Patented Jan. 15, 1952

2,582,469

# UNITED STATES PATENT OFFICE

2,582,469

## METALLURGY

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No Drawing. Application August 11, 1948, Serial No. 43,772

10 Claims. (Cl. 75—11)

1

This invention relates to metallurgy and has for an object the provision of an improved method or process for producing ferrochromium. More particularly, the invention contemplates the provision of a method or process which can be employed advantageously and economically to produce high-grade ferrochromium products from various grades of chromium ore, including the usual commercial ores and some ores of too low grade to be treated commercially by means of heretofore customary methods or processes. The invention further contemplates the provision of a method or process which can be employed advantageously and economically to produce high-grade metallic chromium-bearing products from various grades of chromium through the use of various grades and types of carbonaceous reducing materials such, for example, as low-grade coal of too poor quality metallurgically to be employed commercially in heretofore customary methods or processes for recovering chromium from its ores. Another object of the invention is to provide an improved method or process for producing various grades of high-carbon ferrochromium and low-carbon ferrochromium from various grades of chromium ore.

In the smelting of refractory ore such as chromite ore according to heretofore customary practices, it is difficult to establish and maintain molten a bath of the ore of any substantial volume. Consequently, the slags produced in the smelting operations usually are so viscous as to prevent ready settling out of small particles of metals produced by reduction and small particles of unreduced chromite dispersed therein. In order to avoid high chromium losses through discarding slag having metallic chromium and unreduced chromite particles dispersed therein, it is customary to employ fluxes sparingly and thus produce a minimum amount of chromium-bearing slag, which must be discarded ultimately with consequent loss of chromium, or which must be subjected to a concentration treatment at additional expense to recover chromium contained therein.

I have found that improved recoveries of chromium can be obtained in the smelting of chromite ores by modifying heretofore customary practices through controlled fluxing and dilution of the ores in the production of the smelting charge.

I have found, also, that improved recoveries of chromium can be obtained by preheating the furnace charges, of the heretofore customary types and of the types modified to provide for

2

controlled fluxing and dilution, under reducing conditions.

In employing a submerged arc electric furnace or an arc resistance furnace, the types of furnaces employed heretofore in the smelting of chromite ore, it is difficult or virtually impossible to gain any substantial advantage from preheating of the charges, since the charges in the furnaces are heated, in any case, by hot gases escaping and passing upwardly from the smelting zones in the bottom portions of the furnaces.

In accordance with my invention, I reduce or complete the reduction of a charge initially comprising chromite ore in a furnace containing a slag-covered bath of molten ferrochromium and, thus, I am able to obtain a very substantial advantage through the use of a hot or preheated charge. I prefer to employ a furnace of the type of an open arc electric furnace and to introduce the hot charge directly from the preheating operation into the furnace onto a slag-covered bath therein.

I have found that preheating of a charge with controlled reduction can be carried out effectively in a rotary kiln or other sintering equipment, or in a submerged arc electric furnace operated primarily as a melting furnace. The use of a rotary kiln or other sintering equipment results in the production of a hot sintered charge for the reducing furnace, and the use of a submerged arc electric furnace results in the use of a hot molten charge for the reducing furnace.

In the heretofore customary processes for producing ferrochromium, as, for example, through the use of the electric furnace in the treatment of chromium ores, losses of chromium by volatilization can be substantial, and such losses combined with losses in the slags prevent the recovery of more than about eight-five percent of the chromium.

For fluxing the ore to be treated and forming a suitable slag, I may form a charge mixture comprising the chromium ore, lime in the form of limestone and silica. I carry fluxing of the ore beyond the heretofore customary practice, adding lime and silica in such amounts and proportions as to produce with the gangue of the ore a relatively, low-viscosity slag, relatively dilute with respect to refractory oxides and having a base-acid ratio under 2.0 to 1.0 and preferably equivalent to from 0.8 to 1.75 molecules of lime (CaO) to 1.0 molecule of silica ($SiO_2$). It may be economical in some cases to dilute the charge to a point where a fuel-fired furnace, of

the open hearth type, for example, can be employed as the reducing furnace.

The degree of dilution practiced will be determined in each instance by the character of the ore undergoing treatment, the extent of the reduction carried out in the sintering or preheating operation and the nature of the reducing treatment. For example, an ore high in refractory chromic oxide ($Cr_2O_3$) normally will require greater dilution to produce a fluid slag than will an ore low in chromic oxide; if fractional reduction of chromium and iron is carried out in the sintering or preheating operation, the resulting sintered product will be lower in refractory chromic oxide than it would have been if fractional reduction had not been carried out, and, consequently, it will not be necessary to dilute to as great an extent in order to produce a charge capable of being rendered fluid readily in the subsequent reducing treatment; if reduction of the sintered or preheated charge is to be carried out in two stages with selective reduction of iron being effected in the first stage, greater dilution will be required to compensate for the apparent or relative increase in refractory chromic oxide resulting from reduction of the less refractory iron oxide; and, if total reduction of iron and chromium is to be carried out in a single high-temperature reducing treatment employing a molten fluid slag covered bath, dilution to the extent of simply adding sufficient lime and silica to flux the gangue materials of the ore will be satisfactory. In general, effective dilution can be achieved by providing for the production of a product of the sintering or preheating treatment comprising chromic oxide in amount equivalent to about fifteen to thirty percent (15% to 30%) of the weight of the sintered or preheated charge.

In forming a charge in accordance with the invention, I prefer to mix intimately the various components, including the ore, slag-forming or fluxing material and any solid carbonaceous reducing material which may be employed as hereinafter provided. The components may be crushed to any suitable degree of fineness, and any suitable mixing methods and apparatus may be employed. For most effective mixing, I prefer to grind together in a suitable mill the various components of the charge. A charge in which all the materials are finely divided and all particles are small enough to pass through a 4-mesh screen permits effective sintering and effective reduction when reduction is provided for.

I select the components of the charge to provide for the production of a slag having a base-acid ratio equivalent to about 0.8 to 1.75 molecules of CaO to 1.0 molecule of $SiO_2$. Heating of a charge consisting essentially of chromium ore, lime in the form of limestone and silica to a temperature in the range 1300° C. to 1450° C. produces a desired sintered product. Such a sintering treatment results in calcination of the limestone with the production of calcium oxide (CaO) and with chemical combination of the lime with chromic oxide of the ore and the silica. Fixing of the lime (CaO) in chemical combination with the chromic oxide and silica is very important as it prevents picking up of carbon dioxide from the atmosphere and thus facilitates the production of low-carbon ferrochromium very low in carbon.

In practicing my invention, I prefer to employ a low-temperature sintering operation and one or more high-temperature furnace operations.



The low-temperature operation is carried out at a sintering temperature and the one or more high-temperature operations are carried out at melting temperatures—temperatures at which the charges undergoing treatment are melted or are maintained in the molten state.

In the sintering operation, the charge employed may be free of reducing material or it may contain all or a portion only of the reducing material (preferably solid carbonaceous reducing material) required to reduce all of the reducible iron and chromium contained in the charge, and the operation may be carried out at a temperature and for a period of time sufficient to effect reduction of reducible iron and chromium by means of all or by means of a portion only of the reducing material contained in the charge.

The hot sintered product is introduced into a high-temperature melting furnace wherein melting alone may be accomplished or wherein melting and further reduction of iron or of iron and chromium may be accomplished. For melting or for melting and reduction, I may employ either a combustion heated furnace of the type, for example, of an open hearth furnace or an electric furnace of the type, for example, of a submerged arc furnace or an open arc furnace or an arc resistance furnace.

For the production of carbon-bearing ferrochromium of controlled carbon content, I may sinter a charge, free of reducing material, introduce the hot sintered product into a submerged arc type or arc resistance type of electric furnace to produce a molten slag product, introduce the molten slag product into an open arc type electric furnace, and add coal or coke to the molten slag in the open arc furnace to reduce the iron and chromium contained in the slag with the production of molten ferrochromium. By suitably controlling the amount of carbon and the temperature employed, ferrochromium products containing various amounts of carbon may be produced. Products containing 1.5 percent to 7.0 percent, for example, may be produced as desired.

The furnace employed for the high-temperature reduction may be much larger than the furnace employed for melting. Large quantities of ferrochromium can be held in the furnace to refine and produce a constant composition alloy instead of the variable composition grade of alloy produced by other methods.

If desired, the melting furnace may be omitted in the foregoing operation, and the hot sinter may be charged directly into an open arc electric furnace wherein reduction may be carried out by the addition of coal or coke.

If the production of low-carbon ferrochromium is sought, a smelting charge is subjected to a preheating operation, in a rotary kiln, for example, and under neutral or non-reducing conditions to produce a hot sintered product, and the hot sintered product is introduced directly into an open arc electric furnace and subjected therein to the reducing treatment with a non-carbonaceous reducing agent, such, for example, as silicon or aluminum.

In employing a high-iron chromite ore for the production of ferrochromium, I prefer to heat a smelting charge comprising a limited amount of solid carbon not substantially greater than that required to effect reduction of the reducible iron contained in the charge, to a sintering temperature in the range, 1300° C. to 1450° C., to effect

selective reduction of the iron and form a hot sintered product. I introduce the hot sintered product into an open arc electric furnace and form a molten bath comprising a layer of molten iron reduced in the sintering treatment and a molten slag layer containing the unreduced chromium. If the molten iron product contains some chromium reduced in the sintering treatment the chromium may be reoxidized by treatment of the molten iron product with air or oxygen or a solid oxidizer to form chromic oxide which enters the slag. I tap the slag resulting from melting of the sintered product into another open arc electric furnace and subject it while molten to the action of a carbonaceous reducing agent or a non-carbonaceous reducing agent, depending on whether a carbon-bearing or a substantially carbon-free ferrochromium product is desired.

In carrying out a process of my invention employing preheating or sintering followed by reduction in an open arc electric furnace, sintering is carried on continuously, and charging of the hot preheated or sintered charge to the open arc electric furnace is carried on continuously except for short periods of time during which tapping operations are being carried out. Tapping of slag and metal may be carried out at the same time or at different times. Preferably, a furnace sufficiently large to hold a very substantial quantity of molten metal (about 50 tons or more) is employed and tapping of metal is carried out only infrequently. The use of a furnace having such a large capacity permits the production of large quantities of ferrochromium of uniform compositions, and holding of the metal in the furnace at high temperatures for relatively long periods of time permits more effective carbon elimination and control. The slag never is removed completely from the furnace, a protective layer of fluid slag being maintained always in contact with the molten metal. Charging of the hot sintered product always takes place into and through a layer of fluid slag maintained at a high temperature. Charging of preheated or sintered charge material is discontinued for a short period of time during each tapping period to permit clearing of the reducible chromium compounds and settling out of the particles of reduced metal to avoid their loss through being discarded with the slag.

I claim:

1. The method of producing ferrochromium which comprises heating a charge comprising chromite ore, a solid carbonaceous reducing agent and fluxing material to a temperature and for a period of time sufficient to at least sinter the charge and producing a high-temperature product, adding the high-temperature product directly to a molten charge undergoing reduction in an open arc electric furnace and reducing iron and chromium of the chromite ore with the production of molten ferrochromium, and withdrawing molten ferrochromium from the furnace.

2. The method of producing ferrochromium which comprises heating a charge comprising chromite ore, a solid carbonaceous reducing agent and fluxing material and producing a high-temperature sintered product, adding the high-temperature sintered product directly to a molten charge undergoing reduction in an open arc electric furnace and reducing iron and chromium of the chromite ore with the production of molten ferrochromium, and withdrawing molten ferrochromium from the furnace.



3. The method of producing ferrochromium which comprises forming a charge comprising chromite ore, fluxing material and solid carbonaceous reducing material, heating the charge to a sintering temperature and forming a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to a melting and reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten ferrochromium from the furnace.

4. The method of producing ferrochromium which comprises forming a charge comprising chromite ore, fluxing material, including silica and lime, and solid carbonaceous reducing material, heating the charge to a sintering temperature and forming a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to a melting and reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten ferrochromium from the furnace, lime and silica being present in the charge in a molecular ratio lower than 2.0 molecules of CaO to 1.0 molecule of $SiO_2$.

5. The method of producing ferrochromium which comprises forming a charge comprising chromite ore, fluxing material, including silica and lime, and solid carbonaceous reducing material, heating the charge to a sintering temperature and forming a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to a melting and reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten ferrochromium from the furnace, lime and silica being present in the charge in a molecular ratio in the range 0.8 to 1.75 molecules of CaO to 1.0 molecule of $SiO_2$.

6. The method of producing ferrochromium which comprises forming a charge comprising chromite ore, fluxing material including silica and lime and solid carbonaceous reducing material, heating the charge to a sintering temperature in the range 1300° C. to 1450° C. and forming a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to a melting and reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten ferrochromium from the furnace, lime and silica being present in the charge in a molecular ratio lower than 2.0 molecules of CaO to 1.0 molecule of $SiO_2$.

7. The method of producing ferrochromium which comprises forming a charge comprising chromite ore, fluxing material including silica and lime and solid carbonaceous reducing material, heating the charge to a sintering temperature in the range 1300° C. to 1450° C. and forming a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to a melting and reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten

ferrochromium from the furnace, lime and silica being present in the charge in a molecular ratio in the range 0.8 to 1.75 molecules of CaO to 1.0 molecule of $SiO_2$.

8. The method of producing ferrochromium which comprises forming a charge comprising chromite ore, fluxing material, including silica and lime, and solid carbonaceous reducing material, heating the charge to a sintering temperature and forming a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to a melting and reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten ferrochromium from the furnace, lime and silica being present in the charge in a molecular ratio lower than 2.0 molecules of CaO to 1.0 molecule of $SiO_2$ and in amounts sufficient to form with the gangue materials of the chromite ore slag having a relatively low melting point which can be melted in the open arc electric furnace to form a fluid layer covering ferrochromium produced therein.

9. The method of recovering ferrochromium from high-iron chromite ore which comprises heating a charge comprising the chromite ore and fluxing material under reducing conditions and producing a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to an oxidizing treatment in an open arc electric furnace in the presence of iron oxide to re-oxidize any chromium reduced to the metallic state with iron of the chromite ore and form (1) molten slag comprising the unreduced chromium of the chromite ore and the re-oxidized chromium and (2) a molten metal product comprising the iron reduced from the chromite ore and the iron reduced from the iron oxide in re-oxidizing reduced chromium, subjecting the molten slag to a reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten ferrochromium from the furnace.



10. The method of recovering ferrochromium from high-iron chromite ore wihch comprises heating a charge comprising the chromite ore and fluxing material under reducing conditions and producing a high-temperature sintered product containing a portion of the iron of the chromite ore in the metallic state, subjecting the high-temperature sintered product to an oxidizing treatment in an open arc electric furnace to re-oxidize any chromium reduced to the metallic state with iron of the chromite ore and form (1) molten slag comprising the unreduced chromium of the chromite ore and the re-oxidized chromium and (2) a molten metal product comprising the iron reduced from the chromite ore, subjecting the molten slag to a reducing treatment in an open arc electric furnace and forming a molten bath comprising molten slag and molten ferrochromium, and withdrawing molten ferrochromium from the furnace.

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