United States Patent [19]

Corbett et al.

[11] **3,926,246**

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[54] **FLUX FOR CONTINUOUS CASTING OF STEEL**

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[21] Appl. No.: **444,072**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 290,196, Sept. 18, 1972, abandoned.

[52] **U.S. Cl.** **164/56;** 75/94; 106/52; 117/6; 164/82

[51] **Int. Cl.²** .. **B22D 27/20;** C22B 9/10; C03C 3/16

[58] **Field of Search** 75/94; 117/6; 106/48, 52, 106/73.1; 164/82, 56

[56] **References Cited**

UNITED STATES PATENTS

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3,642,052	2/1972	Schrewe et al.	164/82 X
3,649,249	3/1972	Halley et al.	75/94 X
3,685,986	8/1972	Rutes et al.	164/56 X
3,698,466	10/1972	Vogt et al.	164/82 X

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[57] **ABSTRACT**

There is disclosed a flux composition consisting essentially of controlled proportions of alkali metal oxides and phosphorus pentoxide, and desirably with fluorides, alkaline earth oxides, alumina, silica or boria. The flux which is substantially entirely vitrified is characterized by having flowidity, plastic deformation point, and alumina solubility all of which are suitable in the process for continuous casting of steel. In such process, the exposed molten steel surface is covered with a layer of said flux composition.

6 Claims, No Drawings

FLUX FOR CONTINUOUS CASTING OF STEEL

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part of our co-pending application Ser. No. 290,196, filed Sept. 18, 1972 now abandoned. Also related is Paul M. Corbett's co-pending patent Application Ser. No. 342,052 filed Mar. 16, 1973.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to improvements in flux composition for continuous casting of steel and to such process using said flux.

2. Description of the Prior Art

It is well known that to produce a high quality deoxidized carbon steel, it is necessary to add a deoxidizing agent to the molten steel in order to remove the entrapped oxygen normally present. The amount of the deoxidizing agent to be added depends generally on several factors, such as, the extent of the deoxidation required, the amount of carbon present in said steel, and the grain structure desired in the ultimate steel product. Silicon and aluminum, or mixtures thereof have been utilized extensively to deoxidize carbon steel. Thus, to produce a "semi-killed" carbon steel, silicon is added generally to the extent of about 0.1 to about 0.15%. To produce completely killed steel, the amount can be increased up to about 0.25%. Additions of silicon may increase slightly to compensate for the amount of carbon present in the steel; that is, if the carbon content of the steel is low, then the tendency for the steel to absorb a higher amount of oxygen is enhanced and, consequently, additional deoxidizing agents may be necessary. As to the addition of aluminum, it is usually done in the production of fine grain steels which will require upwards of about 0.15% aluminum to produce completely killed steels. Optimum amounts are in the range of 0.05 to 0.1%, however.

The addition of silicon, or aluminum, or both to molten carbon steels is believed to react with the entrapped oxygen to produce the corresponding oxides which often rise or float to the surface or slightly below it in the form of undesirable inclusions that can weaken the steel. In the manufacture of steel peices made by continuous casting, surface defects cannot be tolerated to any great extent, which why, these inclusions at the surface or just below it are particularly undesirable. Heretofore, a number of slag, flux or mold powder compositions, have been proposed for removing these included oxides.

Earlier proposals to suppress these inclusions in killed and semi-killed steels have involved the addition to the molten steel of calcium fluoride alone or in admixture with sodium carbonate and/or sodium nitrate. Normally, such addition is effected during teeming that is, during pouring of the molten steel into an ingot mold. Such additions can help to some extent, but they themselves tend to form undesirable inclusions unless great care is taken. In the continuous casting of steel, use of other flux compositions has been proposed, such compositions including blast furnace slag, window glass, bottle glass, sodium silicate glass, and borax. These, heretofore, have been referred to as low viscosity slags.

In selecting a desirable flux composition for the continuous casting of steel, it is important that the chemical stability of the flux be sufficient to insure the integrity of the thermophysical characteristics of the flux in service. The main reason for this is to avoid the generation of any appreciable quantity of objectionable fumes, toxic gases, decomposition products, or by-products which might be harmful for production personnel or even contaminate the product. Also, such flux compositions must be capable of solubilizing the impurities which are believed to be the cause of most surface or sub-surface imperfections found in continuous casting or rolled sheet materials produced therefrom. Furthermore, the flux composition must have a softening point (or a Plastic Deformation Point) and flowidity such that the layer of the flux on the molten steel maintains its effectiveness throughout the casting process.

Halley, in his U.S. Pat. No. 3,649,249, discloses a synthetic slag composition emminently suitable for use in the continuous casting of steel, such slag having a composition of: silica 10–15%; calcia 0–40%; calcium fluoride 5–40%; sodium oxide 5–35%; potassium oxide 5–35%; lithium oxide and lithium fluoride 0.5–15%; boria 0–30%; with the provision that the boria, calcium fluoride, and lithium fluoride represent, in combination, more than 15% of the composition, all percentages being by weight. Halley and characterized this slag composition as having several particular properties: Specific Flowidity and Plastic Deformation Point both of which can be determined by standarized methods shown in the patent, and solubility of alumina therein in excess of 20%.

Extensive testing of Halley's synthetic slag has shown it to be superior to any of the prior art slags (flux) for suppressing the incidence of surface defects on steels made by continuous castings: nevertheless, such defects to the extent of about 10% of the total surface area often occur with such slag. Fortunately, such defects are not entirely of a serious type. However, even minor defects are undesirable because they require additional time, cost, and effort for their correction.

Fluxes made in accordance with the present invention have compared favorabley even with Halley's slag compositions in the continuous casting of steel. Additionally, the instant fluxes have been utilized successfully in continuous casters employing, alumina-graphite molten metal inlet tubes (shrouds). Furthermore, the alumina content of the instant fluxes can be adjusted within the limits stated herein to suppress the alumina solubility from the shroud at modest sacrifice in raising fusion temperature and lowering flowidity of the flux. Surprisingly, also, the attack of the instant flux on fused silica shrouds is quite tolerable for practical operation. The instant flux compositions do not appear to form immiscible liquid phases at the elevated continuous casting temperatures, an important criterion for past performances.

BRIEF DESCRIPTION OF THE INVENTION

The instant flux composition is substantially entirely in the vitreous state as frit particles. While it is possible to use very small proportions (30% or less based on the weight of the frits) of finely ground milled additives with the frit, which additives can melt down in the caster to augment the composition within the limits stated herein, the flux as all frit appears to operate best and most reliably in continuous casting of steels. The

flux composition in its broad and in its more advantageous final oxide analysis consists essentially of:

Ingredient	Broad Composition Wt. %	Preferred Wt. %
Na_2O	10–30	18–24
K_2O	0–10	0
Li_2O	0–8	2.5–6
SiO_2	0–40	1–20
P_2O_5	5–50	10–40
F, MgO, CaO, BaO, SrO	0–15	0–10
Al_2O_3	0–25	5–20
B_2O_3	0–25	5–20
	0–10	0–6

In a process for the continuous casting of steel utilizing an open-ended mold, the process is improved by covering the molten steel surface at the top of the mold with a layer of such flux composition (usually handled by scoop and maintained several inches thick).

When the foregoing compositional limitations are complied with, the flux flowidity will be in the usual range for continuous casting of steel: (i.e. about 2–16 inches as measured in accordance with U.S. Pat. No. 3,649,249) and advantageously from about 6–10 inches. Similarly, the Plastic Deformation Point of the flux will be between about 1,000° and about 1,600°F. which is useful for the continuous casting of steel. The solubility of alumina will be at most between about 15–17% measured in accordance with the test shown in the abovementioned patent to Halley, U.S. Pat. No. 3,649,249. If the flux composition contains alumina, then the alumina solubility will be diminished correspondingly.

PREFERRED EMBODIMENT OF THE INVENTION

The flux compositions can be made from actual oxides or perferably, for efficiency and economy, from their conventional ceramic raw material equivalents. For example, some raw materials can be used to provide one or more ingredients of the flux, such as, sodium silicate which can provide both sodium oxide as well as silicon dioxide. Similarly, the various carbonates are capable of providing the requisite oxides, such as sodium carbonates and optional oxides such as the alkaline earth metal carbonates. Care should be taken, however, not to include substantial amounts of hydrated components if fluorides are to be present in the composition because of the possible formation of volatile fluorides. It should be appreciated that high purity for the raw materials is not required, and the compositions in accordance with the present invention can have the ordinary small amounts of impurities encountered in ceramic practice without serious shortcomings. In fact, often in the firing of these raw materials some components of the lining of the furnace such as silica or alumina are incorporated into these flux materials and become eventually part of the final products.

The raw batch ingredients for the flux are preferably premixed in the dry state, then melted and cooled to form a frit (i.e., small vitreous particles). Of course, it should be noted that the fusion temperature for most compositions forming in the ranges specified herein will not exceed 2,500°F. One particular range of preferred embodiments is provided below:

Ingredients	% by Weight
Na_2O	20–24
K_2O	5–7
Li_2O	4–6
SiO_2	25–30
P_2O_5	12–16
Al_2O_3	0–15
F	8–12
MgO	0–25
CaO	10–20
BaO	0–25
SrO	0–25

wherein the percentages of the various ingredients are selected to total 100% by weight. The resulting frit usually is crushed and pulverized to form particles in fineness passing at least 20 mesh (Tyler Standard Sieves) and preferably be mostly between 50 and 100 mesh size or even finer; for example, at least 50% passing 100 mesh. Alternatively, and often with advantage, the frit can be used directly from customary quenching. It has been found that the flux can be used in this particulate powder form in the continuous casting process by simply providing a layer on the surface of the molten metal at the top of the mold in the caster. An adequate layer of the flux usually is about 1 to 2 inches in thickness and is maintained in such thickness throughout the continuous casting process by periodic or continuous additions. Typically, the amount of the flux utilized is about 1 pound per ton and generally in the range of 0.2 to 1.5 pounds per ton of steel cast.

The improvement of the present invention will be more readily understood from consideration of the following specific examples which are given for the purpose of illustration and are not intended to be limiting. All parts and percentages are by weight unless specified otherwise.

EXAMPLE 1

A flux composition was prepared by conventionally dry-mixing, fusing, and fritting conventional raw batch ingredients to yield frit of the following preferred analysis: sodium oxide 22.2%, potassium oxide 6.1%, lithium oxide 5.4%, calcium oxide 15.1%, and silicon dioxide 27%, and phosphorus pentoxide 14% and fluoride as F 10.2%. The frit was ground all to pass through a 20 mesh screen, with at least 50% to pass through a 100 mesh screen.

Raw batch ingredients were as follows:

Ingredients	Parts By Weight
Sodium Carbonate	17.74
Sodium tripolyphosphate	21.07
Fluorspar	18.57
Silica	23.27
Lithium Carbonate	11.61
Potassium Carbonate	7.74

The flowidity of the flux (according to the method disclosed in the U.S. Pat. No. 3,649,249 cited herein) was measured to be 9 inches. Similarly the Plastic Deformation Point was about 1000°F. Several thousand pounds of this flux composition were prepared and used in a process for continuously casting steel pieces with surprisingly excellent results. The flux composition was used to cover the molten metal surface at the top of the mold. Minor surface defects appeared on

only a very minute fraction of subsequently worked pieces.

EXAMPLE 2

Following the same procedure described in Example 1 a flux was prepared with the following analysis: Na_2O: 21.2,K_2O:0.0, Li_2O:3.6, CaO;5.0, MgO: 0, BaO: 0, SrO: 0, SiO_2: 1.0, P_2O_5:40.0, F:10.0, B_2O_3: 0.0, Al_2O_3:19.1.

The flux in frit form was ground to pass through a 20 mesh screen, with at least 50% of the ground particles passing through 100 mesh screen.

Raw batch ingredients were as follows:

Ingredients	Parts by Weight
Soduim Silicofluoride	2.5
Soduim Tripolyphosphate	17.4
Lithium Carbonate	7.4
Fluorspar	5.4
Monoammonium Phosphate	38.5
Alumina (Calcined)	15.9
Soduim Fluoride	13.0

The flowidity of the above flux was measured to be 11–12 inches. Similarly the Plastic Deformation Point was about 1000°F. When this flux was used to cover the molten metal surface of continuously cast steel very minor surface and subsurface defects were observed in the subsequently worked pieces. Thus, the above-described flux possesses surprisingly excellent properties for solubilizing or extracting deoxidizing agents in the steel thereby minimizing surface and nearsurface imperfections.

EXAMPLE 3

The same procedure described in Example 1 was followed to prepare the following flux whose analysis, on oxide basis, was determined to be: Na_2O:22.0, K_2O:6.0, Li_2O:2.4, CaO:9.0, MgO:0, SrO: 0, BaO:0, SiO_2: 25.0, P_2O_5: 20.0, $F_{:10.2}$, B_2O_3:0.0, Al_2O_3:0.0.

As to the raw batch ingredients, they were as follows:

Ingredients	Parts by Weight
Soduim Tripolyphosphate	31.4
Potassium Carbonate	8.1
Lithium Carbonate	5.4
Fluorspar	19.4
Silica	24.2
Sodium Carbonate	11.5

The flowidity of the above flux was measured to be 5 inches. Similarly the plastic Deformation Point was about 1200°F. When this flux was used to cover the molten metal surface of continuously cast steel very minor surface and subsurface defects were observed in the subsequently worked pieces. Thus, the above-described flux possesses surprisingly excellent properties for solubilizing or extracting deoxidizing agents in the steel thereby minimizing surface and near-surface imperfections.

EXAMPLE 4

The same procedure described in Example 1 was followed to prepare the following flux whose analysis, on oxide basis, was determined to be: Na_2O:20.9; K_2O:6.0; Li_2O:4.4; CaO:15.0: SiO_2:27.0; P_2O_5:14.0; F:10.1; B_2O_3:2.8.

Raw batch ingredients were as follows:

Ingredients	Parts By Weight
Soduim Tripolyphosphate	21.1
Fluorspar	18.6
Lithium Carbonate	9.4
Sodium Carbonate	16.5
Potassium Carbonate	7.6
Silica	24.3
Anhydrous Boric Acid	2.7

The flowidity of the above flux was measured to be 6 ½ inches. Similarly the Plastic Deformation Point was about 1200°F. When this flux was used to cover the molten metal surface of continuously cast steel very minor surface and subsurface defects were observed in the subsequently worked pieces. Thus, the above-described flux possesses surprisingly excellent properties for solubilizing or extracting deoxidizing agents in the steel thereby minimizing surface and near-surface imperfections.

EXAMPLE 5

In the foregoing examples 2–4 the calcuim oxide was substituted with other alkaline earths (MgO, BaO and SrO) with substantially the same results.

The plastic deformation point (PDP) was determined by a method which is somewhat different from the one disclosed by Halley (U.S. Pat. No. 3,649,249). This method places a button made from the flux (3.0 grams pressed at 5000lb. to produce a button of 3/8 inches in diameter) on a piece of a high-temperature steel (a nickel alloyed steel) which is then introduced into an electric furnace heated to a pre-set temperature. The flux is maintained at that temperature for a period of 3 ½ minutes after which it is removed and cooled. A visual observation is made to determine if the edges of the pressed button have collapsed and become round. If not, the temperature is increased and the same procedure is followed. The temperature that causes the rounding of the edges is then referred to as the plastic deformation or fusion point.

What we claim is:

1. A flux composition having flowidity, plastic deformation point, and alumina solubility suitable for use in the continuous casting of steel, said composition being substantially in the vitreous state as frit particles, and consisting essentially of:

Ingredients	% by Weight
Na_2O	18–24
K_2O	0–10
Li_2O	2.5–6
SiO_2	1–20
P_2O_5	10–40
Al_2O_3	0–25
F	0–10
MgO	5–20
CaO	5–20
BaO	5–20
SrO	5–20
B_2O_3	0–6

and wherein the percentages of said ingredients total 100% by weight.

2. A flux composition having flowidity, Plastic Deformation Point, and alumina solubility suitable for use in the continuous casting of steel, said composition being substantially entirely in a vitreous state as frit particles and consisting essentially of:

Ingredients	% By Weight
Na_2O	20–24
K_2O	5–7
Li_2O	4–6
SiO_2	25–30
P_2O_5	12–16
Al_2O_3	0–15
F	8–12
MgO	0–25
CaO	10–20
BaO	0–25
SrO	0–25.

3. The flux composition of claim **1** wherein:

Na_2O	21.2
Li_2O	3.6
CaO	5.0
SiO_2	1.0
P_2O_5	40.0
F	10.0
Al_2O_3	19.1.

4. A flux composition having flowidity, Plastic Deformation Point, and alumina solubility suitable for use in the continuous casting of steel, said composition being substantially entirely in a vitreous state as frit particles and consisting essentially of:

Ingredients	% By Weight
Na_2O	22.0
K_2O	6.1
Li_2O	2.4
CaO	9.0
SiO_2	25.0
P_2O_5	20.0
F	10.2.

5. A flux composition having flowidity, Plastic Deformation Point, and alumina solubility suitable for use in the continuous casting of steel, said composition being substantially entirely in a vitreous state as frit particles, and consisting essentially of:

Ingredients	% By Weight
Na_2O	20.9
K_2O	6.0
Li_2O	4.4
MgO	15.0
SiO_2	27.0
P_2O_5	14.0
F	10.1
B_2O_3	2.8.

6. In a process for the continuous casting of steel using an open-ended mold for the molten metal, the improvement which comprises covering the exposed surface of said molten metal with a layer of the flux composition of claim **1**.

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,926,246

DATED : Dec. 16, 1975

INVENTOR(S) : Paul M. Corbett and Michael P. Fedock

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Front Page, line [73] correct Assignee to read: SCM Corporation, Cleveland, Ohio, and Republic Steel Corporation, a Corporation of New Jersey.

Column 2, line 12, correct "casting" to "castings"; line 27, cancel "and" and insert "also" therefor; line 44, correct "favorabley" to "favorably".

Column 5, line 38, correct "K_2O: 6.0" to "K_2O: 6.1"; line 39, correct "F: $_{10.2}$" to "F: 10.2".

Claim 1, correct the % by weight of alkaline earth oxide as listed to read as follows:

Ingredients	% by Weight
-	-
-	-
-	-
-	-
-	-
-	-
MgO) CaO) BaO) SrO)	5-20
-	-

Claim 5, in the list of ingredients correct "MgO" to "CaO".

Signed and Sealed this

thirteenth Day of *April 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks