.
16. The method of claims 1-15, wherein the alloy comprises
 - a. calcium in an amount ranging from 1 wt % to 30 wt %;
 - b. manganese in an amount ranging from 1 wt % to 20 wt %;
 - c. silicon in an amount ranging from 40 wt % to 60 wt %; and
 - d. wt % balance of Fe.
17. The method of claims 1-15, wherein the alloy is an alloy consisting essentially of Fe-Mn-Si-Ca.
18. The method of claims 1-15, wherein the alloy is an alloy consisting of Fe-Mn-Si-Ca.
19. The method of claims 1-18, wherein the alloy does not comprise a substantial amount of aluminum, barium, or strontium.
20. The method of claims 1-19, wherein the oxygen content of the deoxidized molten steel is less than the oxygen content of the molten steel prior to combining with the at least one deoxidizing agent.
21. The method of claims 1-20, wherein the deoxidized molten steel is casted into an article of manufacture.
22. The method of claim 21, wherein the article is a long product.
23. The method of claim 21, wherein the long product comprises a bar, a rod, a wire, or a beam.
24. A steel composition produced by the method of any preceding claim.
25. The composition of claim 21, where the steel composition comprises at least one oxide of the alloy of Fe-Mn-Si-Ca.
26. The composition of claim 25, wherein the at least one oxide is present in the steel is SiO₂, MnO, CaO, FeO, or a combination thereof.
27. The composition of claim 25, wherein the steel composition comprises SiO₂, MnO, CaO, and FeO.
28. The composition of claims 21-27, wherein the steel composition has a oxygen content of less than about 23 ppm.

29. The composition of claim 21-27, wherein steel composition has a oxygen content less than about 20 ppm.
30. The composition of of claims 21-27, wherein steel composition has a oxygen content less than about 18 ppm.
31. A steel composition comprising at least one oxide of the alloy of Fe-Mn-Si-Ca.
32. The composition of claim 31, wherein the alloy is an alloy consisting essentially of Fe-Mn-Si-Ca.
33. The composition of claim 31, wherein the steel composition comprises SiO₂, MnO, CaO, and FeO.
34. The composition of claims 31-33, wherein the the steel composition has a oxygen content of less than about 23 ppm.
35. The composition of claims 31-33, wherein the the steel composition has a oxygen content of less than about 20 ppm.
36. The composition of claims 31-33, wherein the the steel composition has a oxygen content of less than about 18 ppm.
37. An article of manufacture comprising the composition of any preceding claim.
38. The article of manufacture of claim 37, wherein the article is a long product.
39. The article of manufacture of any preceding claim, wherein the long product comprises a bar, a rod, a wire, or a beam.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/001754

A. CLASSIFICATION OF SUBJECT MATTER

INV. C21C7/06 C21C7/064 C21C7/076
ADD.

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)
C21C

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 094 666 A (OTOTANI TOHEI) 13 June 1978 (1978-06-13) abstract column 3, line 30 - line 35 -----	1-39
X	JP 2014 025111 A (JFE STEEL CORP) 6 February 2014 (2014-02-06) paragraph [0025] -----	1-39
X	JP 2010 159437 A (NIPPON YAKIN KOGYO CO LTD) 22 July 2010 (2010-07-22) paragraph [0025] -----	1-39
X	JP 2009 249678 A (NIPPON STEEL CORP) 29 October 2009 (2009-10-29) paragraph [0028] -----	1-39



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"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)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

22 December 2015

Date of mailing of the international search report

08/01/2016

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Gimeno-Fabra, Lluís

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2015/001754

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4094666	A	13-06-1978	CA 1092830 A	06-01-1981
			DE 2738379 A1	30-11-1978
			FR 2392120 A1	22-12-1978
			GB 1585278 A	25-02-1981
			US 4094666 A	13-06-1978

JP 2014025111	A	06-02-2014	NONE	

JP 2010159437	A	22-07-2010	JP 5428020 B2	26-02-2014
			JP 2010159437 A	22-07-2010

JP 2009249678	A	29-10-2009	JP 5272480 B2	28-08-2013
			JP 2009249678 A	29-10-2009
