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2,706,152

## METHOD OF SULPHUR REMOVING FROM PIG IRON

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This invention relates to the removal of sulphur from pig iron. The presence of sulphur in pig iron is generally deemed undesirable whether the ultimate intended use of the pig is for the manufacture of castings or as feed material for one of the steel-making processes. The presence of sulphur in iron for castings tends to cause shrinkage, cracking and bleeding in the ultimate cast article. In pig iron to be used for refining into steel sulphur is undesirable because it is not readily removed by the usual methods of refining employed in the manufacture of steel. The removal of sulphur in the steps which transform pig iron to steel accordingly requires additional processing time or additional processing steps as well as additional fluxing materials beyond those normally employed in the manufacture of steel. The sulphur problem in pig iron and steel has become a problem of increasing importance over the years as the deposits of higher quality ores, coals and other raw materials have been depleted and the amount of sulphur contamination has increased as it has become necessary to go to lower grade raw materials.

Several methods of removing sulphur from iron have been proposed but without completely satisfactory results. In general the processes heretofore proposed have been objectionable because of the high costs and the poor control of the process. For example, it has been proposed to externally desulphurize pig iron by the addition of sodium carbonate. However, the control is poor and it is virtually impossible to predict how much sulphur will be removed in successive runs. Moreover, the slag resulting from the treatment is very corrosive on ordinary refractory materials and must be skimmed off of the metal before it can go to the mixer. Another method which has been proposed is that of tumbling the molten pig iron with dry lime in a tumbling barrel. This method, like the sodium carbonate method, is hard to control and the results are unpredictable. A third method of desulphurizing pig iron was proposed by Heuer in Patent No. 2,193,593, issued March 12, 1940. According to the Heuer process it was proposed to remove the pig iron from the furnace to a special vessel where it was covered with a special slag, then treated with reducing agents producing an oxygen activity in the slag lower than the equilibrium conditions during the reaction of carbon and oxygen to form carbon monoxide. All of this was done as a batch treatment under a reduced pressure atmosphere in the special ladle from which air was evacuated. The Heuer process has not been generally adopted probably because it is a batch process, it requires special apparatus and a special slag and it requires holding the metal under reduced pressure for extended periods of time.

It has generally been believed that sulphur could not successfully be removed from pig iron without following one of the processes above described or some other equally elaborate process. It has also been generally believed that it was necessary to hold the metal being desulphurized in contact with the treating material over extended periods of time while the system attained or approached equilibrium. The various desulphurizing processes which have been proposed have accordingly been batch processes.

We have found that all of these complex process steps and treatments can be completely eliminated and that sulphur can be successfully and consistently removed from pig iron by our invention at low cost and under

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conditions which may be readily achieved and maintained at the cast house.

Our invention will best be understood by referring to a specific example of the manufacture of pig iron. An ordinary blast furnace is charged and operated in the usual manner for the manufacture of pig iron. The pig iron is collected in the hearth of the furnace and tapped at regular intervals as it accumulates. The tapped iron is carried through a refractory trough and is usually accompanied by a certain amount of molten blast furnace slag despite the usual practice of tapping the slag through a separate cinder notch in the blast furnace. It is characteristic of our process that the blast furnace slag thus withdrawn is utilized in the desulphurization of the metal promptly after the metal and slag issue from the tap hole of the blast furnace. As the mixed slag and molten iron issue from the tap hole and flow through the refractory trough we add metallic aluminum to the mixture. The slag being lighter than the molten metal rises to the top of the flowing stream in the refractory trough from which it is separated by a skimmer and carried to a separate vessel for disposal. We have found that the conditions of ebullition which take place in the refractory troughs between the tap hole of the blast furnace and the skimmer promote a highly satisfactory desulphurizing action upon the addition of aluminum and that a substantial portion of the sulphur transfers into the slag and is carried with the slag, away from the metal at the skimmer. If there is not enough slag admixed with the pig iron as it leaves the tap hole there will be some loss in overall efficiency of sulphur removal, however, this may be compensated for by introducing a proportion of molten slag into the metal from the cinder notch depending upon the degree of control which is desired.

We have found that by following this process we can remove substantial amounts of sulphur from the pig iron and produce a material, which in sulphur content, is equal to that produced from the highest grade raw materials. The addition of metallic aluminum to molten pig iron in the presence of the slag accompanying the pig iron from the furnace causes a marked migration of the sulphur from the metal into the slag and results in a metal of unexpectedly low sulphur concentration.

In the preferred commercial practice of our invention we add metallic aluminum, preferably in the form of wire or shot, into the molten pig iron in the refractory trough between the tap hole and the skimmer, at which point it is covered by a layer of blast furnace slag into which the sulphur migrates under the influence of the aluminum. Thus treated, the molten metal is almost immediately separated from the slag as both the metal and slag flow from the skimmer into separate ladles. It is at once apparent that the desulphurizing reaction must be a reaction of great rapidity in order to be effective in this practice. This in itself is contrary to all of the beliefs heretofore held by those in the art. As we have pointed out earlier, it has been generally believed, e. g. Heuer, that in order to successfully desulphurize pig iron it was necessary to hold the pig iron in contact with a special desulphurizing slag for extended periods of time.

While we prefer to add the aluminum to the pig iron before the skimmer immediately after it leaves the furnace, it may be added at other places so long as the molten pig iron is in contact with molten blast furnace slag at or shortly after the time the addition of aluminum is made, and is thereafter separated from the slag. For example, the aluminum might be added to the molten metal in the hearth just prior to casting.

It will be accordingly understood that while we have described a preferred practice, our invention may be otherwise practiced within the terms of the following claims.

We claim:

1. The method of removing sulphur from molten pig iron at the blast furnace comprising the steps of adding metallic aluminum to a moving stream of molten pig iron in the presence of molten blast furnace slag, and thereafter separating the slag from the molten iron.

2. The method of continuously removing sulphur from

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molten pig iron at the blast furnace comprising the steps of substantially continuously adding metallic aluminum to a stream of mixed pig iron and blast furnace slag as it leaves the blast furnace, and continuously separating the slag from the metal after the addition of aluminum.

3. The method of continuously removing sulphur from molten pig iron at the blast furnace comprising the steps of tapping molten metal and accompanying slag from the blast furnace into a skimmer, substantially continuously adding metallic aluminum to the molten metal and slag before the skimmer, and continuously separating the slag from the metal after the addition of aluminum.

4. The method of removing sulphur from molten pig iron at the blast furnace comprising the steps of tapping molten metal from the furnace in a moving stream, passing the stream of molten metal beneath a pool of molten slag, substantially continuously adding metallic aluminum to the portion of the molten stream of metal covered by the molten slag, and substantially continuously withdrawing molten metal from beneath the molten slag.

5. The method of removing sulphur from molten pig iron at the blast furnace comprising the steps of tapping molten metal and molten slag from the blast furnace in a moving stream, substantially continuously separating the slag from the moving stream of metal all the while maintaining a layer of slag over the metal at the point of separation, and substantially continuously adding metallic aluminum to the portion of the metal stream covered by said layer of slag.

6. The method of removing sulphur from molten pig iron at the blast furnace comprising the steps of simultaneously tapping molten metal and molten slag from the furnace, bringing the metal and slag into contact with one another to form a moving stream of molten metal and molten slag, adding metallic aluminum to the

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molten metal, and separating the metal and slag into two streams after the aluminum addition.

7. The method of removing sulphur from molten pig iron at the blast furnace comprising the steps of tapping molten metal from the furnace in a moving stream, passing the stream of molten metal through beneath a pool of molten blast furnace slag, substantially continuously adding metallic aluminum to the portion of the molten stream covered by the molten slag, and substantially continuously replacing the molten slag in the pool with slag from the blast furnace.

8. The method of removing sulphur from molten pig iron at the blast furnace comprising the steps of withdrawing molten pig iron with admixed molten blast furnace slag as a flowing stream from the furnace, adding metallic aluminum to the stream, forwarding the stream with added aluminum until substantial flotation of slag has been brought about, and separating the molten slag from the pig iron.

9. The method of removing sulphur from molten pig iron at the blast furnace by adding aluminum to the molten pig iron in the presence of molten blast furnace slag, and thereafter separating the slag from the molten iron.

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