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3,817,765

## SINGLE PASS PREREACTIONED GRAIN AND METHOD OF MAKING

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6 Claims

### ABSTRACT OF THE DISCLOSURE

A fully recrystallized, single pass refractory grain is made by admixing a finely divided MgO-yielding material such as magnesium hydroxide with finely divided low silica chrome ore and firing this admixture, for example in a rotary kiln, without prior compaction, to a temperature of at least 1775° C., the material being exposed to that temperature for at least 10 minutes.

### BACKGROUND OF THE INVENTION

This invention concerns refractory grain, and more particularly a method of making such grain by reacting low silica chrome ore and an MgO-yielding material.

It has long been known to make refractory shapes from granular admixtures of chrome ore and a magnesia material such as magnesite or periclase. It is also known to make refractory shapes from grain made by prereacting these two materials, for example as disclosed in U.S. Pat. 2,775,525 to Austin et al.

In making prereacted grain from chrome ore and magnesia, it is known to calcine the MgO-yielding material, for example magnesium hydroxide, at a temperature in the neighborhood of 1000° C. to produce an active magnesia, to admix this active magnesia with the chrome ore, to compact, for example by briquetting, this admixture, and then to fire the compacts, for example in a rotary kiln, to produce dense refractory material which can be crushed to the desired grain sizing for making refractory products such as bricks.

Obviously, this so-called "double burn" method of making prereacted refractory grain is more expensive than making such grain in a single firing. However, it has been found in previous attempts to produce prereacted grain without calcination of the MgO-yielding material, and particularly without compaction of the chrome and magnesia admixture, that the desired properties of low porosity and good recrystallization of the grain are not achieved.

In addition, in recent years the trend in refractories technology has been toward lower silica contents; hence, the use of beneficiated, low silica chrome concentrates in place of raw chrome ore. The use of these higher purity, low silica materials, however, makes it even more difficult to achieve low porosities in prereacted grain made from magnesia and chrome.

The present invention provides a method of producing dense, completely recrystallized refractory grain directly from chrome ore, and more particularly from low silica chrome concentrates, and MgO-yielding material in a single fire process without the necessity of compacting the raw materials.

### SUMMARY OF THE INVENTION

According to the present invention, a sintered prereacted refractory grain containing less than 2% SiO<sub>2</sub> is

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made from MgO-yielding material and chrome ore by (1) intimately admixing from 20% to 80% by weight of MgO-yielding material, calculated as MgO, substantially all of said MgO-yielding material being less than 44 microns in size and having a median particule size of less than 4 microns, said MgO-yielding material containing less than 0.5% SiO<sub>2</sub> on the ignited basis, with from 80% to 20% by weight of chrome ore at least 95% of which passes a 325 mesh screen (i.e., is finer than 44 microns) and 50% of which is finer than 10 microns, said chrome ore containing less than 3% SiO<sub>2</sub>, and (2) subjecting said admixture without prior compaction to a heat treatment wherein the admixture is exposed to a temperature of at least 1775° C. for at least 10 minutes.

The resulting product is a fully recrystallized, uniform refractory grain of periclase solid solution crystallites with exsolved chromium-containing spinels within the periclase crystallites and containing less than 2% SiO<sub>2</sub>. The grain is substantially free of any of the original chrome ore in unreacted form, and, in a preferred form, has a total porosity of less than 10 volume percent.

### DETAILED DESCRIPTION

The MgO-yielding material may be any such material, for example brucite or magnesite, but a preferred material is magnesium hydroxide, most preferably magnesium hydroxide produced by reacting CaO-containing material such as calcined limestone or calcined dolomite with brine, for example sea water, containing magnesium values in solution. The resulting precipitated magnesium hydroxide (Mg(OH)<sub>2</sub>) is of the desired fine particle size for use in this invention, the median particle or agglomerate size being about 4 microns, and substantially all the particles or agglomerates being less than 44 microns in size. As indicated, the so-called particles of precipitated magnesium hydroxide are actually agglomerates of finer crystallites, the ultimate crystallite size being about 0.2 microns. However, in any case, no matter what MgO-yielding material is used, at least 90% must be finer than 325 mesh, and it will have a median particle size of about 4 microns. The MgO-yielding material will contain at least 95%, and preferably 98% or more, MgO on the ignited basis, the remainder being normal impurities.

The chrome ore can be any such material, but will generally be of the so-called "refractory grade." Such chrome ores are found in the Masinloc region of the Philippines, in the Transvaal and other regions of Africa, in Turkey, and elsewhere. To achieve the required SiO<sub>2</sub> content of less than 3% in the chrome ore, so-called "chrome concentrates" will generally be used, these concentrates being chrome ore material which has been beneficiated to remove silicate materials. Thus, as used in this specification, the term "chrome ore" includes chrome concentrates. Of course, a naturally occurring chrome ore of the requisite SiO<sub>2</sub> content can be used without beneficiation. In any case, it is essential that the chrome ore be ground so that at least 95% passes a 325 mesh screen, and that it has a median particle size of less than 10 microns. It will be understood that the finer the chrome particles, the better the results of the invention.

Milling of the chrome ore, and of the MgO-yielding material where necessary, can be carried out in any suitable apparatus, for example, a vibratory energy mill such as a Sweco mill. A preferred method of milling is wet milling in a ball mill, for example using iron balls.

A particularly preferred method is to admix the MgO-yielding material and the chrome ore and mill them together until both have the requisite fine particle size and are thoroughly interdispersed. It is an advantage of this invention that magnesium hydroxide can be much more intimately interdispersed with the chrome ore than can the calcined magnesias used in the doubleburn process.

The admixed raw materials are then charged, without any compaction, into a kiln, for example a rotary kiln, where they are exposed to a peak temperature of at least 1975° C., and preferably at least 2000° C. It is necessary that the material be exposed to temperatures of at least 1975° C. for at least 10 minutes. It has been found that shorter exposure times result in insufficiently reacted and nonuniform grain.

During firing, the spinel constituents of the chrome ore are dissolved in the MgO, which is extensively recrystallized. At the peak firing temperatures, substantially all the chromium spinel material is dissolved in MgO. However, upon cooling of the refractory material below the peak firing temperature, chromium-containing spinels exsolve from the MgO, appearing as dendrites in the MgO crystallites. The silicate materials originally present in the chrome ore appear as a minor intergranular phase between the MgO crystallites. A very few intergranular spinel crystallites are also present.

#### EXAMPLE

Magnesium hydroxide was produced by reacting calcined dolomite with sea water containing dissolved magnesium sulfate and magnesium chloride. This magnesium hydroxide shows, on the ignited basis, the following typical chemical analysis: 1.2% CaO, 0.3% SiO<sub>2</sub>, 0.1% Al<sub>2</sub>O<sub>3</sub>, 0.2% Fe<sub>2</sub>O<sub>3</sub>, and (by difference) 98.2% MgO, all percentages being by weight. All the particles of Mg(OH)<sub>2</sub> were smaller than 44 microns, and the median particle size was 4 microns.

Masinloc chrome ore concentrates were charged to a steel ball mill with steel balls and dry milled to a median particle size of 9.3 microns. 95% of the milled product was finer than 44 microns. The chrome concentrates showed the following typical chemical analysis: 18.7% MgO, 0.4% CaO, 2.6% SiO<sub>2</sub>, 29.4% Al<sub>2</sub>O<sub>3</sub>, 13.9% FeO, and 35.0% Cr<sub>2</sub>O<sub>3</sub>, all percentages being by weight.

The milled chrome concentrates and damp magnesium hydroxide filter cake were charged to a pug mill in the proportion of 75 parts by weight, dry basis, magnesium hydroxide to 48 parts by weight chrome concentrates. The damp Mg(OH)<sub>2</sub> filter cake contained equal parts by weight water and Mg(OH)<sub>2</sub>; i.e., each 75 parts by weight Mg(OH)<sub>2</sub> brought an equal weight of water to the mixture. From the preceding analyses, it can be calculated that, after ignition, this admixture will contain very close to 60% by weight MgO. After leaving the pug mill, the wet admixture was conveyed by means of a screw conveyor, where further mixing took place, to a rotary kiln. The material was fired to a peak temperature of 2000° C., the residence time of the material in the kiln at temperatures above 1975° C. being about 15 minutes.

The resulting refractory grain showed the following chemical analysis: 1.5% SiO<sub>2</sub>, 7.1% Fe<sub>2</sub>O<sub>3</sub>, 13.6% Al<sub>2</sub>O<sub>3</sub>, 15.2% Cr<sub>2</sub>O<sub>3</sub>, 0.8% CaO, and (by difference) 61.8% MgO, all percentages being by weight. Petrographic examination of the grain showed it to be a thoroughly uniform periclase solid solution-spinel with minor silicate composition, displaying a strong periclase-chrome reaction. The periclase solid solution crystal size ranged from 60 to 120 microns and averaged about 80 microns. The very few irregularly distributed intergranular spinel crystals averaged about 20 microns in size. The inert and well reacted character of the grain is illustrated by the difficulty experienced in putting the material into solution for purposes of running the wet chemical analysis. The poros-

ity of the grain determined by ASTM method C-493-70 was about 9 volume percent.

The grain of the preceding example is to be compared with grain made in similar fashion except that only about 75% of the chrome ore concentrates were finer than 44 microns (i.e., passed a 325 mesh screen). This comparison grain had a similar chemical composition to that of the example, but its porosity was about 15%. Microstructural examination showed it to be much less well reacted than the grain of the example. The crystallite size of the comparison grain ranged from 30 to 150 microns, with an average of about 60 microns. The greater variability of this comparison grain is thus evident. Although the comparison grain contained periclase crystallites with exsolution chrome, it also contained considerable unreacted chrome material. In general, the comparison grain was not as well bonded as the grain of the example.

The grain of the example can also be compared with a double pass grain made from the same raw materials. The magnesium hydroxide was calcined to a temperature of 950° C. to produce an active magnesias, and admixed with the chrome concentrates ground to an average particle size of 10 microns, over 95% of the chrome concentrates being less than 44 microns in size. The dry admixture was compacted in a roll-type press at an equivalent pressure of 35 tons per square inch. The compacts so formed were charged to a rotary kiln where they were exposed to a peak temperature of 1975° C. Microscopic examination showed the resulting grain to be made up of very uniform periclase solid solution-spinel crystallites with minor silicate, and having an average crystallite size of 70 microns. The porosity was about 10%. In other words, even the "double burn" grain made by the more expensive process is not as well reacted as the grain made according to the present invention.

In the specification and claims, percentages and parts are by weight unless otherwise indicated, except that porosities are expressed in volume percent. Mesh sizes referred to herein are Tyler standard screen sizes which are defined in Chemical Engineers' Handbook, John H. Perry, Editor-in-Chief, Third Edition, 1950, published by McGraw Hill Book Company, at page 963. For example, a 100 mesh screen opening corresponds to 147 microns, and 200 mesh to 74 microns. Analyses of mineral components are reported in the usual manner, expressed as simple oxides, e.g., MgO, SiO<sub>2</sub>, although the components may actually be present in various combinations, e.g., as a magnesium silicate.

Having described the invention, what is claimed is:

1. Method of making prereacted sintered refractory grain containing less than 2% SiO<sub>2</sub> from MgO-yielding material and chrome ore comprising (1) intimately admixing from 20% to 80% by weight of MgO-yielding material, calculated as MgO, substantially all of said MgO-yielding material being less than 44 microns in size and having a median particle size of less than 4 microns, said MgO-yielding material containing less than 0.5% SiO<sub>2</sub> on the ignited basis, with from 80% to 20% by weight of chrome ore at least 95% of which passes a 325 mesh screen and 50% of which is finer than 10 microns, said chrome ore containing less than 3% SiO<sub>2</sub>, (2) subjecting said admixture without prior compaction to a heat treatment wherein the admixture is exposed to a temperature of at least 1975° C. for at least 10 minutes, and (3) recovering a refractory grain comprising a uniform periclase solid solution with exsolved chrome-containing spinel within individual periclase crystallites, said grain having less than 10 volume percent porosity and being substantially free of any of the original chrome ore in unreacted form.

2. Method according to claim 1 wherein said admixture is exposed to a maximum temperature of at least 2000° C.

3. Method according to claim 1 wherein said MgO-yielding material is magnesium hydroxide.

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4. Method according to claim 3 wherein said admixture is exposed to a maximum temperature of at least 2000° C.

5. Method according to claim 3 wherein said magnesium hydroxide is the product of reaction between CaO-containing material and brine containing soluble magnesium values. 5

6. Method according to claim 5 wherein said admixture is exposed to a maximum temperature of at least 2000° C.

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