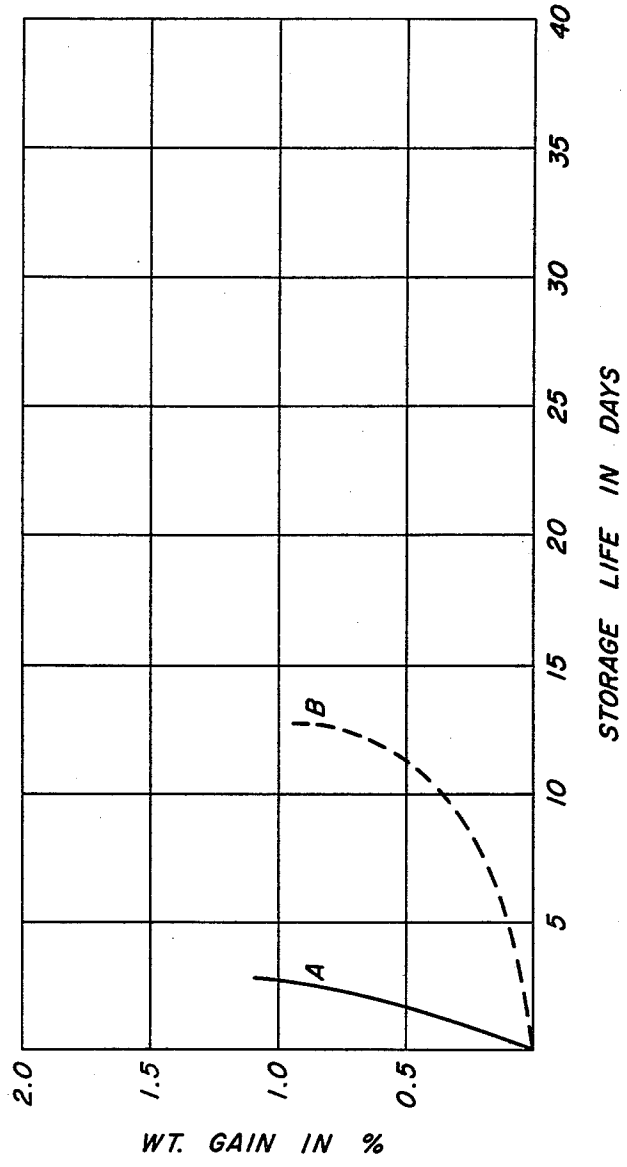
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DOLOMITE FURNACE LINING WITH CARBONACEOUS BOND

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DOLOMITE FURNACE LINING WITH CARBONACEOUS BOND

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This invention relates to a furnace for metallurgical or other high temperature operations; and more particularly, to such a furnace having a metal shell and a basic refractory lining disposed therein; and especially it relates to the refractory batches or shapes which are employed in such lining, and a method for making the same.

A great deal of work has been done in the field of production of refractory dolomite linings for metallurgical furnaces, but many problems have been encountered. For example, burned dolomites in the known methods have shown a tendency to hydrate readily, and this in turn leads to cracking, loss of strength, and eventually can cause complete disintegration of refractory shapes or linings formed therefrom. Under the best of conditions in the past, dolomite refractories have had short storage life because of this hydration characteristic, and it has been customary to begin firing or use of linings comprising such refractory shapes within twenty-four hours after making, in most instances. At most, such shapes even when composed of a magnesitic dolomite having a high content of magnesium oxide have not been successfully stored for longer than five to seven days. It will be understood that where hydration is referred to, carbonation may also or alternatively occur; and therefore it should be understood that these bricks are susceptible to disintegration under normal atmospheric conditions, whether such disintegration stems from hydration or carbonation.

Under the above circumstances it has been necessary for best operation to make such refractories at a location close to where they will be used, so that there will be a relatively short lapse of time between making and firing in the furnace. On the other hand, magnesite or magnesia refractories, while having excellent heat resistance and also having hydration or carbonation resistance greatly superior to that of dolomite, are in general more expensive and also less resistant to fluctuations of temperature, and they tend to spall under such conditions of temperature fluctuation. These characteristics have posed serious problems in the construction of linings for high temperature furnaces, and it is desired to construct furnaces with linings which are resistant to hydration, resistant to spalling, and which are less expensive than all-magnesia or magnesia-chrome linings heretofore known. Dolomites are particularly desirable in some installations, e.g., steel converters where the lime content is believed to be advantageous, and in locations where chromite may be undesirable because of the tendency of molten steel to pick up chromium from such ore.

According to the present invention, therefore, a hydration-resistant, dolomite lining for metallurgical furnaces is provided which overcomes the objections and disadvantages mentioned above and which exhibits other advantages as will become apparent from the description below.

According to the present invention, there is provided a furnace suitable for high temperature operations in various metallurgical processes, such furnace including a metal shell, and a refractory lining disposed therein and consisting essentially of a major portion, or at least 50%, of a coarse grain portion composed of fired, dolomite

grains, and a minor portion, or not over 50%, of finely divided fired dolomite, and a small amount of a non-aqueous cokable carbonaceous bonding agent, for example, tar. The refractory or mineral components, that is, the coarse and fine dolomite, are mixed together and are admixed with the carbonaceous bonding agent, both the dolomite component and the tar preferably being heated prior to mixing. The total mixture is then formed into shape by vibration while applying low forming pressure, such low pressures being insufficient to form dense and strong refractory shapes in and of themselves.

The fired dolomite useful in this invention can be either calcined or deadburned or a mixture of both; and the coarse portion or fraction is useful in various particle sizes, preferably, however, predominantly from ⅜ inch diameter down to 35 mesh. Such preferred coarse portion can include a minor portion of particles down to that retained on a 100 mesh screen. In general, it is preferred that the coarse portion be predominantly of particle sizes retained on, or not less than, 35 mesh. The finely divided dolomite suitably passes through a 100 mesh screen and a substantial amount thereof preferably passes through a 200 mesh screen. The dolomite can be a true dolomite or a magnesitic dolomite or a dolomitic limestone, all of which, as is well known, commonly exhibit hydration tendencies upon standing, even though "deadburned" to an otherwise very useful and well-sintered refractory grain. The coarse grain portion can, if desired, be employed in sizes from kiln run product down to 100 mesh, that is, where the largest particles are about ¾ inch in diameter. In a preferred embodiment, however, the coarse grain portion is as described above.

The finely divided portion of the refractory batch consists of dolomite of particle size essentially passing 100 mesh. Such dolomite can be of the same mineralogical and chemical composition as the dolomite of the coarse grain portion, but alternatively, it can be of different mineralogical or of different chemical composition therefrom. For instance, a true dolomite can be employed as the coarse grain portion, and a magnesitic dolomite or a dolomitic limestone as the finer grain portion, or vice versa.

The cokable carbonaceous bonding material or agent is added in small amount, preferably from 4% to 10% by weight, based on the total weight of the refractory components. For example, with 100 total parts by weight of a mixture of coarser and finer dolomite components, there are admixed from 4 parts to 10 parts by weight of cokable carbonaceous bonding material, such carbonaceous material is suitably coal tar, pitch, tar, asphalt, Gilsonite or the like. If desired, carbon particles can be incorporated also in such carbonaceous material, as is also found useful with dolomite - magnesite - cokable carbonaceous bond mixes and other refractories batches made up with cokable carbonaceous bonding agents. Such carbon particles can be finely divided or, if desired, can be of rather coarse sizes. In a preferred operation, it is advantageous to incorporate in the cokable material a minor amount, up to about 20%, preferably about 2 to 5%, based on the total weight of carbonaceous bonding material, of a surface active agent having a tar-soluble hydrocarbon group containing at least six carbon atoms, and a polar group such as a carboxylic acid or soap of a carboxylic acid, for example, a fatty acid, a long chain aliphatic amine or amide, or a sulfonated or sulfated aliphatic compound containing at least six carbon atoms, or cyclic organic nitrogen compound such as hydroxyethyl-2-n-alkyl-2 imidazole. It is preferred to use a high fixed carbon, hard, or high softening point tar, for instance, a tar having a softening point of at least 50° C., preferably from 50° C. to 90° C., and

having a low moisture content, preferably not over about 0.1% moisture content. Coal tar is an excellent carbonaceous bonding agent for use in the present invention. Preferably, the carbonaceous bonding material is in liquid form or is heated to liquefaction prior to admixture with the refractory components.

In making up a refractory batch according to the present invention, the mineral portion, that is, the coarse and the fine fractions, are intimately intermixed and are thoroughly intermixed with the carbonaceous bonding material. In a preferred embodiment, the coarse grain dolomite is admixed with the carbonaceous bonding agent, and this admixture is then mixed with the finely divided dolomite as described above. In a preferred mode of carrying out this invention, the carbonaceous bonding material is heated to a temperature at which it is in liquid or flowable state, and the refractory material is heated to about the same temperature; and the two materials are then admixed in such heated state, preferably in a sequence of steps described above, although other sequential steps can be practiced, if desired. Preferably, both materials are heated to a temperature of from 120° C. to 220° C., especially when coal tar is employed as bonding material.

The admixed batch can then be applied as patching material in a furnace lining or can be formed into a furnace lining by any desired method, many such methods being well known to the art. The batch can alternatively be formed into bricks, blocks or other shaped articles. Particularly, according to the present invention, a batch is formed into shaped articles in a vibratory press whereby there are employed forming pressures of not over 3000 lbs., preferably not over 1000 lbs., per square inch. In one advantageous mode of operation, the refractory batch is filled into the mold, vibration alone is applied until the mold is filled, and then low pressure is applied to the mass in the mold and gradually increased while still vibrating, up to the top pressure which it is desired to apply, for example, up to 3000 p.s.i. or preferably up to 1000 p.s.i. Vibration is carried out by applying vibrators, as desired, laterally to the mold for the furnace lining section, for example, the bottom section, or for the brick or block. Alternatively, vibrators, as desired, can be applied to the top or the bottom of the bricks or the like. Vibration is then applied in the known way. It has been found that this method of operation is especially advantageous in that it avoids changes of granulometry because it avoids cracking of the coarser dolomite grains, particularly with the weaker dolomites (that is, of relatively low compressive strength). Also, by this method of operation it has been found that the brick or object formed is of high density and of very good strength. The bricks or blocks so made are suitable for storing or shipping and can be burned in after installation in a furnace. In firing it is suitable to heat at such a rate that the coke forms rapidly, but at such rate that the vapors being evolved do not disrupt the face of the brick or block mass, these heating precautions being known to the art.

It is an advantage of the present invention that dolomite furnace linings are produced which have greatly improved hydration resistance; and the refractory product made according to this invention can be stored or held, before installation in the furnace lining, for greatly increased periods of time, thus enabling, for example, the production of the dolomite refractory mass at an economically advantageous factory site with subsequent shipment to the place of use. It is an advantage of this invention that the dolomite refractories made according to this invention exhibit very little swelling or cracking or gain in weight, from either hydration or carbonation, after prolonged storage time relative to the times of storage possible with dolomite refractories made under high pressures. It is a further advantage that after firing and coking of the binder the refractory products made according to this invention exhibit excellent strength, spalling resistance, and resistance to hydration, carbonation, swelling, cracking and gain in weight.

The FIGURE shows in graphic form one advantageous result of the practice of this invention wherein gain in weight is plotted against storage life in days. In the series of tests which provided the results graphically shown in the figure, curve A was determined by preparing a mix consisting of 70% of a batch of deadburned dolomite of grain sizes selected to pass 4 mesh and be retained on 20 mesh, 30% of dolomite of the same batch passing 100 mesh, and 6.75% coal tar calculated on the total weight of dolomite, heating the coal tar to fluidity and heating the dolomite material to the same temperature, admixing while heated and then forming into shapes under a pressure of 8000 lbs. per square inch. The bricks of test A were then held in an open room under normal atmospheric conditions; and the gain in weight was determined each day. At the end of three days the bricks were cracked and disintegrating, that is, they could be broken apart by hand and were unfit for use as components of a furnace lining. To determine curve B, another mix of deadburned dolomite and tar was made up in exactly the same way, and bricks were prepared therefrom by forming in a brick mold by vibration while applying a pressure of 375 lbs. per square inch. The bricks of test B were then stored under the same conditions as those of test A, and the results are shown in curve B, the bricks being in satisfactory condition up to over ten days. Thus, the storage life of bricks made in this way are about three times that of bricks made under pressure. Thus, the bricks made according to the present process, and employing all dolomite material, have a significantly increased storage life over that of bricks made under pressure.

The following example will demonstrate a mode of carrying out the invention:

Example

A refractory batch or mix is prepared using deadburned Natividad dolomite of the following selected grain sizing:

	Percent by weight of mineral
From ⅜ inch to retained on 4 mesh	3.6
From passing 4 mesh to retained on 6 mesh	2.8
From passing 6 mesh to retained on 8 mesh	4.6
From passing 8 mesh to retained on 10 mesh	5.9
From passing 10 mesh to retained on 14 mesh	18.2
From passing 14 mesh to retained on 20 mesh	22.8
From passing 20 mesh to retained on 28 mesh	6.8
From passing 28 mesh to retained on 35 mesh	0.2
From passing 35 mesh to retained on 100 mesh	0.1
Passing 100 mesh	35.0
Total	100.0

The fired dolomite exhibits an average analysis of: 1.3% SiO_2, 6.2% R_2O_3 (Fe_2O_3 and Al_2O_3), 56.6% CaO, 0.4% ignition loss and 35.5% MgO (by difference). The fired dolomite batch mix is thoroughly mixed and is heated to from 180–189° C. and is admixed with 6%, calculated on the total mineral component, of coal tar which has a softening point of 81° C., determined by the well-known cube-in-water method, and which is heated to the same temperature as the dolomite. The whole is thoroughly mixed and is then divided into two portions, A and B. To portion B there is added 0.2% stearic acid based on total weight of batch B and this portion is then thoroughly mixed. Each portion A and B is again subdivided into two batches, A–1 and A–2, and B–1 and B–2.

Batches A–1 and B–1 are formed into bricks of size 9" x 4½" x 3", in a brick press, using 8000 lbs. per square inch forming pressure. Batches A–2 and B–2 are formed into bricks 9" x 4½" x 3", with vibration of the molds and application of low pressures of about 60

lbs. per sq. in. to tailor the bricks properly. The bricks exhibit the following densities:

A–1, using pressure alone and no stearic acid	186.8
A–2, vibration and pressure, no stearic acid	185.8
B–1, pressure alone, and stearic acid	188.6
B–2, vibration and pressure, and stearic acid	187.9

It can be seen that the bricks formed with low pressures, using vibration, have densities approximately as good as those made with high forming pressures, and where the surfactant is used, the density is higher.

Bricks of above mixes B–1 and B–2 were placed as portions of the lining in a test furnace, using mortar of the same composition to form the joints between the bricks, and the furnace was fired up at such rate as to coke the binder rapidly while simultaneously avoiding disruption of the brick surfaces by too rapid evolution of the vapors. The furnace is heated to 1800° F., and is then charged with pig iron and scrap steel, and lime is added to form a slag; and the metal is melted. The molten, slag-covered mass of metal is blown with oxygen introduced through a vertical tube suspended over the melt and terminating a few inches above the normal slag surface. After the blow is completed, as observed by the shortening of the flame, the flow of oxygen is stopped and the metal and slag contents are tapped off. The minimal thickness of the brick at the slag line is measured after eight such blowing cycles. The bricks formed with vibration and pressure and using stearic acid showed about 10% greater remaining brick volume than those formed under pressure alone and using stearic acid. These tests simulate the operation of a top-blown oxygen steel converter.

It is an advantage of the present invention that a dense and strong dolomite brick is obtained by the use of vibration and low pressure, substantially without cracking of the dolomite grains. There is achieved greater hydration resistance, or greater stability toward atmospheric conditions. The incorporation of a surfactant or surface active agent provides a better coating of the grain with the tar or carbonaceous bond, aids in securing greater density and increased resistance to atmospheric influences including hydration and carbonation, as well as greater erosion resistance of the furnace linings.

It has been found further that the addition of a small amount, up to about 2% of the total refractory batch, of a surface active agent or a wetting agent substantially improves the density of refractories made according to the invention and also appreciably further improves the storage life thereof. A suitable surface active agent is a polar compound having a tar-soluble group and a polar group, as described hereinabove. For example, a long chain fatty acid, such as stearic acid, is useful, but other surface active agents can be advantageously employed, such as heptadecylamine, etc.

Other cokable, carbonaceous binders, which are likewise non-aqueous, can be used in the invention, as previously described. When forming shapes according to this invention by filling into a mold or molding zone while vibrating said mold and applying low pressures of up to not over 3000 p.s.i., preferably up to not over 1000 p.s.i., it is preferred to heat the carbonaceous bonding agent described to liquefaction, to facilitate thorough mixing and good tailoring of the product.

Amounts and percentages referred to in the specification and claims are by weight unless otherwise indicated. Mesh sizes referred to herein are Tyler standard screen sizes, which are defined in Chemical Engineers' Handbook, John H. Peery, Editor-in-Chief, second edition, 1941, published by McGraw Hill Book Company, at page 1719. For convenience, the fired dolomite component is sometimes referred to herein merely as "dolomite," and this term is to be understood to refer to dolomite which has been calcined, or fired, or deadburned, for example, by heating from 1550° C. to 1800° C., until deadburned, unless otherwise indicated. Where mineral components are referred to, the term is to be understood to include the metal oxides or compounds and to exclude the carbonaceous bonding agent. In the specification and claims, analyses where given are reported in the usual manner in this art, expressed as simple oxides, although the components may actually be present in combination with each other.

This application is a continuation-in-part of my copending application, Serial No. 804,285, filed April 6, 1959 now U.S. Patent 2,943,240, issued June 28, 1960, and of my copending application, Serial No. 11,579, filed February 29, 1960, and entitled "Furnace Structures," now abandoned.

Having now described the invention,

What is claimed is:

1. In a furnace for operation at high temperatures, a metal shell and disposed therein a refractory lining consisting essentially of an intimate mixture of coarse fired dolomite grains, finely divided fired dolomite and from 4% to 10% of a nonaqueous cokable, carbonaceous bonding material, said lining having been formed by vibration while applying low pressure insufficient in itself to form a dense lining.

2. Method of making a dense refractory shaped product which comprises preparing a refractory batch composed of a major portion of coarse, fired dolomite grains and a minor portion of finely divided fired dolomite, heating said batch to a temperature of from 120° C. to 220° C., heating a nonaqueous cokable carbonaceous bonding agent to such temperature, and admixing with said refractory batch from 4% to 10% of said binding agent to form an intimate and uniform mixture, and forming into shape while vibrating and applying a low pressure insufficient alone to form a dense shape.

3. Method as in claim 2 wherein said pressure is not over 3000 p.s.i.

4. Method as in claim 2 wherein said pressure is not over 1000 p.s.i.

5. Method as in claim 2 wherein said pressure is about 60 p.s.i.

6. Method as in claim 2 wherein there is incorporated in said batch a minor amount, up to 2% based on the weight of the batch, of a surface active agent.

7. Method as in claim 6 wherein said surface active agent is stearic acid.

8. Method as in claim 6 wherein there is incorporated as said surface active agent from 2% to 5% of stearic acid, based on total weight of carbonaceous agent.

9. Dense, unfired shaped refractory consisting essentially of an intimate admixture of at least 50% of coarse, fired dolomite grains, not over 50% of finely divided, fired dolomite, from 4% to 10% tar and from 2% to 5%, based on the weight of tar, of a surface active agent, and formed into shape by vibration while applying low pressure insufficient alone to form a dense shape.

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