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METHOD OF DESULFURIZING IRON AND STEEL WITH METAL HYDRIDES

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1

This invention relates to desulphurizing molten ferrous metal. It relates particularly to the desulphurizing of molten ferrous metal when it is desired that the sulphur content shall be relatively low.

The primary object of this invention is the removal of sulphur, sulphur compounds and contaminating oxides from molten cast iron and steel by either furnace or ladle treatment or by treatment at the spout as the metal flows from the furnace.

Another object of this invention is to produce strong reducing conditions at the slag and metal interface simultaneously with reaction and removal of sulphur and sulphur compounds by action of an alkali metal.

Another object of the invention is to produce strong reducing conditions at the slag and metal interface simultaneously with reaction and removal of sulphur and sulphur compounds and contaminating oxides by introducing a hydride of an alkali metal, which hydride is adapted to dissociate into nascent hydrogen and virgin alkali metal.

Desulphurization of both iron and steel by controlling or modifying the basicity of the slag by the addition of such materials as lime, fluorspar, sodium compounds and barium carbonate is well understood, although the chemical reactions may be somewhat involved. In a general way, the disadvantages of these materials are their limited desulphurizing ability during the relatively short time-temperature interval available in actual foundry practice. That is, in actual foundry practice the temperature of the metal will remain within a suitable range for desulphurizing for a very limited period of time, and therefore most of the common known methods of removing sulphur will not reduce the sulphur content of the metal to a sufficiently low value because the desulphurizing action is relatively slow and the temperature of the metal drops below the minimum working temperature. Furthermore, most generally known practice requires a large volume of slag to produce a reasonably low sulphur value. If a large volume of slag is not employed the slag will begin to give its sulphur content back to the molten metal and prevent reduction of the sulphur content to a satisfactory value. Where the sulphur is removed as a sulphide, conditions necessitate a stable sulphide and a high sulphur-carrying basic slag; otherwise the sulphur would readily be transferred back to the molten iron or steel.

It is commonly assumed that desulphurization

2

results from the formation of sulphides and sulphate, although it is more than probable that much of the sulphur may be lost in gaseous form according to the degree of action with the agent used, and the temperature and reducing conditions of melting.

I have found that the best conditions for desulphurizing are hot melting under strong reducing conditions at the slag and metal interface, with an active gas condition in the molten iron or steel during the process of desulphurization. Further, strong reducing conditions will reduce contaminating oxides, and thereby remove the influence of the oxide and facilitate the removal of sulphur. Oxide reduction is therefore a part of the sulphur removal process. To do this within the limited time available presents a number of practical difficulties, and one of the greatest, particularly in the spout and ladle, is temperature loss of the molten iron or steel itself. In the removal of sulphur, therefore, speed of action is of vital consideration, and this is true also in the furnace, for the removal of the sulphur from metal to slag is a gradual process, and too active or too much slag by volume can become a serious handicap in the melting operation. On the other hand, if a large amount of slag is not used the process reverses, causing the metal to take sulphur from the slag, and this reversal can cause serious limitations.

With the foregoing factors to be considered, I have found that removal of contaminating oxides and thereafter rapid desulphurization can be obtained, and the sulphur content of molten iron or steel reduced to a satisfactory low value by introducing metallic hydrides. Metallic hydrides will break down into metal and nascent hydrogen, and I have found hydrides of alkali metals to be readily available and very satisfactory. For example, lithium hydride, sodium hydride, potassium hydride, calcium hydride, magnesium hydride and barium hydride are alkali hydrides which are highly active reaction agents for desulphurization, and other examples of metallic hydrides would include zirconium hydrides and titanium hydrides.

These metallic hydrides are not merely metals holding hydrogen in the occluding state, but are true compounds possessing different physical and chemical properties than the elements from which they are produced. One of their most useful properties is that they dissociate on heating into pure metal and nascent hydrogen, thus providing the maximum desulphurizing power of the metal in the presence of one of the strongest reducing

agents, namely nascent hydrogen. It is a well-known fact that nascent hydrogen, such as that evolved from a hydride, is more active chemically than hydrogen of the same purity by other means.

The use of an alkali metal hydride for removing sulphur does not limit the treatment of the molten iron or steel for other purposes, such as carbide stabilization or graphitization. Further, the hydride may be introduced into the molten metal in conjunction with a material such as sodium carbonate, lithium carbonate, lime, magnesia, fluorspar, or any of the well-known materials commonly used to increase the basicity and fluidity of the slag.

In actual practice, although I have demonstrated that it is possible to desulphurize in a furnace or cupola, I prefer to draw the metal into a ladle to form a pool of metal, and cover the pool with a sulphur-carrying slag, and then introduce the hydride directly into the molten metal either in the pool or as the metal runs down the spout from the furnace. However, I have added the hydride to the surface of a pool of molten metal at the metal and slag interface and find that satisfactory results may be obtained in that manner. It is to be understood that the hydride may be added to the pool or mass of the molten metal whether in the furnace or the ladle.

As previously stated, however, the preferable method is to introduce the hydride into the pool of molten metal and allow the hydrogen to bubble up through the molten metal and produce an active gas condition which helps to rapidly circulate the molten pool and helps remove the sulphur content at a faster rate. The sulfur may be removed in the form of sulphides transferred from the molten pool into the slag covering the molten pool, or it may be evolved as a gaseous material, or both, dependent upon the type of hydride employed and the temperature of the molten pool. I have evolved chemical equations setting forth my theory of sulphur removal, but regardless of whether or not the chemical reactions do take place as I believe, it is not my intention to limit this invention by any theory or hypothesis, but only to set forth the fact that a hydride of an alkali metal will reduce the sulphur content of molten iron or steel if it is introduced onto the surface, or into a pool of the molten metal in a ladle, or into the spout as the metal is tapped from a furnace into a ladle.

In actual tests which I have made to demonstrate the effectiveness of hydrides for removing sulphur from molten metals, I have been able to reduce a cupola-melted cast iron having a high sulphur content to a sulphur content below .009 percent, and this has been accomplished by the addition of hydrides in quantites as low as one-half of one per cent by weight of the metal treated. Ordinary desulphurization treatment with sodium bicarbonate and high basic slags did not reduce the same iron to a value much lower than .045 per cent.

The obvious advantages of removing sulphur by this improved method are that no expensive apparatus is required to stir the metal, and no vacuum machine is required. This invention provides a method of sulphur removal which is the essence of simplicity and is foolproof in its operation. The actual amount of the hydride necessary to produce the desired sulphur reduction is dependent upon the amount of sulphur originally contained by the molten iron, and the degree of purity desired in the finished product.

A further distinct advantage of this invention is that less expensive iron may be produced because the original charge into the furnace may be made without particular attention to the sulphur-bearing qualities of the charged materials.

Although the invention has been described in its preferred form with a certain degree of particularity, it is understood that the present disclosure of the preferred form has been made only by way of example and that numerous changes in the details and the combination and arrangement of steps may be resorted to without departing from the spirit and the scope of the invention as hereinafter claimed.

What is claimed is:

1. The treatment of molten ferrous metal to reduce the sulphur content thereof, comprising the steps of providing a mass of molten ferrous material, covering said mass with basic molten slag, introducing a reagent to said mass, said reagent having the formula R_xH_x, where R is an alkali metal and x denotes the valence relationship, and thereafter separating the molten ferrous metal from any slag thereon.

2. The treatment of molten ferrous metal for the purpose of removing sulphur gases, sulphur compounds and contaminating oxides, comprising the steps of providing a molten ferrous emtal, covering said metal with a basic slag, adding to the molten ferrous metal at least one hydride of an alkali metal, said hydride addition being introduced in conjunction with a material, to increase the basicity and sulphur-carrying capacity of the slag.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,515,794	Scott et al.	Nov. 18, 1924
1,869,496	Osborg	Aug. 2, 1932
1,869,979	Osborg	Aug. 2, 1932
1,869,980	Osborg	Aug. 2, 1932
1,931,144	Gilbert	Oct. 17, 1933
2,110,066	Heuer	Mar. 1, 1938

OTHER REFERENCES

Lithium, Theoretical Studies and Practical Applications, pages 18 and 19. Edited by H. Osborg. Published in 1935 by the Electro-Chemical Society, New York, N. Y.