United States Patent Office 3,134,668 Patented May 26, 1964

3,134,668

LIQUID IRON-BASED METAL AND METHOD OF PRODUCING SAME

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No Drawing. Filed Mar. 6, 1961, Ser. No. 93,364
3 Claims. (Cl. 75—60)

This invention relates to the stabilization against an increase in N_2 content of hot liquid iron-based metal in the presence of nitrogen and is particularly concerned with a liquid metal of this type containing a stabilizing element of the group VI–A metals of the periodic system with an atomic number between 32 and 85 in an amount sufficient to retard the nitrogen absorption rate of the liquid metal.

The present invention is particularly useful in connection with a solution of iron-based metal in processing in a converter process employed in steelmaking operations. In the converter process, air is generally blown through a solution of iron-based hot metal to reduce the amount of impurities present, for instance, carbon, silicon and manganese. Nitrogen, however, generally present in air, is consequently brought into contact with the hot metal. The nitrogen content of the metal out of the blast furnace is generally low due to the relatively high amounts e.g. 4 percent of carbon present, however, as the carbon content is reduced during the air blowing operation, the nitrogen content tends to increase as a result of existing temperatures and equilibrium favoring such an increase during the operation. Accordingly, steel produced by a converter process possesses different properties from those of steels produced by other methods, e.g. the open hearth process or the oxygen converter process. Tests of the physical properties of converter steel with steel produced by the other processes show a difference in properties that varies with nitrogen content. A strong absorption of nitrogen takes place during the converter process when air is blown through the liquid hot metal. For instance, typical nitrogen analyses in steel manufactured by the open hearth process range from 0.003 to 0.007 weight percent nitrogen, but converter steels, steels manufactured by the converter process, show nitrogen contents ranging from 0.010 to 0.030 weight percent.

The high nitrogen content gives the converter steel greater strength, higher yield limit, greater aging liability, and greater hardness and brittleness as compared with open hearth steels, for instance. In certain applications, high nitrogen steel is of some advantage. However, in general the high nitrogen content is undesirable since it detrimentally affects the properties of the resultant steel, primarily by reducing the ductility of the steel, but also since it can alloy with other elements in the steel. In steels prepared for cold drawing or pressing, a relatively high nitrogen content is of considerable disadvantage.

The relatively high nitrogen content in converter steels has presented a problem which is presently unsolved. In one process, a duplex process, air blown converter steel is conveyed to another steel production furnace, generally an open hearth or electric steel furnace, and subjected to further refining which lowers the nitrogen content. Clearly, it would be of great economic advantage if such a duplex process could be avoided, and a steel with low nitrogen content could be produced directly in a converter using air.

Another suggestion has been to enrich the air with oxygen to produce an oxidizing gas with a low nitrogen content. However, this procedure is not particularly successful in reducing the nitrogen content of converter steel. The nitrogen content of a steel which is in equilibrium with a gas phase is directly proportional to the square root of the partial pressure of nitrogen in the gas mixture. In order to prevent the absorption of nitrogen into the steel by lowering the nitrogen content of the gas phase, it is necessary to go to an almost nitrogen free gas, such as is practiced in oxygen steelmaking where pure oxygen is blown on the liquid iron bath.

In accordance with the present invention, a converter steel with a lower nitrogen content than normal exhibiting properties comparable with a high quality open hearth steel can be produced by reducing the nitrogen absorbing properties of a solution of the liquid iron-based metal charge. This is accomplished by adding a group VI–A metal with an atomic weight between 32 and 85 to the charge which reduces the reaction rate between nitrogen and the liquid metal charge. A periodic table such as is shown on page 449, Handbook of Chemistry and Physics, fortieth edition, published by Chemical Rubber Publishing Co., Cleveland, Ohio, may be used for this purpose. Any of the elements, selenium, tellurium, or polonium or any combination thereof can be added to the charge of liquid iron-based metal prior to or early, i.e. before significant amounts of nitrogen are absorbed, in the course of the blow in the converter process in order that nitrogen pickup is prevented or considerably retarded. It is necessary according to the invention that stabilizing metal, i.e. selenium, tellurium, or polonium, be added to the metal charge prior to the point that appreciable carbon reduction has taken place or, in the case of charges containing high silicon contents, prior to the time that a considerable temperature increase is observed during blowing. The stabilizing metals can be added to the metal charge individually or in mixtures, in pure form as elemental materials, in compound form e.g. selenium oxide, selenium telluride and tellurium oxide, or as part of an alloying addition, e.g. manganese alloy containing 5 percent selenium, a silicon-selenium alloy, a ferro-alloy containing one or more of the stabilizing elements. The actual procedure used in making the addition can take place in the converter unit itself or outside of it in the transfer ladles used to supply material to the converting unit.

The particular form in which the materials are added to the converter charge is also of relatively little consequence. Loss of stabilizing metal in the charge by vaporization of the stabilizing elements, which are volatile elements having relatively low boiling points, can be minimized by employing the stabilizing element or metal in compound or alloy form. The high temperatures involved in converting processes are sufficient to cause decomposition of compounds or solution of alloying stabilizing metals in the solution of hot iron-based charge for processing to steel, and consequently would not decrease the effectiveness of the stabilizing metal. It is expected that the addition of these materials in any form would permit them to dissolve into the steel bath and exhibit their influence on the nitrogen absorption properties of the liquid metal by markedly decreasing the rate of nitrogen absorption during processing.

The stabilizing metals of the present invention are incorporated into a solution of iron-based hot metal in stabilizing amounts to retard the nitrogen absorption rate of the iron-based metal for instance, to maintain the nitrogen content in the resulting steel product generally to less than about 0.009, preferably to less than about 0.006, and these amounts will generally range from about 0.01 to 10, preferably 0.05 to 1, weight percent of selenium, tellurium, and/or polonium.

The temperatures at which this process will prove feasible are generally overlapping to the range of temperatures used in standard converter practice. The rate of absorption of nitrogen into the hot liquid iron-based metal is temperature dependent and increases with in-

creasing temperature. Accordingly, converters operating at lower temperature ranges during the practice of this invention will tend to yield products e.g. steel, with a lower nitrogen content. The temperature ranges over which the process is applicable include temperatures generally from the melting point of carbon-saturated iron and iron alloys, about 2000° F., up to and beyond 3200° F. The standard operating temperatures employed in converter practices generally range from about 2400° F. to 3000° F. and these temperatures would be quite suitable for practicing the present invention.

The present invention is applicable in both acid and basic (referring to the lining material and slag used) converter steelmaking processes and may be used in connection with any pneumatic process involving iron-base materials in the liquid state which are contacted with gas phases containing nitrogen for instance, cupola type melting operations and gas-fired furnaces for melting or refining steel which would include open hearth and electric furnace processes.

The following examples will serve to illustrate the present invention, but they are not to be considered limiting.

Example I

A typical converter heat in which the stabilizing elements of the present invention are used to delay reaction with nitrogen is carried out in the following manner. Scrap materials are first charged to a Bessemer converter unit, hot metal is added to the scrap materials in the unit to form a charge, and solid selenium in an amount of approximately $\frac{1}{10}$ of 1 percent is added to the charge. The Bessemer converter is returned to a blowing position and the process is started by blowing air through the metal charge out which contains about 0.003 percent nitrogen at this point, for about 15 to 20 minutes to reduce impurities including about 4 percent carbon, 1.5 percent silicon and 0.75 percent manganese.

The elements manganese, silicon, and carbon are oxidized and reduced in the melt to a suitable end point e.g. less than about 0.5 percent, the metal is poured into a transfer ladle and treated in the same manner as standard converter heats to produce a steel containing less than about 0.006 percent nitrogen.

Example II

The procedure of Example I is followed except 9 percent tellurium is used instead of the selenium.

Example III

The procedure of Example I is followed except 5 percent polonium is used instead of the selenium.

An experimental result which is of particular significance is the following: The reaction rate coefficient which is a measure of the rate at which nitrogen is absorbed by liquid iron is approximately 0.01 cubic centimeter per square centimeter-second. The rate coefficient for liquid iron to which 0.5 weight percent selenium had been added measured under precisely the same conditions was 0.0015 cubic centimeter per square centimeter-second. This result shows that a selenium content in liquid iron of less than 0.5 weight percent (some selenium was lost by volatilization) absorbs nitrogen at a rate which is lower than the rate in iron not containing selenium by a factor of 67.

In laboratory simulated heats of converter steel which were carried out by blowing a jet of air on the surface of an iron-carbon alloy containing 4.3 weight percent carbon until the carbon had been lowered to the range typical of steels also showed the marked influence of the alloying elements, selenium and tellurium. In one heat, which was typical of the series investigated, one part per thousand by weight (0.1%) of selenium was added to a 40 pound iron-carbon alloy. The carbon content was blown from 4.3 down to a range typical of steel production and the temperature of the melt was observed to go from below 2500° F. to over 2800° F. The time of blowing was approximately 15 minutes. This laboratory simulation very closely approximated the Bessemer converter practice as it is known today. The vacuum-fusion analysis for nitrogen on the heat described above was 0.0024 weight percent, far below the nitrogen content which is typical of good open hearth practice, and about one-tenth of the nitrogen content of typical commercial converter steel.

We claim:

1. In a method for producing steel in a converter by contacting a metal melt with air, the step comprising incorporating into the metal melt an element selected from the group consisting of selenium, tellurium and polonium in an amount sufficient to reduce the rate of nitrogen absorption during the air blowing of the melt in the converter.

2. In a method of producing steel by blowing air through a metal melt, the step comprising incorporating into the metal melt an element selected from the group consisting of selenium, tellurium and polonium in an amount sufficient to reduce the rate of nitrogen absorption during the air blowing of the melt.

3. In a method of producing steel by blowing a gas containing oxygen and nitrogen through a metal melt, the step comprising incorporating into the metal melt an element selected from the group consisting of selenium, tellurium and polonium in an amount sufficient to reduce the rate of nitrogen absorption during the gas blowing of the melt.

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