PROCESS FOR THE PRODUCTION OF LOW SILICON, MEDIUM-TO-LOW CARBON FERROMANGANESE

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Fig. 1.

Fig. 2.

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The present invention relates to the production of ferromanganese. More particularly, the present invention relates to an improved ladle process suitable for the production of medium-to-low carbon ferromanganese.

At the present time, ladle processes for producing ferromanganese are known and practiced commercially as exemplified in the disclosures of U.S. Patent 3,074,793 to Kohlman and U.S. Patent 3,138,455 to Carosella and Chynoweth. Both of these patents describe the reaction of a melt of oxidic manganese-containing material with a silicon reducing agent in a ladle to provide ferromanganese alloy and a manganese-containing slag. In general, the processes of the aforementioned patents are highly successful in producing high quality ferromanganese alloys. However, in order to increase the reduction of the manganese values from the melt and thus obtain high manganese recoveries, it is frequently necessary to repeatedly pour the ladle contents from one ladle to another to thereby increase contact between the metal and oxide phases, and hence promote the reduction reaction. Up to the present time, repouring has been considered the optimum manner of promoting the interaction of large quantities of molten materials in ferromanganese production and considerable equipment has been designed and constructed for this purpose. However, the extent to which repouring can be utilized is limited by the relatively long handling times involved and the concurrent cooling effect which can result in the freezing of significant amounts of material in the ladles. Consequently, repouring must often be discontinued before the reaction between the oxidic and metallic phases has reached equilibrium and before the optimum amount of manganese has been reduced from the oxidic phase.

It is therefore an object of the present invention to provide an improved ladle process for the production of ferromanganese in which re-pouring of molten material from one ladle to another is made unnecessary.

It is a further object of the present invention to provide an improved ladle process for the production of low silicon, medium-to-low carbon ferromanganese from oxidic manganese material wherein greater quantities of manganese are reduced from the oxidic melt or slag than has been previously attainable on an industrial scale.

Other objects will be apparent from the following description and claims taken in conjunction with the drawings in which:

FIGURE 1 shows a diagram of a ladle process in accordance with the present invention.

FIGURE 2 shows a ladle particularly suited for the practice of the present invention and

FIGURE 3 shows a graph comparatively illustrating advantages of the present invention.

A process in accordance with the present invention comprises the steps of: (1) preparing a melt of oxidic manganese-containing material in which the amount of oxygen combined with manganese is no greater than about that represented by the formula MnO; (2) transferring the melt to a ladle and also introducing into the ladle a molten silicon reducing agent, such as silicon metal or a silicon-containing manganese-iron alloy, to provide a molten metal phase in the lower portion of the ladle and molten oxidic manganese-containing material floating on the metal phase (3) introducing gas under pressure into the molten metal phase to cause turbulence in the metal phase to the extent that molten metal is continually forced upward through the oxidic material and falls back downward through the oxidic phase and (4) continuing the introducing of gas until the metal phase has a desired ferromanganese composition.

In the practice of the present invention a suitable manganese containing melt, i.e., one containing 25 percent or more manganese, is prepared by any convenient technique. For example, certain commercially available manganese-bearing materials, such as ores which have been calcined to nodules can often be fused with lime, in the absence of carbon, to provide a suitable oxygen-depleted melt. With other materials such as raw manganese ores, carbon can be admixed with ore and lime and the mixture smelted, for example in a submerged arc electric furnace, to provide the required oxygen level in the melt. The carbon admixed with the ore can be in any suitable form, including coal and the lower grades of coke, and is preferably present in an amount to reduce substantially all of the manganese values to the manganese, i.e., divalent state, but not to the elemental state. Also, by-product manganese-containing slags can be used. Regardless of the manner in which it is obtained, the low oxygen content is required in the manganese-containing melt so that the subsequent ladle reaction is controllable and not excessively violent.

When a suitable low oxygen, manganese-containing melt has been prepared, preferably containing between about 25 to 50 percent manganese, which can be accomplished, for example using a smelting furnace such as indicated schematically as 10 in the process diagram of FIGURE 1, the molten material, at a temperature of about 1350 to 1800° C. is transferred into a ladle as indicated at 12. A molten silicon reducing agent, in the temperature range of about 1250 to 1450° C., preferably one containing 4-32% silicon, 60 to 80% Mn, 0.03 to 1.60% C balance Fe, is also introduced into the ladle with the result that a metal phase is provided at the lower portion of the ladle as indicated at 16 with the manganese containing oxidic melt floating on top as indicated at 18. The amount of silicon reducing agent in the ladle is that which is sufficient to provide reduction of manganese values in the oxidic melt to provide the desired ferromanganese alloy. Lime can also be added to the ladle and is usually present in an amount that will provide a base to acid ratio of from 0.1 to 1.6 in the final slag.

Generally, the starting ratio of oxidic material to metal ranges from 1:1 to 4:1 by volume. With suitable amounts of manganese-containing oxidic material, silicon reducing agent and lime in the ladle, gas, under pressure is introduced below the surface of the metal phase, and the velocity adjusted until turbulence is developed in the metal phase whereby metal is forced upward through the manganese-containing oxidic material and falls back down through the manganese-containing oxidic material. This condition can be readily achieved by slowly increasing the gas input and observing the surface of the material in the ladle. When it is observed that portions of molten metal are being forced up through the layer of oxidic material and pass back down through the oxidic material, in a steady, rapid, but not unbroken succession the gas input is sufficient; at lower gas inputs, the improved results hereinafter described are not obtained due to insufficient mixing of the process reagents. Also, if the gas pressure is increased to the extent that a blast, i.e., a continuous
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stream of gas passes up through the metal and oxidic material, the results are also unsatisfactory in that insufficient mixing is obtained. That is to say, in the present invention, an essentially intermittent passage of gas is required.

The mechanism of the aforementioned gas agitation is to promote a continuously changing contact between the silicon-reducing agent and the manganese-containing oxidic material whereby manganese is reduced by the silicon and passes into the metal phase and silicon is converted to silica and combines in the oxidic slag phase.

This gas agitation is continued until the reduction reaction is essentially complete which can be determined for example by analyzing successive samples of the metal phase so as to observe when equilibrium is reached. When the reduction reaction is completed, the oxidic, i.e., slag phase is decanted from the ladle and either thrown away or re-used depending upon the manganese content, and the metal phase can be cast into molds.

To illustrate the particular advantages of the present invention, a series of tests were conducted using the gas-mixing procedure of the present invention and the previously known re-pouring technique to produce medium-to-low carbon ferromanganese (70-90% Mn, 0.04-1.5% C, 0.1-14% Si, bal. Fe).

In practicing the present invention, a ladle of the type shown in FIGURE 2 was employed. This ladle comprises an outer shell 20 formed of steel, a refractory lining of rammed perlclase and magnesia 22, a refractory base of rammed magnesia 24, and a tuyere 26, which is surrounded by a core arrangement 28 suitably formed of a castable alumina refractory material such as Purotabl 25. Tuyere 26 is suitably formed of stainless steel and gas is passed through hose 30 via tuyere 26 into the ladle. The following examples will further comparatively illustrate the benefits of the present invention.

Example

Molten silicon reducing agent (Mn 65%, Si 18%, C 1.6%, bal. Fe) in the amount of 780 pounds at a temperature of about 1300° C. was poured into a ladle of the type shown in FIGURE 2. The dimensions of the ladle were inner diameter 2.5 feet, height 3.0 feet. A molten manganese-bearing oxidic material (MnO 36.6%, CaO 25.7%, MgO 2.9%, Al₂O₃ 8.1%, SiO₂ 26%) in the amount of 1100 pounds at a temperature of about 1500° C. was poured into the ladle. With the aforementioned materials in the ladle, the molten metal was then poured and the molten metal was covered by about 1.08 feet of oxidic material. A space of about 1.5 feet remained empty at the top of the ladle. Argon gas under pressure was introduced into the molten metal through a tuyere, 0.125 inch in diameter, centrally located at the bottom of the ladle and the gas flow was increased until vigorous agitation of the ladle contents occurred and molten metal was continually heated above the surface of the oxidic material, and fell back down through the oxidic material, but did not cause significant splashing of material out of the ladle. The gas flow for this condition was about 215 s.e.f.h.

The gas flow was continued for about 10 minutes after which the oxidic slag material and the molten metal were poured into a magnesia lined pot.

The recovered metal (852 lbs.) analyzed 74% Mn, 11.2% Si, 1.4% C, bal. Fe; the manganese content of the slag material was 17.2%; and the base-to-acid ratio of the slag was 0.88. The ratio by weight of metal product to slag was 0.88 to 1 and the overall recovery of manganese was 97.4%.

The above procedure was repeated in 15 additional tests in which the materials and processing conditions were essentially the same except for the lime content of the charge which was varied to provide base-to-acid ratios ranging from 0.1 to 1.5. In all instances the alloy product was medium-to-low carbon ferromanganese containing 72 to 78% Mn, 6 to 12% Si, 1.1 to 1.5% C, bal. Fe.

Fifteen further tests were conducted in which the materials and processing were essentially the same except (1) that the lime content of the charge was varied to provide base-to-acid ratios ranging from 0.1 to 1.6 and (2) that re-pouring was used instead of gas agitation. The re-pouring technique involved pouring the contents of the first ladle into a substantially identical second ladle, re-pouring back to the first ladle, and then once again re-pouring from the first to the second ladle. In all instances the alloy product was medium-to-low carbon ferromanganese containing 72 to 78% Mn, 6 to 12% Si, 1.1 to 1.5% C, bal. Fe.

The results of the aforesaid tests, based on the base-to-acid ratio and unreduced manganese retained in the slag are shown in the graph of FIGURE 3.

As can be seen, the graph of FIGURE 3, for a base-to-acid ratio of 1.0, almost 50% more manganese is recovered using the gas mixing practice of the present invention compared to the previously standard re-pouring technique (14% Mn in slag compared to 20%).

From another point of view, to obtain a slag containing a particular manganese, e.g., 20% Mn, a much lower base-to-acid ratio can be used with the present invention, as compared to re-pouring. This means that substantially less lime is required and consequently a larger volume of metal can be produced in a given ladle. Also, with the use of less lime, less manganese is entrapped in the slag phase and hence manganese recovery is higher.

Since the present invention involves the mixing of molten phases of different densities to promote the interreaction thereof, and is not a refining or gas-reaction process wherein gas is a significant process reactant, a rather wide variety of non-reactive gases can be effectively employed. For example, all of the inert gases can be used and air can also be used since the temperatures and gas velocities involved do not lead to any significant re-oxidation of manganese. Nitrogen, carbon monoxide and carbon dioxide can also be used effectively.

What is claimed is:

1. A process for the production of manganese-containing alloys which comprises providing in a ladle a melt of oxidic manganese-containing material in which the amount of oxygen combined with manganese is no greater than about that represented by the formula MnO₉ together with a silicon reducing agent to thereby provide a molten metal phase in the lower portion of the ladle and molten oxidic manganese-containing material floating on and covering the metal phase, and reacting the molten metal and oxidic material by introducing gas under pressure into the molten metal phase to cause turbulence in the metal phase the pressure of the gas being sufficient to cause intermittent passage of gas through the molten metal and oxidic phase and being at a rate sufficient to cause a portion of molten metal to be continually forced upward through the oxidic phase in a steady, rapid, but broken succession and to fall back downward through the oxidic phase.

2. A process for the production of medium-to-low carbon ferromanganese comprising providing in a ladle a melt of oxidic manganese-containing material in which substantially all of the manganese values are in the manganeseous state together with a molten metal reducing agent containing between about 4 and 32 percent silicon to provide a molten metal phase in the lower portion of the ladle and molten oxidic material floating on and covering the metal phase, and reacting the molten metal and oxidic material by introducing gas under pressure into the metal phase to cause turbulence in the metal phase the pressure of the gas being sufficient to cause intermittent passage of gas through the molten metal and oxidic phase and being at a rate sufficient to cause a portion of molten metal to be continually forced upward through the oxidic phase.
phase in a steady, rapid, but not unbroken succession and to fall back downward through the oxidic phase.

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