SLAG-MAKING METHODS AND
MATERIALS

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Filed: Dec. 3, 1970

Appl. No.: 94,898

U.S. Cl. ...................... 75/60, 75/30, 75/54,
75/93, 75/94

Int. Cl. ...................... C21c 5/36, C22b 9/10

Field of Search ............ 75/54, 93, 94, 55,
75/30, 60

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ABSTRACT
A lime product is intimately combined with a halogen
compound and preferably one or more other fluxes to
form a reactive flux addition which is used in steel
making. The flux addition is obtained by burning a
CaCO₃ bearing material in the presence of auxiliary
fluxes or by briquetting a mixture of lime and auxiliary
fluxes, including a halogen compound.

2 Claims, 4 Drawing Figures
Fig. 1

- Base
- 2% KCl
- 2% CaCl₂
- 2% NaCl
- 2% CaF₂

Increasing Solubility vs. Minutes
Fig. 2

% FREE CaO

INCREASING SOLUBILITY

MINUTES

0 10 20 30 40

0 5 10 15 20 25 30 35 40

BASE

0.5% CaCl₂

1.0% CaCl₂

6.0% CaCl₂

3.0% CaCl₂

10% CaCl₂
Fig. 3

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Fig. 4
SLAG-MAKING METHODS AND MATERIALS

BACKGROUND OF THE INVENTION

The present invention relates generally to the art of steel making, and more specifically to new methods and materials which improve both the rate and the efficiency of slag development in steel making processes such as the basic oxygen process.

In recent years the basic oxygen process has rapidly replaced open hearth steel making because of the speed with which iron can be refined. The heat times for the basic oxygen process are well under one hour as compared to 4 to 6 hours for similar sized heats in the open hearth. The speed of the process demands rapid slag formation, and this necessitates the use of a lime product which will go into solution in the slag quickly. Economical considerations require that a rapid solution rate of the lime be obtained without the necessity of adding large amounts of auxiliary fluxes such as fluor spar.

The dissolution of lime in the basic oxygen process is adversely affected by the formation of dicalcium silicate which results from an undesirable reaction between the lime and silicates produced at an early stage in the process. Dicalcium silicate is a refractory material having a high melting point about 3800°F. Since the lime is customarily added to the furnace in pebble form, the dicalcium silicate may coat the pebbles so as to inhibit their dissolution and consequently slow the rate of slag development.

It has been a conventional practice to charge an auxiliary flux into the furnace for the purpose of facilitating dissolution of the lime. Fluorspar is a material commonly used. When added in the conventional manner, the amount and the cost of auxiliary fluxes required to accelerate the slag formation rate to the degree necessary in the basic oxygen process are excessive.

It has also been conventional to oxidize the iron to form iron oxide which acts as a fluxing ingredient to aid lime dissolution. This expedient of forming iron oxide decreases the yield and can result in slags which are extremely erosive to furnace linings made of magnesite or dolomite.

SUMMARY OF THE INVENTION

The present invention provides methods and materials which are effective to decrease slag making time and which make it possible to reduce the amount of fluxes required to make a heat of steel. The invention is particularly concerned with the composition, manufacture and use of a new flux material which has an improved rate of slag solubility and is thus suited for use in modern methods of producing steel by oxygen blowing, as for example the basic oxygen process. As is well known, in the production of steel by oxygen blowing, scrap and molten pig iron are serially charged to the furnace and then the blowing period is initiated and carried out to turn-down. Lime and preferably one or more auxiliary fluxes are also added to the furnace in sufficient quantity for the formation of slag during blowing.

The invention is based on the discovery that the slag solubility of burned lime which is intimately combined with other fluxing ingredients, including a halogen compound, is faster than that obtained by adding the lime and other fluxes separately to the slag. In addition to achieving a rapid slag solution rate of lime, it has been found that the amount of auxiliary fluxes can be reduced in comparison to the amount required by normal practice.

According to one practice of the invention, lime is intimately mixed with a halogen compound and one or more fluxes selected from the group consisting of iron oxide, alumina, phosphorus pentoxide and manganese oxide, and the mixture is compressed into briquettes suitable for addition to a steel making furnace. An advantage of this practice is that the briquetted mixture may constitute the entire flux requirements for making a heat of steel by the basic oxygen process. When added to the furnace as one ingredient of the briquettes, the amount of the halogen compound, for example, fluor spar, can be reduced by as much as 30 per cent in comparison to normal practice.

According to another practice of the invention, limestone and/or dolomite is calcined in the presence of a halogen compound, as by sintering or in a rotary kiln. Other fluxes, namely, iron oxide, manganese oxide, phosphorus pentoxide and or alumina, also may be included in the mixture prior to calcination.

In addition to exhibiting an improved slag solution rate, the halogen containing lime product comprehended by the invention produces more basic slag with attendant metallurgical advantages and the further advantage of prolonging the life of furnace linings. Since the refractory linings of basic oxygen furnaces are made of dolomite or magnesite, the acid slags which are developed will attack the linings if the lime does not go into solution fast enough. By increasing the rate of lime solution into the slag, the rate of wear on the refractory linings is reduced.

Other advantages obtained by the invention include a simplification of the manner of introducing the flux into the furnace, and an increased resistance to hydration, whereby the lime product has a longer shelf-life than ordinary lime.

Still other advantages and a fuller understanding of the invention will be had by reference to the accompanying drawings and the following detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing slag solubility results of different halogen reacted lime products in comparison to ordinary lime;

FIG. 2 is a graph showing slag solubility results of CaCl₂ reacted lime products;

FIG. 3 is a graph showing slag solubility results of CaF₂ reacted lime products; and

FIG. 4 is a graph showing the slag solubility results of a CaF₂ reacted lime product in comparison to lime and CaF₂ added separately to the slag.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The composition of the new flux material of this invention employs a lime product obtained by burning limestone and/or dolomite to lime (CaO) and dololime (CaO-MgO), respectively. The use of a lime product in the form of burned lime and/or dololime instead of raw limestone or dolomite is preferred in the basic oxygen steel making process because of the speed with which the iron is refined and the consequent need to minimize the additions of any materials which extract heat from the process. Preferred compositions contain the burned lime and/or dololime in an amount of at least 50 per-
3,771,999

According to another preferred procedure of this invention, the new flux material is prepared by mixing a halogen compound and any auxiliary fluxes which are desired with a CaCO₃ bearing material, namely, limestone and/or dolomite, and heating the mixture to burn and reduce the CaCO₃ content to lime. The calcination temperature should be below the boiling point of the halogen additive in order to react and diffuse it in the stone and thereby obtain a halogenated product exhibiting maximum slag solubility. The stone-flux mixture may be calcined in a rotary kiln or other conventional calcining apparatus. Alternatively, the mixture may be sintered in a conventional manner, as on a travelling grate sinter strand, to affect calcination.

Preferred mixtures for use in the above-described calcining practice consist of at least 50 percent limestone and/or dolomite, and more preferably are at least 50 percent limestone. Specifically preferred mixtures consist in parts by weight of at least 50 percent limestone, from 0 to 30 percent dolomite, from 0.5 to 15 percent halogen compound, from 0 to 30 percent iron oxide, and from 0 to 30 percent of a flux selected from the class consisting of MnO, Al₂O₃, and P₂O₅.

For sintering use, the above mixtures are combined with coke or other fuel. In order to obtain good sintering rates and proper diffusion of the halogen additive into the lime product, it has been found desirable to use a stone having a maximum size of \( \frac{6}{8} \) inch and a minimum size of plus 100 mesh. An optimum stone size is 30 percent minus 3 plus 6 mesh, 40 percent minus 6 plus 20 mesh, and 30 percent minus 20 plus 100 mesh.

The following are specific examples of the preferred embodiments and practices of the invention.

**EXAMPLE 1**

A series of tests were conducted to show the improved slag solubility rates of a lime product produced by calcining a mixture of limestone and halogen additive. The tests were conducted using a homogeneous limestone having a particle size of minus \( \frac{4}{2} \) inch and plus \( \frac{4}{2} \) inch. Four sample mixtures were prepared to include a 2 percent by weight addition of the additive, the selected halogen compounds being NaCl, CaCl₂, and CaF₂. A fifth comparison sample consisted solely of the limestone without a halide addition. All samples were burned at a temperature of 2,150°F. for one hour, cooled and then crushed to a size of minus 5 plus 6 mesh.

The crushed samples were reacted with a lime deficient slag and the rates of solution into the slag were determined. This was done by mixing the burned lime samples with lime-deficient slag-forming mixture in a proportion of 3 parts lime grain to 1 part slag mixture. The slag-forming mixture was a synthetic composition simulating an early BOF slag without lime, and had an approximate composition of 56% SiO₂, 38% Al₂O₃, 3.7% TiO₂, 19% Fe₂O₃, 8.5% MgO, and 9% MnO. A series of crucibles containing each of the lime grain-slag mixtures were placed in a gas fired furnace at 2,700°F. Crucibles containing each mixture were withdrawn from the furnace at two minute intervals from 4 to 10 minutes. The crucibles were then weighed and the free lime determined by the sugar method.

FIG. 1 is a plot of free lime against time in the furnace and indicates the rate of lime solubility into the slag. It will be seen that in all cases limestone calcined with a halide addition yields a lime product superior to...
lime calcined in the absence of the addition. It will also be seen from FIG. 1 that the best solubility is obtained with the CaF₂ addition.

EXAMPLE 2
Sample mixtures were prepared consisting of the limestone used in Example 1 and CaC₂ in amounts by weight of 0.5, 1.0, 3.0, 6.0 and 10 percent. The five sample mixtures and a comparison sample consisted solely of limestone were calcined at 1,800°F for one half-hour. Slag solubility test results conducted with these sample mixtures are plotted in FIG. 3 and show an improvement in solubility with all additions of fluorspar.

EXAMPLE 3
Another series of sample mixtures were prepared using the same limestone as in previous examples with additions of various amounts of CaF₂ and the mixtures were calcined at 1,800°F. for one half hour. Slag solubility test results are shown in these sample additions are plotted in FIG. 3 and show an improvement in solubility with all additions of fluorspar.

EXAMPLE 4
A 2% CaF₂ reacted lime was prepared in the same manner as in Example 3. Slag solubility tests were run on samples of reacted lime and on samples prepared by adding 2 percent by weight addition of CaF₂ to a lime grain-slag mixture. The results also include comparison lime grain-slag samples with no CaF₂ addition. The results are plotted in FIG. 4. As shown, the addition of CaF₂ to the slag improved lime solubility after 10 minutes in the furnace. In all instances, the lime solution of the CaF₂ pre-reacted lime was far superior to that obtained by adding lime and CaF₂ separately to the slag.

EXAMPLE 5
Approximately 1,100 tons of raw materials were used to prepare a sinter mix consisting of 78.7% dolomite, 13.9% Fe₂O₃, and 7.4% CaF₂, and 189 tons (17.1% coke breeze were added to the mix. The raw dolomite was crushed and washed to remove all fines of minus 100 mesh. A size and approximate chemistry of the raw materials is given in the following table.

Raw Material Screen Analysis

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<th>%</th>
<th>BOF ppt. Dust</th>
<th>Dolomite</th>
<th>Fluorspar</th>
<th>Coke Breeze</th>
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Chemical Analysis

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The mix was prepared in a pug mill according to conventional procedures, including wetting to "glistening". This mix was then sintered on a conventional traveling grate sinter strand to obtain the desired product in basic oxygen process slag making operations. The chemistry of the sinter product was as follows: 4.14% FeO, 16.82% Fe₂O₃, 3.68% SiO₂, 0.9% Al₂O₃, 34.10% CaO, 24.4% MgO, 10.83% CaF₂, 0.09% P, and 0.33% Mn.

Results of a series of tests using the sinter product to make slag in a basic oxygen furnace confirmed better lime solution in comparison to a product made in the identical manner from a mix which did not include the CaF₂ addition. The per cent of lime solution in the slag was calculated by the following formula:

\[
\text{percent lime solution} = \frac{100}{1.19} \left( \frac{\text{CaO} - 1.19 \text{ P}_2\text{O}_5}{\text{SiO}_2} \right) \times 100
\]

Using this formula, the sinter product with the CaF₂ addition had a lime solution of 79.8 percent in comparison to a 74.9 percent lime solution for the sinter product with no CaF₂ addition.

EXAMPLE 6
Briquettes of the following approximate composition were produced by using a conventional briquetting press:

- 7.75 percent by weight CaO
- 14.5 percent by weight CaO-MgO
- 3.1 percent by weight CaF₂
- 4.9 percent by weight iron oxide (BOF dust)

The briquettes were used in a basic oxygen furnace to supply the total flux requirements for the production of 80 heats of steel or 14,768 tons of ingots.

All heats were of good quality. Tests run on the first 32 heats indicated a yield of 88.67 percent compared to an average yield of 87.53 percent from 32 heats which were made by charging lime and auxiliary fluxes separately in the furnace according to conventional practice.

It was found that when the flux was added in the form of briquettes less flux was required per ton of steel than when the lime and auxiliary fluxes were charged separately. More importantly, the heats made with the briquettes averaged about 168 pounds of flux per ton of steel compared to an average of about 233 pounds of flux per ton of steel in conventional practice.

Other advantages resulting from the use of the briquettes included less slopping, fewer rebows and less slag volume. The heats shaped up faster and were...
smoother to blow. The material was uniform and dependable, and the slag was fluid on all heats.

Many modifications and variations of the invention will be apparent to those skilled in the art in the light of the foregoing detailed disclosure. It will be understood therefore, that the invention can be practiced otherwise than as specifically described.

What is claimed is:

1. A method of producing steel by oxygen blowing comprising:
   a. the serial steps of:
      i. charging scrap into a steel making furnace,
      ii. charging hot metal into the furnace, and
      iii. blowing by directing oxygen on or into the charge, and
   b. charging lime and auxiliary fluxes into the furnace in sufficient quantity for the formation of slag during blowing,
   c. said lime and auxiliary fluxes being added to the furnace in the form of briquettes consisting essentially of the following ingredients in amounts by weight: over 50 percent lime, from 0.5 to 15 percent of at least one halogen compound, and from 1 to 30 percent of at least one material selected from the class consisting of iron oxide, MnO, Al₂O₃, and P₂O₅.

2. A method as claimed in claim 1 wherein said briquettes contain at least 70 percent by weight lime.