Patented Feb. 5, 1946 2,394,304

UNITED STATES PATENT OFFICE

2,394,304

REFRACTORIES

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No Drawing. Application August 26, 1944, Serial No. 551,449

23 Claims. (Cl. 106—59)

This invention relates to refractory bodies of the type generally known as "chrome-magnesite" or "chrome-magnesia" refractories. Such refractories are well known and widely used in the metallurgical industries, particularly in the construction of basic open hearth furnaces for the production of steel. The use of refractories of this type in the basic open hearth furnace has been largely restricted to service in front walls, back walls, end ports and other parts of the furnace above the hearth level. They have been used to a limited extent in roof service, such use being restricted to a few courses of brick lengthwise of the furnace along the skews. But up to the present time complete roofs have not been successfully nor economically used.

Among the purposes of this invention are the development of a superior brick of the chrome-magnesia type for the general services in which such brick are now used in basic open hearth furnaces, and the development of a brick of the chrome-magnesia type which is practically and economically adapted to roof service. Other advantages of the invention will become apparent from the description which follows.

The destruction of basic refractories in service is caused by reaction with iron oxides, reaction with slags, failure under load, spalling, mechanical breakage, and other factors. Exposure of the brick to attack by iron oxides and by slags at high temperature is inherent in open hearth practice. Under service conditions failure under load and spalling are influenced to a large degree by the above reactions. The temperature of failure under load may drop considerably as the brick are exposed to, and react with, iron oxides and slags. The type of spalling changes as the brick absorbs or is coated by the materials to which it is exposed. The furnace operator has no control over these factors; that is, he cannot avoid exposing the brick to furnace dusts and slags; therefore, improved refractory performance with respect to these factors is to a large degree a matter of improved refractories. On the other hand, mechanical breakage, and often destruction by pure thermal shock, that is, spalling uninfluenced by furnace conditions, are to some extent controllable by the operator, and failures due to them are not always blamable on the refractories. Therefore, improved refractory performance with respect to controllable factors is a function of operating practice. The product of this invention yields greatly improved performance with respect to the factors over which the operator has no control, and practically eliminates the most destructive influence on the furnace refractory, namely the "bursting" or swelling due to attack by iron oxide at high temperature.

The product of this invention combats the most active cause of destruction by providing a refractory with greatly increased resistance to iron oxides and slags at elevated temperatures. Its resistance to failure under load at service temperature is eminently satisfactory and measured in laboratory tests is of the same magnitude as the load test values of the chrome-magnesia refractories heretofore used. The spalling characteristics of the brick are greatly improved, especially in roof service, where it has been noticed that heretofore used brick of the chrome-magnesia type tend to absorb or become coated with iron oxide, then spall or peel in sections of appreciable thickness, sections up to 1½" thick separating from the entire exposed face of the brick. In service spalling of the product of this invention takes place very slowly, occurring as a slow breaking off of very small or thin flakes, apparently of the magnitude of $\frac{1}{16}$" to possibly ½" in thickness.

The objects of the invention are accomplished by making the refractory body from a mixture composed of 50 to 75 parts by weight of chrome ore, 25 to 50 parts by weight of periclase, 5 to 12.5 parts by weight of iron oxide and up to 10 parts by weight of high silica clay. Under certain conditions, as explained later, the clay may be eliminated from the mixture. On firing, either previous to, or after, installation for service in a furnace, there is obtained a refractory body comprising chromite spinel, in a matrix of periclase, forsterite, and magnesioferrite.

The novelty of the invention lies in the addition of an appreciable proportion of iron oxide to the brick forming mix. Chrome ore-periclase mixes, or other mixes which will yield chromite-forsterite refractory bodies are well known to the art, and clay (and similar materials such as pyrophyllite) are used in some instances, but the use of iron oxide bearing materials has always been avoided as extremely detrimental, so that the results obtained by the product of this invention are unobvious and unexpected.

Several reasons can be advanced for the greatly improved resistance of the body thus formed to iron oxide attack at high temperatures. It is known that the addition of iron oxide to a straight chrome ore body will, on heating, cause the body to swell and lose its refractoriness. It is also known that the addition of iron oxide to periclase will cause the body to shrink on heating.

Bodies made from mixtures of chrome ore and periclase, such as the heretofore used chrome-magnesia refractories, show an increase in refractory qualities as the amount of periclase in the mix is increased from about 10% to about 40%, but such bodies are very susceptible to attack, particularly by iron oxides at high temperatures.

In the product of this invention, the iron oxide addition increases the resistance to attack by iron oxide at high temperatures. The function of the iron oxide is not completely understood at the moment. It is known that some of the periclase in the mixture reacts with the silica and silicates present to form forsterite. Another portion of the periclase reacts with at least some of the iron oxide to form magnesioferrite ($MgO.Fe_2O_3$), a compound with a high melting point. It is further known that Fe_2O_3 goes into solid solution in periclase, the amount dissolved varying as the temperature changes. Magnesioferrite and periclase form a continuous series of solid solutions, their relative amounts changing upwardly and downwardly with increases or decreases in temperature, but it seems that such continuous changes in mineralogical composition can take place while maintaining the stability of the body against attack by outside oxides or slags. There is also the possibility that under service conditions the exposed face of the body tends to glaze to some extent, forming a protective face similar to that obtained on silica brick in open hearth roof service.

In the practice of the present invention, the following materials are used:

Chrome ore.—50 to 75 parts by weight. Chrome ore containing less than 6% of silica, less than 15% total iron as FeO, less than 1% CaO and with sum of Cr_2O_3 and Al_2O_3 approximately 60% is preferred. Excellent results were obtained with chrome ore analyzing Cr_2O_3 30.73%, total iron as FeO 12.50%, Al_2O_3 29.73%, SiO_2 5.35%, CaO 0.93% and MgO 18.47%. Chrome ore of approximately this analysis was used to make the brick in the examples described herein. The chrome ore should be dense and close grained, so that on grinding hard grog is obtained. The chrome ore used in the practice of this invention is ground to substantially all passing a 6 mesh Bureau of Standards screen, and substantially all remaining on a 100 mesh Bureau of Standards screen.

Periclase.—25 to 50 parts by weight. The periclase preferred is relatively pure, and deadburned to the point at which substantially no residual shrinkage remains. Preferably it should contain less than 6% SiO_2, less than 0.5% Al_2O_3, less than 2% CaO, and more than 90% MgO. Excellent results were obtained with periclase analyzing MgO 91.5%, Fe_2O_3 0.6%, Al_2O_3 0.3%, SiO_2 5.8%, porosity 13.0%. Periclase of approximately this analysis was used to make the brick in the examples given herein. The periclase is preferably ground to substantially all through a 100 mesh Bureau of Standards screen, with at least 80% passing a 200 mesh Bureau of Standards screen. The practice of the invention is not limited to periclase of the mesh ratio described. Excellent results have been obtained with periclase ground to pass a 20 mesh Bureau of Standards screen, with 45% passing a 200 mesh Bureau of Standards screen.

Iron oxide.—5 to 12.5 parts by weight. A relatively pure source of iron oxide in a fine state of subdivision is preferred. Such sources are pyrites cinder containing 90% or over Fe as Fe_2O_3 on the dry basis, or aniline sludge of the same analysis. Excellent results have been obtained with aniline sludge analyzing on the dry basis total Fe as Fe_2O_3 92.5%, SiO_2 3.8% with small amounts of carbon and other impurities. Aniline sludge offered a further advantage for experimental purposes in that it is obtained in a very fine state of subdivision, over 90% passing a 200 mesh Bureau of Standards screen as received, eliminating the need for fine grinding, since in the practice of this invention the iron oxide is preferably at least 90% minus 200 mesh. The iron oxide addition may be made directly to the refractory mix, or it may be added in the form of a high iron periclase. The latter method provides the advantage of large iron oxide additions to the magnesite before deadburning, aiding in the production of periclase with very low residual shrinkage. Brick have been made both ways with good results, so the choice of a method would be determined by the relative economics with available equipment.

Although the total Fe, reported as Fe_2O_3, is of the same magnitude, that is approximately 92%, in both the aniline sludge and the pyrites cinder, it is recognized that the actual form of the iron present differs in the two materials. In the pyrites cinder the iron is actually present as Fe_2O_3, while in the aniline sludge the iron is present as Fe_2O_3 and FeO, and sometimes as Fe. Apparently, the degree of oxidation, that is, whether the iron in the materials is in the ferric or ferrous condition, does not affect the quality of the finished product.

High silica clay.—Up to 10 parts in weight. The clay used in the examples described analyzed SiO_2, 75 to 85%, Al_2O_3, 5 to 11%. Because the material is so highly siliceous (the X-Ray pattern shows strong lines of alpha quartz) it is not a clay in the regularly accepted sense of the term. In fact very finely divided silica can be used, but the clay described is advantageous over silica in that it imparts some plasticity to the mix and aids in pressing the mixture into brick form. The inclusion or omission of the clay depends upon the desired qualities of the product, as will be brought out later.

Brick made of the compositions covered by the above ranges have been compared to the chrome-magnesia brick heretofore in wide use in the steel industry. The product of this invention is at least equal to the previously used chrome-magnesia brick in the refractory qualities usually considered. However, in its resistance to attack by iron oxide at high temperatures, tremendous and unexpected improvement is obtained. The same is true regarding resistance to thermal shock (spalling) on many of the combinations, falling within the scope of this invention.

Several methods can be used to measure the resistance of a refractory body to iron oxide at high temperatures. The method used to obtain the figures given in the examples described was found to give concordant quantitative results in the laboratory, and the results were confirmed by field tests under operating conditions. The tests were run as follows: A 3" by 3" by 4½" section was cut from the brick to be tested. The test piece was placed in the furnace on a 3" by 3" face, with a pellet of iron oxide weighing 150 grams on top of it. The piece was heated to 3000° F. in an oxidizing atmosphere, reaching 3000° F. in five hours, and held at 3000° F. for three additional hours. The pieces were then cooled. The face on which the iron oxide pellet was placed was

carefully measured before and after the test. The "iron oxide absorption" was then reported as the percentage area expansion of this face. The tests were run in a special furnace in which 30 pieces could be tested simultaneously, and all comparative tests were made during the same burn. Each burn also contained standard commercial chrome-magnesia pieces for "controls."

The combination of starting materials is chosen to yield a product having the most desirable characteristics for the purpose intended. The data in the following table of examples shows how the proportion of starting materials may be varied within the ranges covered, thus varying the refractory characteristics slightly in one direction or another, without seriously affecting the ability of the product to resist iron oxide attack at high temperatures. The ingredients of the brick forming mixture are dry mixed and tempered in a wet pan with the addition of water and temporary binders to a consistency which will permit pressing. The temporary binders referred to are such materials as sulphite pitch, starch, etc. which are regularly used in brick plant practice as a means of imparting dry or "green" strength to the pressed brick to permit handling in travel from the dryer to the firing kiln. Such binders have no relation to the chemical bonding agents later mentioned. The mixture is pressed into brick, which are dried and fired to a temperature in excess of 2700° F. In practicing the invention, it is preferable to use the well known "dry-press" process for forming the brick, and to fire the brick in a tunnel kiln. This procedure is preferable only, and the practice of the invention is not limited to it. The desirable firing temperature will vary somewhat with the composition of the brick, but 2700° F. is an operable minimum temperature, and a temperature to yield optimum results in any case can readily be determined by an experienced operator.

In the following table of examples, typical combinations are shown, with the percentage expansion on exposure to iron oxide in each case. The standard given at the top of the list is a typical commercial brick of the heretofore used chrome-magnesia type, containing no iron oxide added as such.

Example	Chrome ore	Periclase	Iron oxide	Clay	Expansion
	Parts	*Parts*	*Parts*	*Parts*	*Percent*
Standard	75	25	None	2.5	40.00
1	75	25	10	2.5	23.32
2	70	30	10	2.5	20.32
3	70	30	5	5.0	9.78
4	65	35	10	2.5	7.61
5	65	35	5.0	2.5	10.88
6	65	35	5.0	5.0	15.91
7	60	40	10	2.5	3.33
8	60	40	5.0	2.5	9.78
9	60	40	5.0	10.0	15.96
10	60	40	10.0	10.0	15.67
11	60	[1] 28	[1] 12	None	5.70

[1] In this example a mixture of 70 parts of periclase with 30 parts of iron oxide was nodulized, and the brick forming mix consisted of 60 parts of chrome ore and 40 parts of the finely ground nodules

The eleven examples in the table illustrate the flexibility of the process of the invention, and serve as a guide to the practice of the invention. Heretofore used chrome-magnesia refractories were made from a mixture of 70 to 80 parts of chrome ore, 20 to 30 parts of periclase and optionally up to 10 parts of clay, this range covering the majority of the products of this type. The "standard" used for comparison in the above table can therefore be considered an average of the previous practice. Some of the manufacturers used various amounts of olivine, or other forsterite bearing material as mineralizers, but such additions will have no effects, either good or bad, on the product of this invention, since the silicates of the starting materials are converted to forsterite in the final product.

It is noted that the addition of 10 parts of iron oxide to the standard mix decreased the iron oxide attack by 50%. Increasing the proportion of periclase with respect to the chrome ore makes a further improvement, so that 60 parts of chrome ore, 40 parts of periclase, 10 parts of iron oxide and 2.5 parts of clay, yield a refractory with an iron oxide attack value of only 3.33%. In other words, the "bursting" of chrome-magnesia brick due to the attack of iron oxide has been virtually eliminated. Varying the proportions of iron oxide, of clay, and the chrome ore-periclase ratio within the ranges of the invention shows that very desirable and unexpected results are obtained, with some leeway as to proportions should any particular combination be desirable. Example 11 is illustrative of the point that it is not necessary to add the iron oxide as such, because in this example special periclase was first prepared by calcining a mixture of 70 parts of periclase and 30 parts of iron oxide. Chrome-magnesia brick made by using 40 parts of the special high iron periclase with 60 parts of chrome ore were excellent in all their characteristics.

When chrome ore high in iron is used as the source of the iron, poorer results are obtained, and although such ore falls within the broad scope of the invention, its use is not preferred.

The proportion of clay, if any, to be used is determined by the characteristics of the raw materials available and by the properties desired in the finished brick. For example, when precalcined chrome ore is used, the addition of clay increases the plasticity of the mix going to the brick presses, and results in a brick of greater density and lower porosity and therefore increased resistance to attack by iron oxide and furnace slags. On certain types of crude ore, for instance, the ore from the Selukwe district in Southern Rhodesia, the clay has a similarly beneficial effect. On other types of chrome ore, for example, the ore from central Cuba or from the Masinloc deposits in the Philippine Islands, the effects of the clay on the porosity of the brick are not so pronounced, and in such cases the clay may be omitted, without noticeably deleterious effects.

In some instances, the clay addition causes a slight increase in the "bursting" effect produced by iron oxide attack at high temperatures, but the magnitude of this increase is negligible compared to the advantages obtained. A further advantage of the clay lies in the fact that it introduces an additional small amount of liquid phase into the body at high temperatures, thereby producing a resiliency which has a decidedly beneficial effect on the spalling characteristics of the product. While this effect is not readily measurable in quantitative terms by laboratory tests, it is readily apparent in practice. The entire roof of a large open hearth furnace was constructed with the product of this invention, and after 90 heats showed no loss due to the spalling of thick pieces of the refractory. The loss in roof thickness over this portion of the campaign resulted from very slow flaking in very thin sections, probably $\frac{1}{16}$'' to $\frac{1}{8}$'' thick, so that no spalls were apparent. The wear on the roof

was very much less than the year in similar service of standard chrome-magnesia refractories.

In the practice of the invention a mixture comprising 50 to 75 parts by weight of substantially through 6 mesh on 100 mesh chrome ore, 25 to 50 parts by weight of substantially minus 100 mesh periclase, 5 to 12.5 parts by weight of substantially minus 100 mesh iron oxide, and up to 10 parts by weight of substantially minus 100 mesh clay is dry mixed, tempered, and formed into brick. The mixing, tempering and pressing are done in accordance with approved brick making practices. The preferred procedure is to start with a mixture of 60 parts chrome ore, 40 parts periclase, 10 parts iron oxide and 2.5 parts high silica clay, dry mix thoroughly in a rotary drum mixer, temper in a wet pan with approximately 3% of water and a temporary binder such as sulphite pitch, and press the mixture into brick by the so-called dry press method. The brick shapes are dried and fired, preferably in a tunnel kiln, to a temperature of at least 2700° F. or slightly higher if necessary to obtain a well developed ceramic bond. As a result there is produced a refractory body comprising chromite spinel in a matrix of forsterite, periclase and magnesioferrite, which has all the desirable qualities of the heretofore used chrome-magnesia refractory bodies, and in addition, a greatly increased resistance to attack by iron oxide at high temperature.

Equally good results are obtained in service by the use of unfired, chemically bonded brick of the same compositions. The preparation of the chemically bonded brick differs from the procedure described above in that a chemical bonding agent such as magnesium chloride, magnesium sulphate, sulphuric acid, etc. is added to the starting mixture, either in the dry mixer or in the wet pan. 3% of magnesium sulphate, or 1.5% of sulphuric acid give excellent results. After forming, the brick are dried to about 350° F., and on cooling are ready for shipment to the point of installation.

The novelty of the invention lies in the inclusion of an iron oxide bearing material, and optionally of a highly siliceous clay, in the starting mixture for producing a chrome-magnesia type refractory. The product of the invention is a brick of the chrome-magnesia type with tremendously improved resistance to attack by iron oxide at elevated temperatures, and with greatly improved spalling characteristics due to the elimination of the tendency to spall in thick sections.

I claim:

1. A refractory comprising 50 to 75 parts by weight of chrome ore, 25 to 50 parts by weight of magnesium oxide and 5 to 12.5 parts by weight of iron oxide.

2. A refractory comprising 50 to 75 parts by weight of chrome ore, 25 to 50 parts by weight of magnesium oxide, 5 to 12.5 parts by weight of iron oxide and up to 10 parts by weight of clay.

3. A refractory comprising about 60 parts by weight of chrome ore, about 40 parts by weight of magnesium oxide, about 10 parts by weight of iron oxide, and about 2.5 parts by weight of clay.

4. A shaped refractory body highly resistant to attack by iron oxide at elevated temperatures comprising 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of magnesium oxide less than 100 mesh in particle size, and 5 to 12.5 parts of iron oxide less than 100 mesh in particle size.

5. A shaped refractory body highly resistant to attack by iron oxide at elevated temperatures comprising 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of magnesium oxide less than 100 mesh in particle size, 5 to 12.5 parts of iron oxide less than 100 mesh in particle size, and up to 10 parts by weight of clay less than 100 mesh in particle size.

6. A shaped refractory body highly resistant to attack by iron oxide at elevated temperatures comprising about 60 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, about 40 parts by weight of magnesium oxide less than 100 mesh in particle size, about 10 parts of iron oxide less than 100 mesh in particle size, and about 2.5 parts by weight of clay less than 100 mesh in particle size.

7. An unfired refractory body highly resistant to attack by iron oxide at elevated temperatures comprising 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of magnesium oxide less than 100 mesh in particle size, and 5 to 12.5 parts of iron oxide less than 100 mesh in particle size.

8. An unfired refractory body highly resistant to attack by iron oxide at elevated temperatures comprising 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of magnesium oxide less than 100 mesh in particle size, 5 to 12.5 parts of iron oxide less than 100 mesh in particle size, and up to 10 parts by weight of clay less than 100 mesh in particle size.

9. An unfired refractory body highly resistant to attack by iron oxide at elevated temperatures comprising about 60 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, about 40 parts by weight of magnesium oxide less than 100 mesh in particle size, about 10 parts of iron oxide less than 100 mesh in particle size, and about 2.5 parts by weight of clay less than 100 mesh in particle size.

10. A shaped refractory article formed from a batch mixed with water and about 1.5% of sulphuric acid and comprising 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of magnesium oxide less than 100 mesh in particle size, and 5 to 12.5 parts of iron oxide less than 100 mesh in particle size.

11. A shaped refractory article as in claim 10 in which the batch includes up to 10 parts by weight of clay less than 100 mesh in particle size.

12. A shaped refractory article formed from a batch mixed with water and about 3% of magnesium sulphate and comprising 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of magnesium oxide less than 100 mesh in particle size, and 5 to 12.5 parts of iron oxide less than 100 mesh in particle size.

13. A shaped refractory article as in claim 12 in which the batch includes up to 10 parts by weight of clay less than 100 mesh in particle size.

14. The process of making refractory bodies highly resistant to attack by iron oxide which comprises mixing and tempering 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts of per-

iclase less than 100 mesh in particle size, and 5 to 12.5 parts of iron oxide less than 100 mesh in particle size, pressing the mixture into shapes and drying the shapes.

15. The process of making refractory bodies as in claim 14 which comprises the inclusion of up to 10 parts by weight of clay in the starting mixture.

16. The process according to claim 14 which comprises the use of about 1.5% of sulphuric acid in the starting mixture.

17. The process according to claim 14 which comprises the use of about 3% of magnesium sulphate in the starting mixture.

18. The process of making refractory bodies which comprises mixing and tempering about 60 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, about 40 parts of magnesium oxide less than 100 mesh in particle size, about 10 parts of iron oxide less than 100 mesh in particle size, and about 2.5 parts by weight of clay less than 100 mesh in particle size, adding sulphuric acid in the amount of about 1.5% of the weight of the batch while tempering, pressing the mixture into shapes, and drying the shapes at about 350° F.

19. The process of making refractory bodies which comprises mixing and tempering 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of periclase less than 100 mesh in particle size, and 5 to 12.5 parts by weight of iron oxide less than 100 mesh in particle size, pressing the tempered mixture into brick, drying, and firing the brick to a temperature of at least 2700° F.

20. The process of making refractory bodies which comprises mixing and tempering 50 to 75 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, 25 to 50 parts by weight of periclase less than 100 mesh in particle size, 5 to 12.5 parts by weight of iron oxide less than 100 mesh in particle size, and up to 10 parts by weight of clay less than 100 mesh in particle size, pressing the tempered mixture into brick, drying, and firing the brick to a temperature of at least 2700° F.

21. The process according to claim 20 in which the periclase is less than 20 mesh in particle size.

22. The process according to claim 14 in which the periclase is less than 20 mesh in particle size.

23. The process of making chrome-magnesia refractory bodies which comprises mixing and tempering about 60 parts by weight of chrome ore approximately 6 mesh to 100 mesh in particle size, about 40 parts by weight of periclase less than 100 mesh in particle size, about 10 parts by weight of iron oxide less than 100 mesh in particle size and about 2.5 parts by weight of clay less than 100 mesh in particle size, pressing the tempered mixture into brick and firing the brick to a temperature of at least 2700° F.

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