⑲ Europäisches Patentamt
European Patent Office
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⑪ Publication number: **0 060 706**
A1

⑫ EUROPEAN PATENT APPLICATION

㉑ Application number: **82301304.0**

㉒ Date of filing: **15.03.82**

(51) Int. Cl.³: **F 27 D 3/15**

㉚ Priority: **16.03.81 JP 37642/81**
16.03.81 JP 37645/81

㊸ Date of publication of application: **22.09.82**
Bulletin 82/38

(84) Designated Contracting States: **DE FR GB SE**

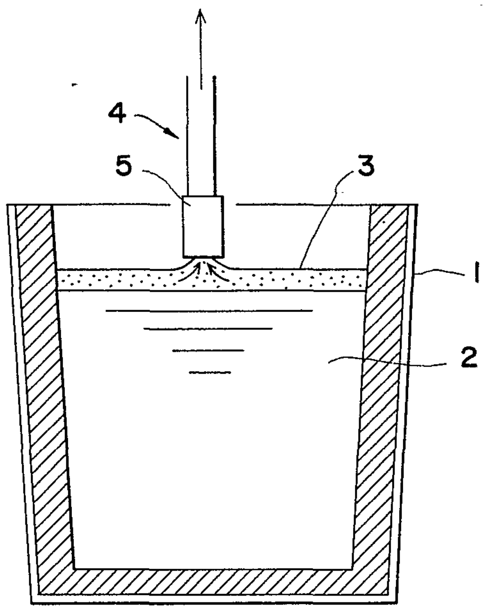
(71) Applicant: **Nippon Steel Corporation,**
6-3 Ote-machi 2-chome Chiyoda-ku, Tokyo 100 (JP)

(72) Inventor: **Matsunaga, Hisashi, No. 1, Fuji-cho Hirohata-ku, Himeji City Hyogo Prefecture (JP)**
Inventor: **Ishikura, Katuhiko, No. 1, Fuji-cho Hirohata-ku, Himeji City Hyogo Prefecture (JP)**
Inventor: **Imamura, Katuyosi, No. 1, Fuji-cho Hirohata-ku, Himeji City Hyogo Prefecture (JP)**
Inventor: **Kato, Fujio, No.1, Fuji-cho Hirohata-ku, Himeji City Hyogo Prefecture (JP)**
Inventor: **Mineyuki, Seizo, No. 1, Fuji-cho Hirohata-ku, Himeji City Hyogo Prefecture (JP)**
Inventor: **Minami, Akiyoshi, No. 1, Fuji-cho Hirohata-ku, Himeji City Hyogo Prefecture (JP)**

(74) Representative: **Lewin, John Harvey et al, Elkington and Fife High Holborn House 52/54 High Holborn, London WC1V 6SH (GB)**

(54) Method for removing slag on the surface of molten metal by suction.

(57) A method of removing slag from the surface of molten metal by suction after adding a fluidity modifier to the slag to increase its fluidity is disclosed.



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This invention relates to a method for removing slag from the surface of molten metal by suction. More particularly, the invention relates to a method that achieves easy discharge of slag through suction by increasing its fluidity.

Molten iron from a blast furnace is freed of slag before it is poured into a vessel, but the separation of molten iron from slag is often incomplete and the blast furnace slag floats on the surface of the molten iron in the vessel. Performing various types of refining operation in one vessel is common practice in modern steelmaking plants, and in this case, slag is formed by reaction of the molten iron with a flux added in each refining stage, and floats on the surface of the melt.

Complete separation of the slag from the molten iron is an important factor for achieving easy treatment of the iron in subsequent steps. Several methods have been proposed for separating slag from the molten iron. In one method, molten slag is poured from a tilting vessel. This method is simple but is unable to achieve complete separation of the two materials. In another widely used method, slag is skimmed manually or by mechanical force, but this method is not preferred for the following reasons:
1) the temperature of the molten iron is decreased since its surface is exposed to the atmosphere;
2) the operator is exposed to very high temperatures; and 3) it takes much time to skim all the slag from the molten iron. A more effective method is to use a slag cleaner that is positioned above the slag and draws it off by suction. A typical slag cleaner is illustrated in Fig. 1, wherein a slag cleaner 4 with a suction head 5 is positioned slightly above the surface of the slag 3 floating on molten iron 2 in a vessel 1.

The suction head 5 is connected to a vacuum pump or other vacuum source, and slag 3 is drawn through the head and discharged overhead. A conventional slag cleaner is described in U.S. Patent No. 4,160,662. One great problem with the slag is that its composition and physical properties such as temperature vary across the section of the molten metal and it contains some portions having low fluidity. It is difficult to draw off low-fluidity slag by the slag cleaner and it can only be removed by mechanical force.

In desiliconization of molten iron, solid oxide such as iron oxide is injected into the melt, and the resulting slag has a low total Fe content and hence a low fluidity. After desiliconization and discharging the slag, the molten iron is dephosphorized or, instead, it is desulfurized and dephosphorized simultaneously, followed by discharging of the resulting slag. In this case, dephosphorization or simultaneous desulfurization and dephosphorization is achieved by using a flux mainly composed of CaO and supplying solid oxide (e.g. iron oxide) or gaseous oxygen or both. In either case, the resulting slag has a high melting point and hence low fluidity. This phenomenon is particularly conspicuous when dephosphorization and desulfurization are performed simultaneously because the slag to be treated must have a low total Fe content. One method of simultaneous desulfurization and dephosphorization after desiliconization and slag discharge is described in U.S. Patent No. 4,295,882. In this patent, desiliconization basically consists of supplying oxygen into a molten bath in the form of gaseous oxygen, solid oxide or both and removing Si in the melt as SiO_2. The slag formed has a high SiO_2 content. In the subsequent step of simultaneous desulfurization and dephosphorization, a $CaO-CaCl_2/KCI$ flux is used and oxygen is supplied in the form of gaseous oxygen, solid oxide or both. For efficient dephosphorization, the slag to be treated desirably has a basicity (weight ratio of CaO/SiO_2) of at least 3.0 and a total Fe content of 15 wt % or less. However, the slag obtained by treating slag having a fairly high basicity and low total Fe content has a low fluidity and cannot be completely removed by a slag cleaner unless much time is spent, or the cleaner is replaced by less efficient mechanical skimming.

Therefore, one object of the present invention is to provide a method that increases the fluidity of slag on molten metal so that it can be easily removed by a suction-type slag cleaner.

Another object of the present invention is to provide a method for forming slag of increased fluidity without causing any adverse effect on dephosphorization or simultaneous dephosphorization and desulfurization.

These objects of the present invention can be achieved by the following methods.

1) A method of removing slag from the surface of molten metal by suction after adding a fluidity modifier to the slag to increase its fluidity.

2) A method according to Item 1) wherein the slag floating on the surface of the molten metal is a blast furnace slag.

3) A method according to Item 1) wherein the slag floating on the surface of the molten metal is one which has been formed by desiliconization of the molten metal.

4) A method according to Item 1) wherein the slag

floating on the surface of the molten metal is one which has been formed by dephosphorization of the molten metal.

5) A method according to Item 1) wherein the slag floating on the surface of the molten metal is one which has been formed by simultaneous desulfurization and dephosphorization of the molten metal.

6) A method according to any of the preceding items wherein the fluidity modifier is one or more materials selected from the group consisting of CaF_2, sintered ore, iron ore, gaseous oxygen, slag from desiliconization, water-quenched slag from desiliconization.

7) A method according to Item 6) wherein the fluidity modifier is in a solid particulate form.

8) A method according to Item 7) wherein the fluidity modifier is a particulate slag or pulverized slag produced by water-quenching the slag from desiliconization.

9) A method according to Item 1) wherein the fluidity modifier is in a solid form and is added in an amount of from 50 to 200 kg per tonne (1000 kg) of the slag.

10) A method according to any of Items 1 to 9, wherein the fluidity modifier is added to the slag in the final stage of each refining operation.

11) A method according to any of Items 1 to 9, wherein the fluidity modifier is added to the slag after completion of each refining operation.

12) A method according to any of Items 1 to 9, wherein the addition of the fluidity modifier starts in the final stage of each refining operation and ends after completion of each refining operation.

Reference is now made to the accompanying drawings, in which:

FIG. 1 illustrates how a slag cleaner with a suction head 5 positioned above slag 3 floating on the surface of molten iron in a vessel 1 draws off the slag and discharges it overhead.

FIGS. 2 to 5 are graphs comparing the efficiency of drawing slag by suction according to the method of the present invention with that of the conventional method, in which:

FIG. 2 is a graph showing the relation between drawing time and slag removal efficiency observed when several of the fluidity modifiers according to the present invention are added to the slag formed by simultaneous desulfurization and dephosphorization of molten metal that follows desiliconization and slag discharge;

FIG. 3 is a graph showing the relation between drawing time and slag removal efficiency observed when both gaseous oxygen and CaF_2 are added to blast furnace slag as fluidity modifiers; and

FIG. 4 is a graph showing the relation between drawing time and slag removal efficiency observed when water-quenched slag from desiliconization is added to the slag formed by dephosphorization of molten metal subsequent to desiliconization and slag discharge; and

FIG. 5 is a graph showing the relation between drawing time and slag removal efficiency observed when water-quenched slag from desiliconization is added to the slag formed by simultaneous desulfurization and dephosphorization of molten metal that follows desiliconization and slag discharge.

The present invention achieves easy removal of slag by suction by means of lowering the melting point of the slag and increasing its fluidity. The slags to be treated by the method of the present invention include blast furnace slag floating on the surface of molten metal and those slags which are formed by purifying molten iron with a flux and which contain various impurities in a removable form. One of the purification operations that produce the slag to be treated by the present invention is desiliconization. The other purifications are dephosphorization and simultaneous desulfurization and dephosphorization that follow desiliconization. In either post-treatment, the slag to be treated desirably has a high basicity and total Fe content for achieving efficient dephosphorization, but the resulting slag then has a low fluidity. Therefore, the principal object of the present invention is to increase the fluidity of such slag.

The fluidity modifier used in the present invention is preferably one or more materials selected from the group consisting of CaF_2, sintered ore, iron ore (fine ore is preferred), slag from desiliconization, water-quenched slag from desiliconization and gaseous oxygen. Sintered ore is preferred since it contains not only iron oxide but also a suitable amount of SiO_2. The slag from desiliconization is the slag formed by desiliconization which is the first step of several purifications to be performed on the molten metal from a blast furnace. This slag has a very high SiO_2 content since it contains melt-derived Si in the form of SiO_2.

On the basis of the fact that the fluidity of slag can be increased by reducing its basicity, the present invention adds the high SiO_2 slag to the blast furnace slag, the slag from dephosphorization, or the slag from simultaneous desulfurization and dephosphorization, to thereby form a slag having a low basicity (say, less than 3.0), and hence a high fluidity. In the method of the present invention, the slag formed by desiliconization can be used as a fluidity modifier for the slag produced in the subsequent step of dephosphorization or simultaneous desulfurization and dephosphorization. The slag used as a fluidity modifier preferably has a uniform and small size of, say, 2 mm. To obtain such particulate slag or pulverized slag, the slag from desiliconization may be water-quenched after being drawn off by a slag cleaner. Such slag is called "water-quenched slag from desiliconization" and can also be used as a fluidity modifier in the present invention.

To confirm the effectiveness of the present invention, the inventors desiliconized molten iron, discharged the resulting slag, performed simultaneous dephosphorization and desulfurization on the molten iron at 1310-1320°C with a CaO flux and oxygen, added 200 to 600 kg of various fluidity modifiers to 3 to 4 tonnes (in this specification "tonne" means 1000 kg) of the resulting slag, and drew off the slag by suction. FIG. 2 shows the relation between drawing time and slag removal efficiency observed in this experiment. When the slag was drawn by suction according to the conventional method without adding any fluidity modifer,the surface temperature of the slag was decreased as time went by, and only about 40% of the slag could be removed because of its low fluidity. On the other hand, when sintered ore or CaF_2 was added as a fluid modifier, the melting point of the slag was reduced, its fluidity was increased, and the efficiency of slag removal was increased remarkably: about 80% when sintered ore was used, about 90% when CaF_2 was used, and almost all the slag could be removed when both sintered ore and

CaF_2 were used. When water-quenched slag from desiliconization or iron ore was used, the result was almost the same as obtained by using sintered ore.

FIG. 3 shows the relation between drawing time and slag removal efficiency observed when gaseous oxygen was blown for 2 to 5 minutes onto 800 kg of blast furnace slag floating on 70 tonnes of molten iron at 1365°C after 40 kg of CaF_2 was added to it. Almost all the slag could be removed by the method of the present invention, whereas only 60% of untreated blast furnace slag could be removed by suction alone.

The fluidity modifiers of the present invention can be added to blast furnace slag at any time, but this is not so with the slag formed as a result of various refining operations, and the timing of addition is very important. The fluidity modifiers could be added in either the early or middle stage of each refining operation, but in fact, various troubles occur. For instance, if CaF_2 is added in the early or middle stage of desiliconization of molten iron, the resulting slag forms so much that continued desiliconization becomes difficult. If CaF_2 is added in the early or middle stage of simultaneous dephosphorization and desulfurization following desiliconization of molten iron and slag discharge, the resulting slag also foams considerably and continued dephosphorization and desulfurization become difficult. Furthermore, dephosphorization is inhibited if simultaneous dephosphorization and desulfurization is performed by supplying solid oxide overhead. If sintered ore is added in the early or middle stage of simultaneous dephosphorization and desulfurization, the total Fe content of the resulting slag becomes greater than the value (7 to

8%) suitable for desulfurization, and not only is the desulfurization efficiency decreased but also re-sulfurization occurs. If water-quenched slag from desiliconization is added in the early or middle stage of dephosphorization or simultaneous dephosphorization and desulfurization, the basicity of the slag being treated is decreased to reduce the dephosphorization efficiency.

As a result of various studies on the timing of addition of fluidity modifiers that can increase the fluidity of slag to an easily removable level without incurring the above mentioned problems, the present inventors have found that the desired slag can be formed by adding the fluidity modifiers in the last stage of each refining operation, after completion of each refining operation, or by starting the addition in the last stage of each refining operation and ending it after completion of each refining. The term "the last stage of each refining operation" means, but it is not limited to, less than 6 minutes, say, 3 to 5 minutes, before completion of each refining operation.

CaF_2 is capable of increasing the fluidity of slag in a short time, so excessive slag foaming can be avoided by stopping the process of slag formation as soon as the desired slag fluidity is obtained. If sintered ore is added in one of the three stages mentioned above, little or no reduction occurs in the refining efficiency due to increased total Fe content of the slag being refined. At the same time, sintered ore contains SiO_2 which decreases the basicity of the slag being treated, but there is no possibilty of re-sulfurization since the timing of its addition enables rapid slag formation. When the slag from desiliconization or water-quenched slag from desiliconization is used in the subsequent refining operation, it is added in one of the following stages: i) after completion of dephosphorization or simultaneous desulfurization and dephosphorization, ii) in the last stage of dephosphorization or simultaneous desulfurization and dephosphorization, or iii) the addition starts in the last stage of the respective refining operations and ends after completion of those refining operations. By adding the slag (or water-quenched slag) from desiliconization after dephosphorization or simultaneous desulfurization and dephosphorization has been practically or completely finished, the possibilty of reduced refining efficiency due to low basicity of the slag being refined can be eliminated.

The advantages of the present invention are now described in greater detail by reference to the following Examples and comparative Examples which are given here for illustrative purposes only and are by no means intended to limit its scope.

Example 1 (Treatment of Blast furnace Slag)

Gaseous oxygen was blown for 4 minutes onto the surface of 800 kg of slag floating on 70 tonnes of molten iron (0.40% Si, 0.105% P, 0.028% S) at 1365°C after 40 kg of CaF_2 were added to the slag. Almost all the slag could be drawn off by sucking with a slag cleaner for 3.5 minutes. Only 450 kg of untreated slag could be removed by the same slag cleaner.

Example 2 (Treatment of Slags Formed in Various Refining Operations)

The results of treatment of slags formed in various refining operations are listed in Table 1 below.

Table 1

		Ex. 2-1		Ex. 2-2		Ex. 2-3	Ex. 2-4
		desiliconization - addition of CaF_2		simultaneous dephosphorization and desulfurization addition of CaF_2		simultaneous dephosphorization and de sulfurization addition of sintered ore and CaF_2	dephosphorization addition of CaF_2 and sintered ore
		added in initial stage	added in last stage	added in initial stage	added in last stage	added in last stage	added in last stage
amount of molten iron (tonne)		100	100	100	100	100	100
iron composition before treatment (%)	Si	0.65	0.60	0.10	0.09	0.12	0.10
	P	0.115	0.125	0.119	0.117	0.120	0.115
	S	0.020	0.018	0.025	0.033	0.026	0.020
temp. before treatment (°C)		1350	1350	1390	1380	1360	1390
refining method		solid oxide injected	same as first column	CaO flux and solid oxide injected	same as third column	same as third column	same as third column

(to be cont'd)

Table 1 (cont'd)

		Ex. 2-1		Ex. 2-2		Ex. 2-3	Ex. 2-4
		desiliconization - addition of CaF_2		simultaneous dephosphorization and desulfurization - addition of CaF_2		simultaneous dephosphorization and desulfurization - addition of sintered ore and CaF_2	dephosphorization - addition of CaF_2 and sintered ore
		added in initial stage	added in last stage	added in initial stage	added in last stage	added in last stage	added in last stage
amount of slag formed (Kg)		2000		3000		3250	2500
fluidity modifier	type and amount	CaF_2 300 Kg	CaF_2 300 Kg	CaF_2 250 Kg	CaF_2 250 Kg	sintered ore 400 Kg CaF_2 170 Kg	same as fifth column
	timing of addition	4 min. after start of refining	20 min. after start of refining	4 min. after start of refining	17 min. after start of refining	21 min. after start of refining	17 min. after start of refining
refining time		interrupted in 10 min.	23 min.	interrupted in 8 min.	20 min.	25 min.	17 min.
method of slag removal		-	vacuum slag cleaner	-	vacuum slag cleaner	same as fourth column	same as fourth column
drawing time		-	11 min.	-	10 min.	9 min.	8.3 min.

(to be cont'd)

Table 1 (cont'd)

		Ex. 2-1		Ex. 2-2		Ex. 2-3	Ex. 2-4
		desiliconization - addition of CaF_2		simultaneous dephosphorization and desulfurization addition of CaF_2		simultaneous dephosphorization and desulfurization addition of sintered ore and CaF_2	dephosphorization addition of CaF_2 and sintered ore
		added in initial stage	added in last stage	added in initial stage	added in last stage	added in last stage	added in last stage
percent slag removal (wt%)		-	100	-	90	100	100
iron composition after treatment (%)	Si	0.43	0.12	0.04	0.01	0.01	0.01
	P	0.115	0.124	0.073	0.014	0.012	0.007
	S	0.020	0.018	0.021	0.014	0.013	0.018
temp. after treatment (°C)		1335	1320	1350	1310	1320	1330

Notes to Table 1:

In Example 2-1, when CaF_2 was added in the early stage of desiliconization (comparative run), considerable slag foaming occurred and the refining operation had to be suspended after 10 minutes. The final Si content was as high as 0.43%. When CaF_2 was added 3 minutes before the end of the desiliconization (run of the present invention), no slag foaming occurred and the desired desiliconization could be achieved. All the slag formed could be removed by eleven minutes of sucking.

In Example 2-2, when CaF_2 was added in the early stage of simultaneous dephosphorization and desulfurization (comparative run), considerable slag foaming took place and the refining operation had to be suspended after 8 minutes. The final P and S contents were as high as 0.073% and 0.021%, respectively. When CaF_2 was added 3 minutes before the end of the refining operation (run of the present invention), no slag foaming occurred and the desired dephosphorization and desulfurization could be achieved. Ninety percent of the slag formed could be removed by ten minutes of sucking.

Example 3-1 (Dephosphorization)

Iron ore was added to 100 tonnes of molten iron (0.55% Si, 0.018% S, 0.115% P) at 1340°C in a vessel and desiliconized for 15 minutes under agitation with gas while oxygen was blown from above. The treated iron had 0.15% Si, 0.018% S and 0.115% P. The resulting slag was water-quenched as it was drawn from above by a slag cleaner of Kubota, Ltd. The so treated slag had a SiO_2 content of 45% and comprised particles less than 2 mm in size. After discharging the slag, a CaO flux was added to the molten iron in the same vessel, and the iron was dephosphorized for 15 minutes under agitation with an impeller while iron oxide was added and oxygen was blown from above. After completion of the dephosphorization, 300 kg of the water-quenched slag from desiliconization was added. The resulting slag had a basicity of 2.2 and was drawn off by a slag cleaner . The dephosphorized iron had 0.01% Si, 0.017% S and 0.015% P.

FIG. 4 compares the efficiency of removing the slag from dephosphorized iron in Example 3-1 according to the present invention and that of removing slag without addition of the water-quenched slag from desiliconization. One can see from this figure that the slag could be removed in a short time by the method of the present invention. However, in the conventional method wherein no water-quenched slag from desiliconization was added, the slag became increasingly hard (less fluid) as the surface temperature of the molten iron was decreased, and only about half of the slag could be removed.

Example 3-2 (Simultaneous desulfurization and dephosphorization)

Molten iron was desiliconized as in Example 3-1, and after discharging the resulting slag, a $CaO/CaCl_2$ flux was added to the molten iron in the same vessel, and the iron was desulfurized and dephosphorized simultaneously for 20 minutes under agitation with an impeller while iron oxide was added and oxygen was blown from above. Three minutes before completion of the refining operation, 500 kg of water-quenched slag from desiliconization prepared as in Example 3-1 were added. The resulting slag had a basicity of 2.5 at the time of completion of the refining operation, and it was drawn off by a slag cleaner. The refined iron had 0.01% Si, 0.009% S and 0.012% P, and these values were exactly the same as intended.

FIG. 5 shows the efficiency of removing the slag from simultaneously desulfurized and dephosphorized slag in Example 3-2 according to the present invention and that of removing slag without addition of the water-quenched slag from desiliconization. One can see from this figure that the slag could be removed in a short time by the method of the present invention, whereas in the conventional method which did not use water-quenched slag from desiliconization as a fluidity modifier, only about 30% of the slag could be removed.

CLAIMS:

1. A method of removing slag from the surface of molten metal by suction characterised in that the slag is removed after adding a fluidity modifier to the slag to increase its fluidity.

2. A method according to claim 1, wherein the slag floating on the surface of the molten metal is a blast furnace slag.

3. A method according to claim 1, wherein the slag floating on the surface of the molten metal is one which has been formed by desiliconization of the molten metal.

4. A method according to claim 1, wherein the slag floating on the surface of the molten metal is one which has been formed by dephosphorization of the molten metal.

5. A method accordng to claim 1, wherein the slag floating on the surface of the molten metal is one which has been formed by simultaneous desulfurization and dephosphorization of the molten metal.

6. A method according to any of the preceding claims, wherein the fluidity modifier is one or more materials selected from CaF_2, sintered ore, iron ore, gaseous oxygen, slag from desiliconization, and water-quenched slag from desiliconization.

7. A method according to claim 6, wherein the fluidity modifier is in a solid particulate form.

8. A method according to claim 7, wherein the fluidity modifier is a particulate slag produced by water-quenching the slag from desiliconization.

9. A method according to claim 1, wherein the fluidity modifier is in a solid form and is added in an amount of from 50 to 200 kg per tonne (1000 kg) of the slag.

10. A method according to any of claims 1 to 9, wherein the fluidity modifier is added to the slag in the final stage of each refining operation.

11. A method according to any of claims 1 to 9, wherein the fluidity modifier is added to the slag after completion of each refining operation.

12. A method according to any of claims 1 to 9, wherein the addition of the fluidity modifier starts in the final stage of each refining operation and ends after completion of each refining operation.

FIG.1

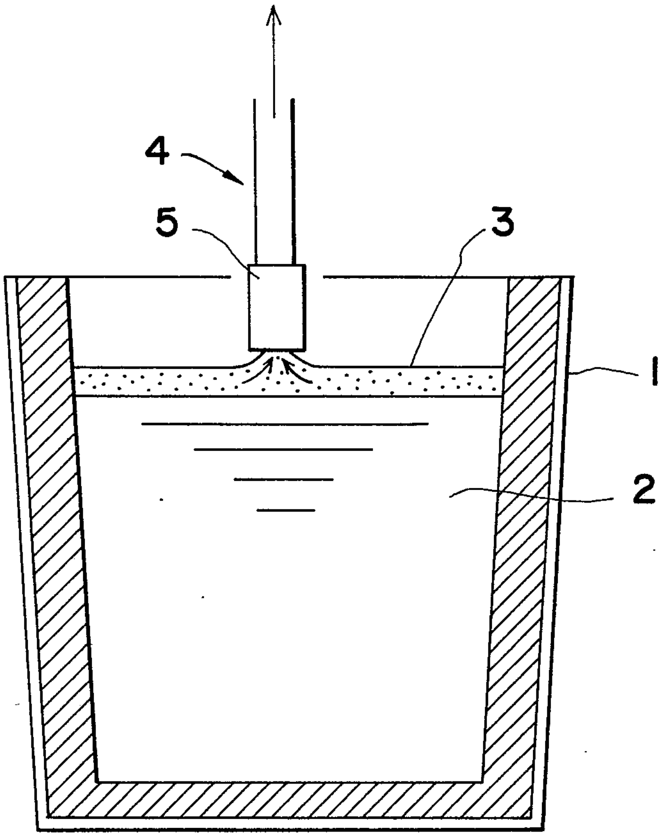


FIG.2

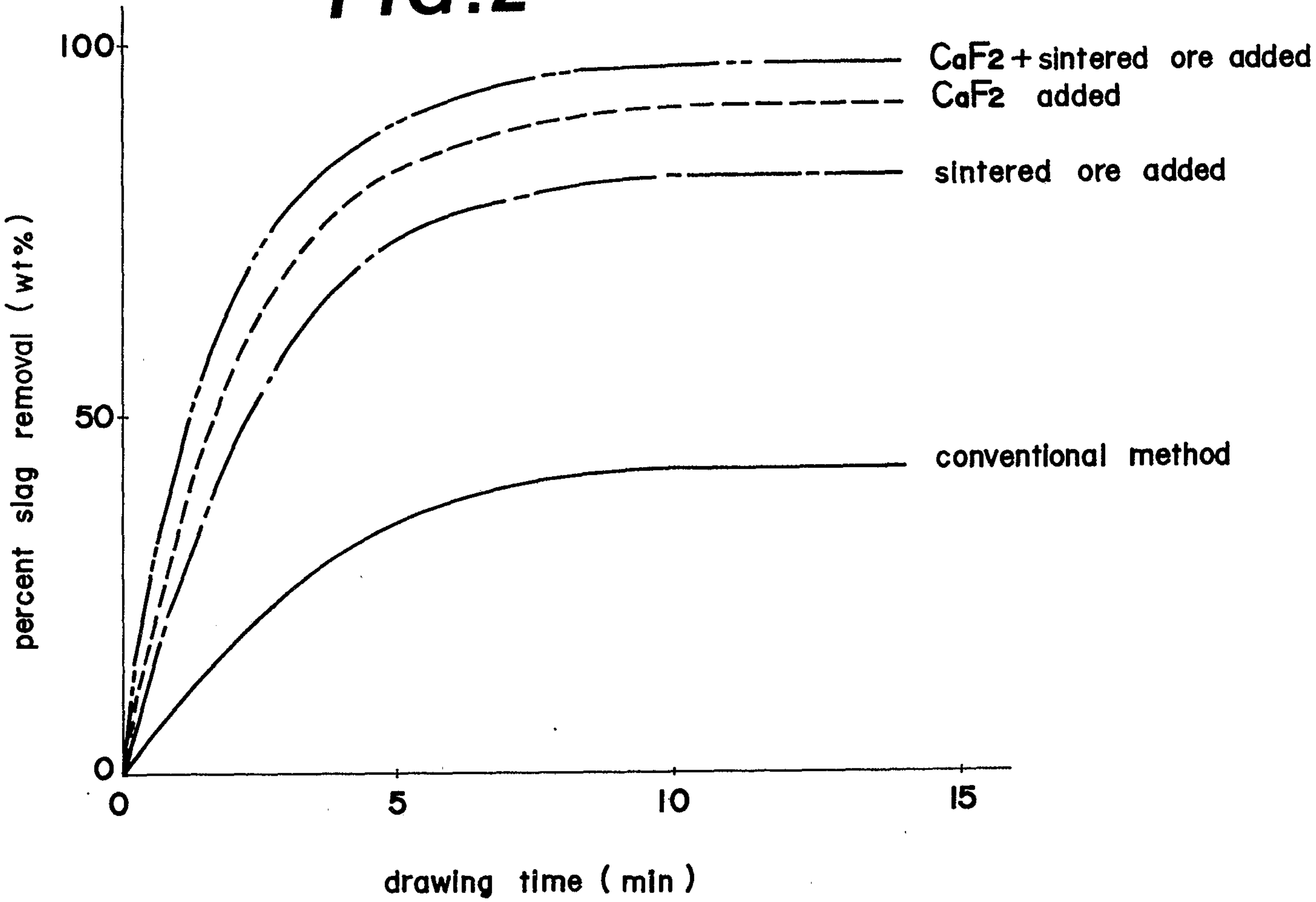
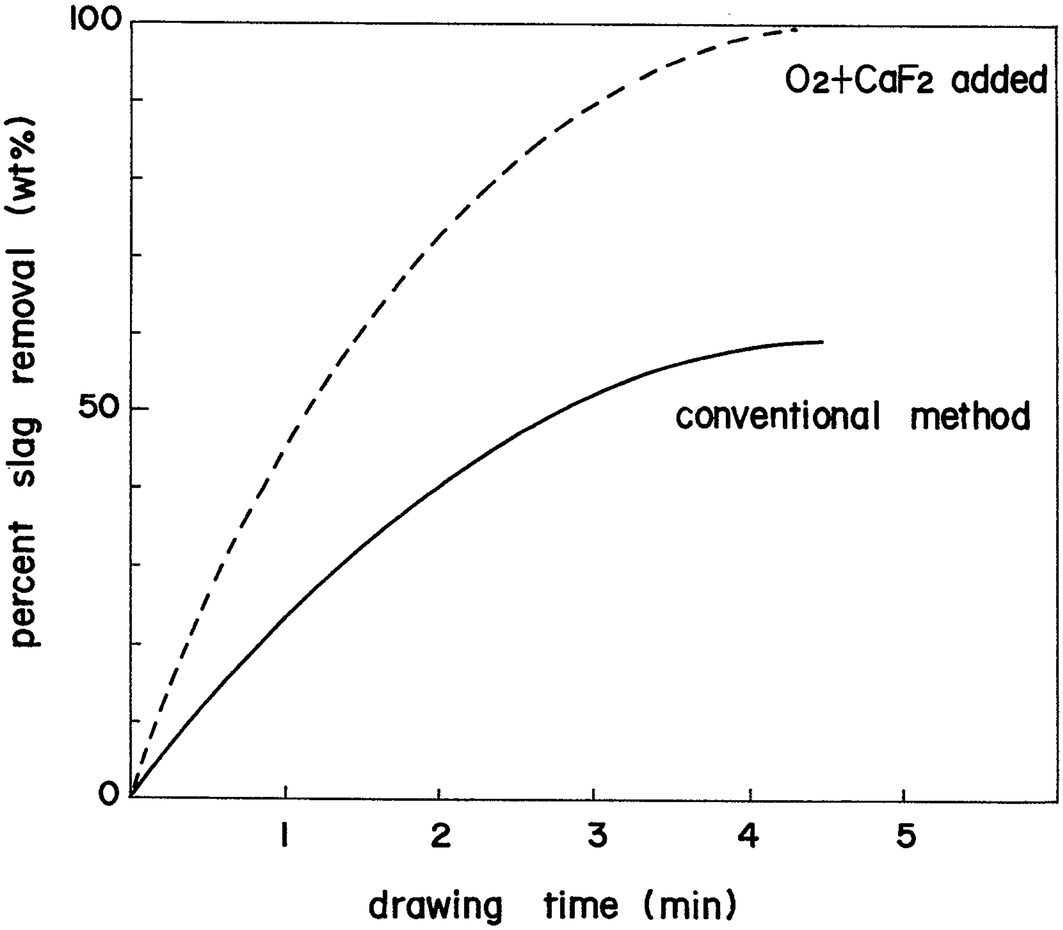

100
50
0
percent slag removal (wt%)
0
5
10
15
drawing time (min)
CaF2 + sintered ore added
CaF2 added
sintered ore added
conventional method

FIG.3


100
50
0
percent slag removal (wt%)
1
2
3
4
5
drawing time (min)
O_2+CaF_2 added
conventional method

4/4

FIG.4

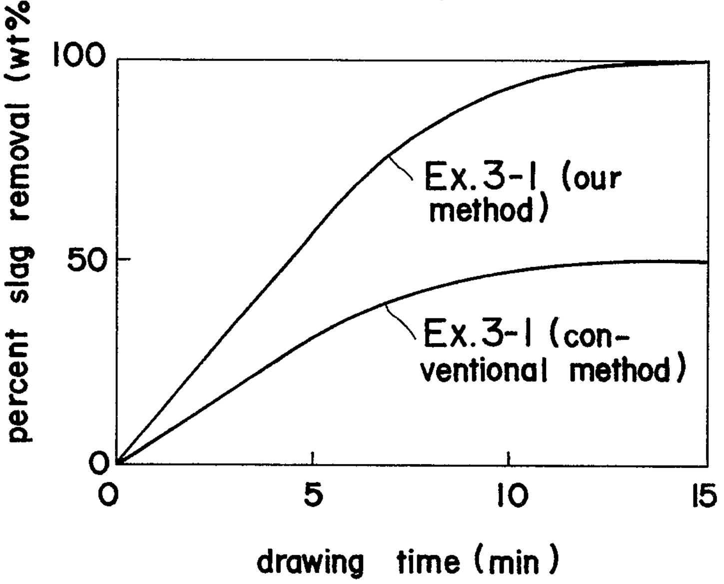
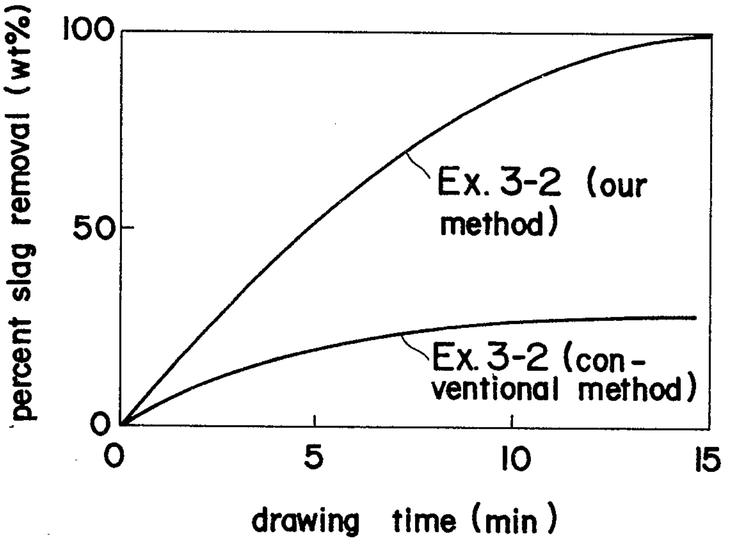

percent slag removal (wt%)
100
50
0
0
5
10
15
drawing time (min)
Ex.3-1 (our method)
Ex.3-1 (conventional method)

FIG.5


percent slag removal (wt%)
100
50
0
0
5
10
15
drawing time (min)
Ex. 3-2 (our method)
Ex. 3-2 (conventional method)

0060706

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 82 30 1304

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ^{3})
Y	BE - A - 699 180 (C.N.R.M.) * claims 1-13; page 3, lines 10-24; page 1 *	1-5	F 27 D 3/15

Y	FR - A - 2 327 320 (MERCIER CORPORATION) * claims 1-19 *	6,7, 9-12	

A	FR - A - 2 258 459 (KUBOTA)		
A	FR - A - 2 051 700 (REPUBLIC STEEL CORPORATION)		
A	FR - A - 2 259 908 (CARAD)		TECHNICAL FIELDS SEARCHED (Int. Cl. ^{3})
	-------		F 27 D C 21 B C 21 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	10.06.1982	ELSEN

CATEGORY OF CITED DOCUMENTS

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