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PROCESS FOR REDUCING DETERIORATION IN EQUIPMENT HANDLING MOLTEN MATERIALS

Virgil S. Tadsen, Rossford, Ohio, and Gerhard J. Derge, Pittsburgh, Pa., assignors, by mesne assignments, to Chas. Pfizer & Co., Inc., New York, N.Y., a corporation of Delaware

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This is a continuation-in-part of U.S. patent application Serial No. 251,757, filed January 16, 1963 entitled "Improved Process Slags, and Refractories for Reducing Deterioration of Refractories in Equipment Handling Molten Materials," now abandoned.

The present invention has particular utility in metallurgical processes which utilize vessels lined with basic refractories that are in contact with molten slags which contain calcia, and has greatest application in steel producing processes which utilize slags containing calcia as well as silica and/or alumina, and magnesia refractories.[1]

The metallurgical equipment which is utilized in the refining and handling of molten steels is generally constructed by means of steel shells that are lined with a refractory which in turn contains the molten metal. Slags of molten metal oxides and/or other compounds are usually used in these processes to cover the molten metals, and to aid in the purification of the molten metal. The slaps which are used in the various metallurgical processes are of two groups: one group is basic in character and is known as "basic type" slag, and the other group is acidic in character and is known as "acid type" slag. Silica, alumina, and phosphates cause slags and refractories to be acid in character; while CaO and MgO are the principal ingredients which cause refractories and slags to be basic in character. Where acid refractories are used to line metallurgical equipment, it is necessary that the slags be acid in character; and where basic refractories are used to line metallurgical equipment, it is necessary that the slags be basic in character.

"Basic type" slags, in which the basic material is principally calcia, are known as "calcia type" slags, and have particular advantages in the manufacture of steel, inasmuch as they have high heat conductivity and remove sulfur and phosphorous from the molten metal, and accordingly, "calcia type" slags have wide spread use in steel making processes. Various steel making equipment may be operated with "calcia type slags," as for example, open hearth furnaces, Bessemer converters, electric furnaces, and basic oxygen furnaces, e.g. those in which the processes disclosed in Blast Furnace and Steel Plant, July 1961, pages 621–632, and cited references, and in Ceramic Bulletin 39, No. 5, 1960, pages 261–263, are practiced; and when such is the case, magnesia refractory is the preferred material for lining the equipment. The term "steel making processes," as used herein, refers to all of the foregoing processes. In equipment that is lined with a basic refractory, it is necessary that the molal ratio of the basic ingredients of the slag to the acid ingredients of the slag be greater than 1.5:1 e.g. at least about 1.6:1; the ratio should preferably be between 2.0:1 and 4.5:1; and most desirably between 2.5:1 and 3.5:1. These ratios are frequently stated less accurately on a weight basis.

Magnesia refractories are obtained by burning magnesium oxide containing materials—for example, magnesium carbonate ores containing some impurities, or the magnesium hydroxide that is precipitated from solutions, including sea water. During the burning process, the carbon dioxide or water, as the case may be, is driven off leaving magnesium oxide with minor amounts of impurities.

Magnesium oxide can exist in either of two states which differ in structure and properties. During the initial burning of the magnesium carbonate, the alpha or amorphous state of MgO is first achieved. Amorphous magnesia is quite reactive; it hydrates readily and is an active fluxing agent for metals. Upon further burning of the amorphous magnesia, the MgO changes over to its beta phase which is crystalline in character and highly thermal resistant. This beta phase is commonly called periclase. The melting point of periclase varies depending upon the impurities contained or associated therewith, and can be as high as 2800° C. The transition of magnesia from its alpha to its beta phase may be quite slow. The burning of magnesium carbonate to periclase crystals is promoted by the molten glassy materials that are generally formed by the impurities found in the magnesium carbonate ores. These impurities generally include SiO_2, Al_2O_3, Fe_2O_3 and CaO; and refractory manufactures may add small amounts of some of these materials to provide a molten flux which speeds up and catalyzes the substantially complete conversion of the alpha phase MgO into the periclase form.

The periclase crystals that are formed during burning of magnesium carbonate- or hydroxide-containing raw materials are quite small and must be held together by a binder in order to form refractory shapes. CaO, MgO, tar or pitch, and minor amounts of other materials added to or present in the raw materials before burning form this binder.

The amount of binder forming materials used generally comprises between about 6% and about 20% of the refractory, and these materials melt at the burning temperature to form a glassy phase around the periclase particles, or form a carbon binder. The other binder forming materials used may vary, but generally include CaO, MgO, Fe_2O_3, Cr_2O_3, Al_2O_3, and SiO_2 so as to form forsterite and spinals or other glassy materials, frequently in combination with tar or pitch.

After the $MgCo_3$ ores or precipitates are burned they are crushed and mixed with various additional binder materials, which may be temporary or permanent in nature, to hold the refractory grains in place. The additional binder materials may be more of the glassy phase materials, or they may be an asphaltic tar. The tar acts as a temporary binder, and is ultimately converted to a carbon binder. In one form commonly used, the crushed burned material is mixed with approximately 5% of asphalt and is pressed into the form of bricks at up to 100,000 pounds per square inch. The asphaltic material acts as a temporary binder which holds the brick together until it is used. Either by prior heating or during use, some of the tar or asphaltic material is decomposed to carbon and the glassy phase-forming binder materials which were incorporated during burning unite and cooperate with the carbon to form a binder network or binder networks. Since the particles of periclase generally key each other together and do not move provided they are not subjected to undue load prior to "burning in," refractory materials so formed can be used at temperatures above the softening or melting point of the glassy phase bond material.

Metallurgical equipment that is lined with refractories, including those enumerated above which are lined with magnesia brick, must either be taken out of operation periodically for lining replacement, or other provision must be made for lining maintenance. The deterioration of the magnesia refractory in steel making equipment is appreciable; and basic oxygen furnaces, for example, must

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[1] The term "magnesia refractories," as used herein, means refractories such as brick and rammed or monolithic linings containing substantial proportions of magnesia, frequently from about 35 percent by weight to virtually 100 percent.

currently be taken out of service frequently in order to have their working linings renewed. The actual cost of the lining, and the labor for installing it, is appreciable, as is the lost production during the relining operation; so that a sizable percentage of the cost of steel can be attributed to the direct and indirect costs of replacing the working lining of the metallurgical equipment used in its manufacture. It has been determined that approximately 15 pounds of refractory are consumed for every ton of steel that is produced in basic oxygen furnaces.

Accordingly an object of the present invention is the provision of new and improved means for reducing the deterioration of magnesia refractory materials used in steel making processes.

A more particular object is the provision of new and improved means for reducing the deterioration of magnesia refractories that are in contact with molten "calcia type" slags.

Another object of the present invention is the provision of new and improved slag forming materials for steel making processes of the "basic type" which greatly reduce the deterioration of the refractory used in the equipment involved, expedite operation by rapid formation of proper slag, or both.

Still another object of the present invention is the provision of new and improved binder materials for refractories which are used with specific slags, as, for example, the binder of the magnesia refractory for use with "calcia type" slags.

A further object of the present invention is the provision of a new and improved slag-making material which fluxes more rapidly than do presently used materials.

Still other objects and advantages of the present invention will become apparent to those skilled in the art to which the invention relates from the following description, which is intended only to illustrate and disclose, but in no way to limit the invention.

The present invention is based upon a realization that, at the elevated operating temperatures of steel making equipment, molten slags contained in the equipment form a liquid-solid ceramic system with the binders and the refractory of the ceramic linings of the equipment, and approach equilibrium with respect to each other by the migration of elements from one to the other. According to the invention, the binder and the slag that are used together may be tailored to one another, so that the main constituents of each match closely, and no great change in either is necessary for the two to reach equilibrium. If, for example, the molten slag that is in contact with a particular magnesia refractory contains all of the major alkaline earth metal oxides of which the refractory and binder are made, the driving force tending to cause the major constituents of the binder to go into solution in the slag is reduced; there is reduced dissolution in the slag; and the life of the refractory is increased. The term "alkaline earth metals" as used herein includes all the metals of Group II*a* of the periodic table having an atomic number from 12 through 56, i.e., magnesium, calcium strontium and barium, more particularly calcium and magnesium, and the term "alkaline earths" is used as meaning the oxides of these alkaline earth metals.

In the work which led to the present invention, it was found that when calcia and slag conditioners were charged to a particular basic oxygen furnace to produce a slag on top of a metal melt, the concentration of magnesium oxide in the slag changed from approximately 0% to 5% by weight. Observation of the phenomena involved at the elevated operating temperatures is practically impossible. It has now been demonstrated, however, that the MgO in the slag came from particles of periclase that were eroded or dissolved from the refractory during operation of the equipment.

The binder materials which hold the periclase particles in place in the refractory are of the same general nature as is the slag that is in contact therewith at the elevated operating conditions. The molten slag and the refractory binder make up a liquid-solid ceramic system which tends to reach an equilibrium state at the operating temperature of the equipment. The migration of the binder materials to the slag and vice versa loosens the periclase particles in the brick to speed up the deterioration of the surface of the brickwork. These concepts have been demonstrated by adding alpha phase magnesia in the form of dolomitic quick lime to the slag-forming materials charged to the same furnace. It was found that the rate of deterioration of the refractory was reduced substantially.

The ceramic binder materials that are formed during the making of present day magnesia refractory are either composed principally of spinels and silicates of magnesia, or include spinels and silicates of magnesia. One of the silicates which is commonly formed is forsterite ($2MgO.SiO_2$), although aluminum silicate may also be formed. The spinels which are usually formed are $MgO.Al_2O_3$. $MgO.Fe_2O_3$ and $MgO.Cr_2O_3$, or mixtures thereof. The overall composition of the ceramic binders of the refractory will, of course, be mixtures of the above spinels and silicates, and may include still others not mentioned, forming a highly complex mixture. The important feature for present consideration is that the ceramic binders that are usually formed and used contain MgO. The MgO that remains in the binder after firing is readily available to be fluxed out by slag as will later be described. The MgO constituent of the spinels and silicates is believed to be fairly reactive so that it is also fluxed to some extent by the slags. In any event, all commercial magnesia refractories include some form of MgO which goes into solution with calcia-iron-silica slags.

It is believed that the mere balancing of the concentrations of the major ingredients of the slag and refractory is not the sole phenomenon by which the great reduction in refractory deterioration is accomplished according to the invention. All of the exact reasons are not fully understood, inasmuch as exacting analyses cannot be made of the slag and refractory during operation of the furnace at the temperatures which are involved. It appears that the introduction of magnesia into a slag causes the formation of an adherent protective layer upon the surface of the magnesia refractory, and that this is an important contributing reason for the great reduction in refractory wear that is achieved by the present invention. Preferably the magnesia concentration in a "calcia type" slag should be between approximately 4% and approximately 12% by weight.

It is known that one of the first reactions which takes place in a steel making process is the conversion and oxidation of the dissolved silicon in the iron to molten impure silica. The molten silica thereafter reacts with other materials such as iron oxide, CaO and MgO. Before the molten silica has reacted with the basic constituents of the slag forming charge, it is highly corrosive to basic refractories, and experience has shown that an appreciable amount of the total loss of basic refractories occurs during the first few minutes of the steel making operations, during and immediately following the time that dissolved silicon is oxidized to silica. It has further been found that the speed with which the silica is neutralized is a function of the surface area of the alkaline earth metal oxides. While deterioration of magnesia refractory is reduced by the addition of any form of active magnesia, as above stated, a further decrease in deterioration of the magnesia refractory is achieved by the use of highly active pebble or finely divided alkaline earth metal oxides having a surface area greater than approximately 3.5 square meters per gram as determined by nitrogen absorption techniques. In fact, a decrease in deterioration of any basic refractory can be achieved by the use of any highly active pebble or finely divided alkaline earth metal oxide having a surface area greater than approximately 3.5 square meters per gram as determined by nitrogen absorption techniques, if it is used in sufficient quantities to react with the silica formed in situ to form a slag wherein the base to acid molal ratio is greater than 1:1 and thereby prevent the silica from contacting the refractory. It is necessary only to introduce the above mentioned highly active alkaline earth metal oxide in the region adjacent the refractory lining of the equipment in which processing is carried out, to prevent the silica formed in situ from contacting the refractory, and slower acting alkaline earth metal oxides can be used to neutralize the silica in interior portions of the equipment where there is no contact with the refractories. In any equipment using a magnesia refractory and wherein dissolved silicon is oxidized to silica, a reduction in lining deterioration can be achieved by using highly active calcia having a surface area greater than approximately 3.5 square meters per gram as determined by nitrogen absorption techniques instead of the conventionally used calcia, and the very best results can be achieved by using both the alpha magnesia and the calcia in the highly active form above described. The activity of calcia and magnesia, of course, varies with the calcining methods that are used in production, and the calcia and alpha magnesia in the metallurgical grade of dolomitic lime produced by the Gibsonburg Lime Products Company, of Gibsonburg, Ohio, give excellent results. When slags are formed by charging calcia or calcia and magnesia, having somewhat less than about 3.5 square meters per gram surface area, there is an increase in lining deterioration. This increase is particularly serious in rapid refining processes such as the basic oxygen process.

It has been found that the MgO in the slag gradually converts to the periclase form, which settles out in lower temperature portions of the slag as small solid crystals which mechanically thicken the slag. Inasmuch as the refractory is slightly cooler than the main body of slag, the layer of slag adjacent the refractory is more viscous and tends to be retained on the surface of the refractory. The conversion of MgO to periclase is a time rate function and the viscous layer adjacent the refractory of the furnace tends to be retained in the furnace when the main body of slag is dumped. As a consequence, more of the MgO in the viscous layer is converted to periclase after dumping, and in turn, further thickens the layer. As a result, a furnace which is operated using a slag charge containing dolomitic lime builds up a viscous slag layer on its refractory which greatly retards erosion thereof. What is more, the concentration of MgO in the viscous layer increases progressively, and equilibrium between the refractory and the viscous layer is approached. In addition, the viscous nature of the slag layer adjacent to the refractory lining impedes the passage of constituents which are not in equilibrium with respect to the main body of slag.

The present invention makes still other advantages possible. It is preferred to charge calcined dolomite, not only because it is low in cost, but also because the MgO is combined with approximately an equal molal percentage of CaO. Approximately equal percentages of CaO and MgO form, at a comparatively low temperature, melts having a high degree of fluidity. While it has been thought that the addition of MgO to a CaO type slag would lower the fluidity of the slag, it has been found that the addition of calcined dolomite causes the opposite effect and, in fact, makes it possible to eliminate the fluoride salts normally used in slag charges to induce fluidity. Fluoride salts are known to be detrimental to refractories; and in slag-charging compositions according to the invention, it is preferred either to eliminate the fluoride salts, or to keep their concentrations to a very low value, preferably below 3%.

With respect to the fluidity of slags containing magnesia derived from additions of dolomitic lime, and the thickening which occurs as the dissolved MgO is converted to periclase, it has been found that the MgO converts quite slowly to the periclase form when its concentration is below approximately 10 molal percent. Particular advantages occur, therefore, by the charging of the alpha MgO in the form of dolomitic lime because of its higher solution rate and lower melting point as a consequence of the presence of the alpha MgO in approximately a 1:1 molal ratio with CaO, since this is a low melting composition which melts readily, supplying alpha magnesia to the slag early in the heat. By controlling the amount of dolomitic lime that is added, relative to the total content of slag forming materials, to provide an MgO to CaO molal ratio of from 1:15 to 1:3, the rate of thickening is most favorably controlled.

As previously mentioned, the present invention not only contemplates tailoring the composition of the slag to the refractory binder as one of its embodiments, but also contemplates tailoring the composition of the binder to that of the slag charging materials as another embodiment. It is known that MgO combines with silica to form forsterite and that MgO will also combine with alumina, or ferric oxide to form high melting spinels. By using dolomitic lime in place of the usually used calcia lime as part of the binder material for the periclase particles of the refractory, a binder material is produced which is at first highly fluid at normal refractory firing temperatures, so that it flows around and encases the periclase particles. Thereafter some of the alpha MgO is transformed to periclase and the remaining MgO and the CaO form high melting forsterite and spinels which match those of the slag adjacent the refractory when both CaO and MgO are present in the slag.

In the manufacture of the refractory, therefore, dolomitic lime can be added to the $MgCO_3$ or $Mg(OH)_2$ raw materials in place of the CaO and other constituents which are presently added to make up the glassy phase-producing binder.

The CaO content of the calcined dolomite may form a spinel with alumina or ferric oxide, and will at the same time provide a CaO content in the binder which tends to match that of the slag. Most of the MgO of the dolomitic lime forms periclase, while the remaining portion may also form a spinel with alumina, ferric oxide, or other sesquioxides. Periclase particles are substantially insoluble in the slag-binder ceramic system, and to the extent that the MgO forms periclase, it does not enter into the reactive slag-binder system but hardens the binder around the original periclase crystals.

In order to demonstrate the beneficial results which are achieved according to the present invention, Table I has been prepared giving the pertinent information of some of the heats which have been run in a basic oxygen furnace. It will be understood, however, that the invention may be used with the various other types of metallurgical equipment utilizing slag in contact with basic magnesia refractory, and that the conditions which exist in the basic oxygen furnace are considered to be the most severe.

The basic oxygen furnace in which the various heats listed in Table I were made was lined with a high magnesia basic refractory having an MgO content of 76%. Each of the heats listed in the table was conducted by charging the furnace with a weighed amount of molten metal from a blast furnace. The composition of the metal had been previously determined. In accordance with the analysis of the metal, as received from the blast furnace, the amount of basic oxides required for the removal of the silicon, phosphorous, and sulphur of the metal charge was determined and added. Oxygen or oxygen-enriched air was directed at the surface of the slag and metal for a period of between 20 to 40 minutes following which the slag and metal were sequentially poured off into ladles and an analysis of their compositions was made. Because of the type of operation involved, weighing of the slag poured off was not feasible and the total weight of the slag was calculated, utilizing the amount of CaO which was charged to the furnace as CaO lime and as dolomitic lime. The CaO content of the CaO lime added was taken as 92%, and analysis indicated that it also contained approximately 1% MgO. The dolomitic lime on the other hand contains approximately 40% MgO by weight, and approximately 56% CaO by weight. From the total amount of the CaO added to the furnace, and from the percentage of the CaO found in the slag that was poured from the furnace, the total weight of slag was calculated.

A similar calculation was made to determine the total MgO charged to the furnace in both the CaO lime and the dolomitic lime. Knowing the total amount of slag that was poured from the furnace and the percent of MgO that was contained therein, the MgO content removed from the furnace was calculated. By subtracting the total MgO charged from the MgO removed from the furnace, a figure was obtained representing the amount of MgO which must have been removed from the refractory lining of the furnace.

Heat A is given as typical of the prior art heats wherein no dolomitic lime was used in the slag charge, and the only MgO which was present in the charge occurred as an impurity in the CaO lime. As previously indicated, this is only approximately 1%. It will be seen from this typical heat that, generally, about 1.4 parts of refractory are lost during each heat, when no MgO is charged to the slag forming materials. Heat B is given as typical of the results which are achieved when approximately 10% of the alkaline-earth metal oxides which are charged to the furnace are added in the form of magnesium oxide along with the usual prior art spar material. As is typical of this type of charge using both MgO and fluorospar (CaF_2), from approximately 0.7 to approximately 0.9 part of refractory is lost per heat.

Table I

Heat	Hot Metal Comp.				Analyses as Refined Percent by Weight				Start Temp., ° F.	Slag Charge, Parts by Wt.				Ratio CaO+MgO/Si+P+S
	Parts by Weight	Analyses as charged percent by Weight			C	Mn	P	S		Fe_2O_3 Pellets	Spar	CaO Lime	Dolom. Lime [1]	
		Si	Mn	S										
A	440	1.08	.40	.031	.08	.39	.008	.023	2,890	4	2	3.5	None	2.7
B	440	1.02	.40	.045	.21	.42	.011	.024	2,900	4	2	3.2	6.5	3.1
C	440	1.02	.40	.045	.06	.37	.011	.026	2,990	4	None	2.8	6.5	2.8
D-1	430	1.20	.45	.031	.15	.78	.012	.021	2,930	4	2	3.0	6.5	------------
D-2	440	1.20	.45	.031	.12	.46	.010	.020	2,930	4	2	3.0	6.5	------------
D-3	430	1.24	.46	.028	.15	.39	.012	.019	2,910	4	2	3.2	6.5	------------
D-4	430	1.28	.46	.024	.15	.39	.011	.019	2,930	4	2	3.4	6.5	------------
D-5	430	1.28	.46	.024	.08	.40	.010	.020	2,920	4	2	3.4	6.5	------------

Heat	Analysis, Percent by Weight				Parts by Weight								
	Fe	CaO	MgO	SiO_2	CaO From Lime	CaO From Dolom.	Total CaO Added	Calcul. Parts Slag	MgO From Lime	MgO From Dolom.	Total MgO	MgO in Slag	MgO From Brick
A	17.0	47.1	2.54	17.4	32.2	None	32.2	68.5	0.35	None	0.35	1.73	1.38
B	16.2	47.3	5.45	15.2	29.2	3.74	33	69.5	0.32	2.67	2.98	3.78	0.80
C	16.4	46.0	5.47	16.3	26	3.74	29.8	65	0.28	2.67	2.95	3.55	0.60
D-1	14.6	47.0	3.77	18.0	27.6	3.74	31.4	66.7	0.30	2.67	2.96	2.52	−0.45
D-2	12.3	53.1	5.15	15.0	27.6	3.74	31.4	59.2	0.30	2.67	2.96	3.05	0.09
D-3	12.5	49.5	6.12	16.5	29.2	3.74	33	66.4	0.32	2.67	2.98	4.07	1.08
D-4	11.9	52.1	4.42	16.5	30.6	3.74	34.4	66	0.33	2.67	3.00	2.92	−0.09
D-5	10.3	56.2	5.36	15.7	30.6	3.74	34.4	61.4	0.33	2.67	3.00	3.28	0.28

[1] The dolomitic lime had a surface area of 3.5 square meters per gram as determined by nitrogen absorption techniques.

Heat C is given as typical of the results achieved when approximately 10% of the total alkaline earth metal oxide slag charge is in the form of magnesium oxide and when no fluorspar is added to the charge. As shown in the Table, heats so made will generally give less than a 0.7 part loss of refractory during the run.

It will be understood that the data given for the heats A, B and C are only typical, and that there may well be a fluctuation in the results which are achieved from one heat to the next using what appear to be identical charging materials. The variations which are observed in various heats using similar charging materials are, of course, attributable to the fact that a layer of the slag materials adheres to the side surfaces of the refractory and that in some instances a greater amount of this material is poured from the furnace with the slag than in others. Variation in the amount of slag which remains on the refractory may be attributable to purely mechanical reasons and may also be attributable to variations in viscosity as a consequence of the differences in the temperature achieved during the various heats, the duration of the various heats, and minor variations of the composition of the resulting slag.

Heats D-1 through D-5 give the data obtained from five consecutive heats, and generally indicate the variations which may be observed in the calculations of the amount of refractory which is lost in any given heat period. In heat D-1, for example, there is shown a net gain of brick work of 3.45 parts while in heat D-3 there is a loss shown of 1.08 parts. The average for the heats D-1 through D-5, however, is 0.18 part, which is striking when compared with a typical prior art loss of furnace refractory of over 1.4 parts per heat, on a comparable basis, using conventional high CaO content lime.

Test results indicate that a tailoring of the slag to provide a dissolved MgO content of from between approximately 3 and approximately 15% of the total slag forming ingredients causes a very marked reduction in the amount of refractory that is lost during each furnace heat. Best results are achieved with between approximately 5% and approximately 10% of dissolved MgO. The above data further shows that an even further reduction in the loss of refractory is obtained by eliminating the fluoride containing materials which are normally added to the slag forming materials. As previously indicated, the MgO is preferably added in the form of dolomitic lime, or equivalents thereof from natural or purposely combined materials, and, as previously indicated, the amount of dolomitic lime which is used can be varied over a considerable extent so that amounts up to approximately 30% of the total charge can be in the form of the dolomitic lime. There appears to be no criticality in the lower limit of the amount of dolomitic lime which is charged, inasmuch as the beneficial effect which is achieved is generally proportional to the amount used. In order that a substantial advantage will be achieved, however, over the prior art calcium oxide lime slag forming materials, more than approximately 10% of the charge should be in the form of the dolomitic lime. A preferred range of dolomitic lime is between 15 and 20% of the total slag forming charge materials.

While the data given show the beneficial effects which are achieved utilizing slag forming materials that incorporate active MgO in contact with conventional refractory, a still further reduction in refractory lining consumption can be achieved by using the MgO slag forming materials of the present invention in combination with the improved refractory of the present invention wherein dolomitic lime is utilized as a major percentage of the refractory binder forming materials.

It will be apparent from the foregoing detailed discussion that the instant invention is concerned with refining slags which are used in contact with basic refractories, and particularly magnesia refractories having particles of periclase held together by a refractory binder which includes magnesia. The slags must have a base to acid molal ratio greater than 1:1, preferably greater than about 1.6:1, more desirably between 2.0:1 and 4.5:1 and should most desirably have a base to acid ratio of between 2.5:1 and 3.5:1. Since there is a change in the chemical composition of such slags during the refining process, and since such change involves an increase in the percentage of constituents other than alkaline earth metal oxides, it will be appreciated that the flux charge must contain considerably more than 60 percent of the alkaline earths. While the charging of magnesium carbonate or the like to metallurgical equipment may produce active magnesia in situ, such a procedure is not generally desirable because carbon dioxide or the like which is released causes extensive and uncontrolled foaming of the slag, and absorbs a considerable amount of heat from the metallurgical process. However, appreciable reduction in lining wear can be achieved in this way if appropriate steps are taken to compensate for the heat loss and to prevent foaming.

Not only must the slags of the invention have a base to acid ratio as specified above, but they must contain at least 10% and preferably more than 12% by weight of SiO_2, or 30% by weight of Al_2O_3, or an appropriate mixture of SiO_2 and Al_2O_3. Where a mixture of SiO_2 and Al_2O_3 forms the acid portion of the slags, the percent of SiO_2 therein when divided by 12% and added to the percent of Al_2O_3 therein divided by 30% should be at least equal to 1. In addition to having a proper base to acid ratio, and an amount of the acid ingredients as specified above, the slag must contain calcia as its principal basic constituent and must have a proper magnesia to calcia ratio in order that the slag will have the proper heat transfer characteristics. For best results the magnesia to calcia ratio should be not greater than about 1:3, should preferably be more than about 1:15, and for best results should be between about 2:15 and about 1:4. Higher percentages of MgO cause the slag to become more viscous and refractory, to hinder heat transfer to the metal, and the ratio of MgO to CaO should never be greater than 1:1. According to the invention it has been found that refractory wear can be effectively reduced by using MgO in the above percentage ranges, without decreasing the heat transfer, the fluidity, and other desirable characteristics which calcia-silica and calcia-alumina type slags have.

It will be seen that the objects heretofore enumerated, as well as others, have been accomplished, and that there has been provided a new and improved method of reducing the deterioration of the refractory used in metallurgical processes and equipment. According to one embodiment slag and refractory binder compositions are tailored relative to each other to provide a solid-liquid ceramic system at operating temperatures which is more nearly in equilibrium than are slag and binder compositions used heretofore. It is further to be understood that while the invention has been described in considerable detail, it is not limited to the particular embodiments shown and described; and it is intended to cover hereby all novel adaptations, modifications, and arrangements thereof which come within the practice of those skilled in the art to which the invention relates.

What we claim is:

1. In the operation of metallurgical equipment of the type wherein molten metal is covered by molten calcia type refining slags having a final composition including at least 10 percent by weight of SiO_2 and a base to acid molal ratio of at least 1.6 to 1 in contact with a magnesia refractory and which is exposed to a highly oxidizing atmosphere: the method of reducing the deterioration of the magnesia refractory by charging to the metallurgical equipment slag forming ingredients containing active MgO and CaO in particulate form, the ingredients including from approximately 10.0 percent to approximately 30.0 percent by weight of exposed calcined dolomite, and the limiting of the concentration of fluoride containing salts in the slag to less than approximately 3.0 percent by weight.

2. In the operation of metallurgical equipment of the type wherein molten metal is covered by molten calcia type refining slags having a final composition including at least 12 percent by weight of SiO_2 and a base to acid molal ratio between 2.0 to 1 and 4.5 to 1 in contact with a magnesia refractory and wherein a highly oxidizing atmosphere is blown into contact with the molten metal: the method of reducing the deterioration of the magnesia refractory by charging to the metallurgical equipment slag forming ingredients containing active MgO and CaO in particulate form, the ingredients comprising approximately 20.0 percent by weight of exposed calcined dolomite.

3. In the operation of metallurgical equipment of the type wherein molten metal is covered by molten calcia type refining slags having a final composition including at least 12 percent by weight of SiO_2 and a base to acid molal ratio between 2.0 to 1 and 4.5 to 1 in contact with a magnesia refractory and wherein a highly oxidizing atmosphere is blown into contact with the molten metal: the method of reducing the deterioration of the magnesia refractory by charging to the metallurgical equipment slag forming ingredients containing active MgO and CaO in particulate form, the ingredients comprising approximately 20 percent by weight of exposed calcined dolomite, and the limiting of the concentration of fluoride containing salts in the slag to less than approximately 3.0 percent by weight.

4. In the operation of metallurgical equipment of the type wherein molten metal is covered by molten calcia type refining slag having a final composition including at least 10 percent by weight of SiO_2 and a base to acid molal ratio of at least 1.6 to 1 in contact with a magnesia refractory and wherein a highly oxidizing atmosphere is blown into contact with the molten metal: the method of reducing the deterioration of the magnesia refractory which includes the step of introducing slag forming ingredients containing from approximately 10 percent to approximately 30 percent by weight of dolomitic lime into the equipment, said slag forming ingredients being in such proportions as to provide a magnesia to calcia molal ratio in the slag of from about 1:15 to about 1:3 at least at the interfaces between the slag and refractory, whereby conversion of the magnesia in the dolomitic lime to periclase occurs at the interface and physically thickens the slag adjacent the interface, there-

by minimizing solution of the refractory binder in the slag and consequent refractory deterioration.

5. In a method for operating metallurigcal equipment lined with a basic magnesia-containing refractory which method includes the steps of charging to the equipment, in contact with the magnesia refractory lining, a calcium compound which is reactive to neutralize SiO_2 and form a calcium oxide-containing refining slag, and molten ferrous metal containing silicon, and treating the metal with a highly oxidizing atmosphere to form a slag which causes deterioration of the refractory and which has a final composition including at least 10 percent by weight of SiO_2 and a base to acid molal ratio of at least 1.6 to 1: the improvement of reducing deterioration of the refractory by additionally charging into the equipment exposed calcined dolomite in an amount which provides a slag having a magnesia to calcia molal ratio of from about 1:15 to about 1:3.

References Cited by the Examiner

UNITED STATES PATENTS

1,939,638	12/1933	Hyde	75—55
2,361,416	10/1944	Reece	75—43
2,668,759	2/1954	Tenenbaum	75—52
2,733,141	1/1956	Sims	75—52
2,741,554	4/1956	Rinesch	75—52
2,741,555	4/1956	Cuscoleca et al.	75—52
2,811,436	10/1957	Heuer	75—52
2,906,616	9/1959	Allard et al.	75—51

FOREIGN PATENTS

4,422	1877	Great Britain.
908	1878	Great Britain.
1,313	1879	Great Britain.
810,960	3/1959	Great Britain.

BENJAMIN HENKIN, *Primary Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,288,592 November 29, 1966

Virgil S. Tadsen et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Columns 7 and 8, in Table I, under the heading "Slag Charge, Parts by Weight," sub-heading CaO Lime, thirteenth column, lines 1 to 8 thereof, for

3.5		35
3.2		32
2.8		28
3.0	read	30
3.0		30
3.2		32
3.4		34
3.4		34

Signed and sealed this 24th day of October 1967.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents