Patented Sept. 29, 1953 2,653,867

# UNITED STATES PATENT OFFICE

2,653,867

## REDUCTION OF METAL OXIDES

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No Drawing. Application July 27, 1951, Serial No. 239,028

4 Claims. (Cl. 75—11)

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This invention relates to the reduction of metal oxides to their corresponding metals and more particularly to the reduction of such oxides by smelting with reducing agents, such carbon, silicon, etc., which tend to combine with the reduced metal and considerable amounts of which therefore have remained in the reduced metal as impurities. More specifically, the invention relates to a method for smelting iron oxide to produce directly, without subsequent purification, a high grade iron which is substantially free of such impurities as carbon, silicon, sulfur and phosphorus or any deleterious component of the reducing agent used.

The principal object of the present invention is to provide a method for smelting a high grade metal oxide ore, which is substantially free from objectionable impurities and deleterious elements, such as sulfur and phosphorus, in such a way that objectionable impurities are not introduced during the process of reduction and thus obtain a pure metal product.

It is well known that carbon has a great affinity for many metals, such as iron, chromium, molybdenum, vanadium, tungsten, titanium, etc. Thus, when iron oxide or an iron oxide ore is smelted with coke as a reducing agent, the resulting metal contains a high content of carbon. If the initial oxide material contains silica, the silica also is reduced and a large percentage of silicon remains in the reduced metal as an impurity. However, the presence of a substantial amount of silicon tends to reduce the carbon content of the resulting metal.

The United States patent to Becket No. 854,018 proposes the production of ferro-alloys having a relatively low content of carbon and silicon from a material containing principally chromium oxide and ferrous oxide by smelting this material with ferrosilicon. According to this patent, when an amount of silicon sufficient for complete reduction of the chromium and iron oxides is used, a representative analysis of the ferrochromium shows that the reduced metal contains 0.50 per cent carbon and 0.10 per cent silicon. Furthermore, the patent indicates (page 2, lines 8 to 12) that when a very low silicon content (less than 0.2 per cent) is required in the alloy, a deficiency of reducing agent must be used with a consequent sacrifice in the yield of metal obtained.

Another method for producing ferro-alloys having a relatively low content of carbon and silicon is described by the United States patent to Becket No. 906,854. This method comprises

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smelting the metal oxide ore with a mixture of carbon and silicon, namely, silicon carbide as the reducing agent. This patent also indicates (page 2, lines 19–24) that when a very low silicon content (less than 0.2 per cent) is required in the alloy, a deficiency of reducing agent must be used with a consequent reduction in the yield of metal obtained. The same method as applied specifically to the production of vanadium and its alloys is described by the United States patent to Becket No. 858,325, the latter being a division of Patent No. 906,854.

The present invention provides a method for smelting metal oxides or their ores with a novel combination reducing agent which may be used in large excess over that theoretically required to obtain a maximum yield of metal containing a substantially smaller amount of deleterious impurities, such as carbon and silicon, than has been previously possible. The invention is based upon the discovery that charcoal when used in certain proportions in conjunction with an aluminum ferrosilicon alloy provides a combined reducing agent capable of producing surprising advantageous results in the reduction and smelting of metal oxides. Thus, when a high grade iron oxide ore and a suitable flux is mixed and smelted with a combination reducing agent consisting of charcoal and an alloy of aluminum ferrosilicon in proportions such that the charcoal is calculated to combine with the same weight of oxygen as the combined proportions of aluminum and silicon to form carbon monoxide, alumina and silica, a high grade iron or steel is produced containing negligible amounts of carbon, silicon, aluminum, sulfur and phosphorus even when a large excess of the combined reducing agents over that calculated for complete reduction of the iron oxide is used. This is especially surprising since it is well known that smelting iron oxide with a reducing agent consisting solely of charcoal does not produce satisfactory results. A typical analysis of such an iron or steel product produced using a 20% excess of the combined reducing agent is 0.022 per cent carbon, a trace of silicon, 0.022 per cent phosphorus, 0.024 per cent sulfur, a trace of manganese and a trace of aluminum. The advantages of the invention are the direct production, without subsequent purification, of a metal of extremely high purity and high yield. Other forms of substantially pure carbon may be used in place of charcoal and other materials capable of reducing the metal oxide to its corresponding metal may be used in place of aluminum ferrosilicon with comparable results.

The method of the present invention comprises smelting a metal oxide or metal oxide ore, such as a high grade iron oxide ore, in the presence of a suitable flux, such as lime, and a combination reducing agent consisting of finely divided substantially pure carbon, such as charcoal, and another finely divided solid reducing agent capable of reducing the metal oxide to its corresponding metal to produce a molten burden consisting of slag and the reduced metal. The carbon and the other reducing agent should be used in the proportions hereinafter specified. Any conventional smelting procedure may be employed. However, we prefer to melt a mixture of the metal oxide, flux and combination reducing agent in a suitable electric furnace to form a molten burden at a temperature slightly above the melting temperature of the reduced metal and to feed continuously such mixture in finely divided form upon the molten burden at a controlled rate while withdrawing molten metal and slag continuously or at suitable intervals and separating the metal and slag by known means. The composition and amount of the flux used depends upon the amount and nature of the impurities in the metal oxide or metal oxide ore to be reduced and upon the decomposition of the furnace lining as is understood by those skilled in the art.

Our presently preferred combination reducing agent is finely divided charcoal and a finely divided alloy of aluminum ferrosilicon in about the relative proportions previously stated. However, comparable results in smelting metal oxides may be obtained using a combination reducing agent consisting essentially of substantially pure carbon, such as charcoal, and another reducing agent, such as aluminum ferrosilicon, in relative proportions such that the carbon is calculated to combine with from about 45 to 85 per cent by weight of a given weight of oxygen and the other reducing agent, such as aluminum ferrosilicon, is calculated to combine with from about 15 to about 55 per cent by weight of such given weight of oxygen. As illustrative of other reducing agents which may be used in place of aluminum ferrosilicon, we may mention aluminum, silicon and ferrosilicon and also such reducing agents as calcium, magnesium, etc., which have less affinity for such metals as iron, chromium, nickel, molybdenum, tungsten, titanium, etc., than does carbon, silicon and aluminum.

The combination reducing agent may be used in sufficient amount in excess of that theoretically required for complete reduction of the metal oxide to assure a satisfactory high yield of metal of high purity. An amount of about 20 per cent in excess of that theoretically required usually is sufficient to assure a high yield of high purity metal but in most instances a substantially greater amount may be used, and in some instances as much as 40 per cent excess, without substantially increasing the amounts of deleterious elements in the metal recovered. The maximum amount of the combination reducing agent which may be used without substantially increasing the amounts of deleterious elements in the metal recovered varies with the relative proportions of the components of the combination reducing agent.

The method of the present invention is adapted especially for the production of a high grade iron or steel by the direct reduction of a high grade iron oxide or iron oxide ore. There are many uses in the metallurgical industry for an extremely pure iron or steel. For many of such uses a product in which the combined amount of carbon and silicon is as high as 0.20 is unsuitable. By the practice of the present invention an extremely pure iron or steel product may be produced in which the combined amounts of carbon and silicon do not exceed 0.15 per cent by weight and in which the amount of either carbon or silicon does not exceed 0.10 per cent by weight. The method of the invention is applicable for smelting other metal oxides or oxide ores containing either a substantial or predominating amount of an oxide of a metal other than iron, such as chromium, molybdenum, tungsten, vanadium, nickel, cobalt, etc., to produce a metal product or ferro-alloy. If the metal oxide or oxide ore reduced is of high grade, a metal product having a purity comparable with that above may be produced.

The invention is illustrated further by the following specific examples.

*Example 1*

In this run high grade magnetite ore ground to minus 10 mesh was used. It analyzed 65 per cent acid soluble iron, 5 per cent silica and 30 per cent oxygen in the form of iron oxide. The reducing agent used was a mixture of charcoal (minus 100 mesh) containing 95 per cent carbon and aluminum ferrosilicon (minus 100 mesh) containing 65 per cent silicon, 10 per cent aluminum and 25 per cent iron. The flux used was burnt lime (100 per cent CaO).

The charge consisted of 1000 lbs. of the magnetite ore, 118.4 lbs. charcoal, 175 lbs. aluminum ferrosilicon and 170.9 lbs. burnt lime. The amount of charcoal used was calculated to combine with one half the weight of oxygen combined with the iron of the ore. The amount of aluminum ferrosilicon used was calculated to combine with the other half of the weight of oxygen combined with the iron of the ore. These materials were intimately mixed and the mixture was fed continuously into a single phase arc furnace lined with a magnesia refractory and having two graphite electrodes. The molten burden consisting of slag and steel was poured continuously into a vessel where a liquid separation of the slag and steel was made. The slag was cast as cakes and the steel as ingots. The steel was killed in the usual manner by adding a small amount of silicon, such as ferrosilicon, before casting the ingots.

The following are the amounts of discharge from the furnace:

624.37 pounds of steel
555.3 pounds of slag

The yield of metal was 90 per cent and it contained 0.02 per cent carbon, a trace of silicon, 0.025 per cent phosphorus, 0.020 per cent sulfur, a trace of manganese and a trace of aluminum.

*Example 2*

This run was identical to that of Example 1 except that a 20 per cent excess of reducing agent was used while the relative proportions of charcoal and aluminum ferrosilicon were the same. Thus, the charge consisted of 1000 lbs. magnetite ore, 142 lbs. charcoal, 210 lbs. aluminum ferrosilicon of the same composition and 180.6 lbs. burnt lime. The electrode consumption was 6.5 lbs. A 94 per cent yield of metal was obtained and it contained 0.022 per cent carbon, a trace of silicon, 0.022 per cent phosphorus, 0.024 per cent sulfur, a trace of manganese and a trace of aluminum. The excess reducing agent used substantially increased the yield of metal obtained without increase in the amount of impurities. Operation upon a large scale would be expected to increase the yield of metal and to decrease the melting losses which were mostly dust losses.

The amounts of charcoal and aluminum ferrosilicon used in the above examples were calculated upon the basis of the requirements of the equations

$$C + O \rightarrow CO$$
$$Si + O_2 \rightarrow SiO_2$$

and the aluminum in the aluminum ferrosilicon was assumed to be silicon. This method was used as a matter of convenience since in these instances the difference in the amounts as calculated by this method and the conventional method is negligible.

The components of the combination reducing agent should be substantially free of elements, such as sulfur and phosphorus, which are not reducing agents for the metal oxide to be reduced and the presence of which are known to have a deleterious effect in iron, steel and their alloys. The term "substantially pure carbon" as used herein is intended to mean carbon in a form which is substantially free of elements, such as sulfur and phosphorus, which are not reducing agents for the metal oxide to be reduced and the presence of which are known to have a deleterious effect in iron, steel and their alloys. It will be understood, therefore, that carbon combined with another element which is a reducing agent for the metal oxide, such as silicon carbide, calcium carbide, etc., may be used. Thus, a combination reducing agent consisting of silicon carbide and charcoal may be used.

We claim:

1. In a method of smelting a high grade metal oxide ore in an electric furnace wherein said ore is melted with a flux and a reducing agent, which tends to combine with the metal produced, to form a molten burden comprising a slag and the metal component of said oxide, the smelting temperature being not substantially greater than the melting temperature of the metal produced, the improvement wherein said reducing agent consists essentially of finely divided substantially pure carbon and a finely divided non-carbonaceous reducing agent for said oxide in relative proportions such that said carbon is calculated to combine with from about 45 to about 85 per cent by weight of a given weight of oxygen to form carbon monoxide and said non-carbonaceous reducing agent is calculated to combine with from about 55 to 15 per cent by weight of said given weight of oxygen to form an oxide of said non-carbonaceous reducing agent, said non-carbonaceous reducing agent being silicon or silicon and aluminum and being selected from the group consisting essentially of ferrosilicon, aluminum ferrosilicon and mixtures thereof, said improvement being characterized by the production of a metal in which the combined amount of carbon and silicon does not exceed 0.15 per cent and the amount of either carbon or silicon does not exceed 0.10 per cent.

2. The method as described by claim 1 wherein said carbon and said non-carbonaceous reducing agent are in relative proportions such that the carbon is calculated to combine with about the same weight of oxygen as said non-carbonaceous reducing agent to form carbon monoxide and an oxide of said non-carbonaceous reducing agent.

3. The method as described by claim 1 wherein said metal oxide consists essentially of iron oxide.

4. The method as described by claim 1 wherein said metal oxide consists essentially of a metal oxide selected from the group consisting of iron oxide, nickel oxide, cobalt oxide and mixtures thereof.

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