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This is a continuation-in-part of abandoned application
Ser. No. 391,330 filed Aug. 21, 1964.

This invention relates to the production of castings of
fused cast magnesia-chrome ore refractory having a mi-
crostructure in the as-manufactured state characterized by
improved thermal stability. This more thermally stable
microstructure provides the castings with a greatly im-
proved resistance to the type of spalling that has been
found to occur as a result of subjecting the castings to
repeatedly fluctuated temperatures, especially in the pres-
ence of oxidizing atmosphere, as occurs in the operation
of steelmaking furnaces. Improved resistance of these
castings to basic steelmaking slag corrosion is also afford-
ed by this improved microstructure.

Heretofore, it has been known to use castings, in ap-
propriate shape and size of bricks (usually cut from larger
billet castings), of fused cast magnesia-chrome ore re-
fractory, made principally of about 55 parts by weight
magnesia and 45 parts by weight chrome ore, to construct
arched roofs and other lining parts of reverberatory fur-
naces, such as open hearth steelmaking furnaces, and to
construct linings in basic oxygen steelmaking vessels. Such
refractory castings have exhibited what has been con-
sidered very good resistance to corrosion and erosion by
a variety of basic ferruginous steelmaking slags and slag
vapors, but further improvement in this regard would be
of great benefit to the economics of steelmaking opera-
tions. Although the resistance of these castings to the
above noted type of spalling is an improvement over
earlier basic fused cast refractory casting compositions,
these castings have been subject to the undesirable tend-
ency for chunks or pieces at the hot faces of the bricks
(i.e. the faces exposed to the hot furnace chamber) to
spall off during service, thereby materially reducing the
life of the bricks. Some notable improvement in reducing
this tendency has been accomplished by additions of ti-
tania to the casting composition, but occurrences of this
spalling have still continued in a frequency that is tech-
nically and economically undesirable.

In our studies of these refractory castings to discover
the basis of the spalling problem, we have found their
as-manufactured microstructure to consist essentially of
the following four crystalline phases:

(1) Crystals or grains of periclase with some other
constituents (e.g. FeO, Cr_2O_3, Al_2O_3, etc.) in solid solu-
tion therewith,

(2) Intergranular chrome-containing complex spinel
between and interlocked with the periclase crystals or
grains,

(3) Small size grains or crystals of intragranular
chrome-containing complex spinel within the periclase
grains formed by precipitation or exsolution from the
periclase grains during cooling, indicating that the oxide
content of this spinel was initially in solid solution in
the periclase, and

(4) Forsterite or olivine type of silicate crystals or
grains distributed as a discontinuous minor matrix or
islands between portions of the periclase and intergranu-
lar spinel grains or crystals.

Occasionally a very minor amount (usually less than
1 wt. percent) of isolated islands or particles of free iron
metal occur as a result of abnormal reduction of iron
oxide during melting. Also when fluorine is included in

the composition to improve manufacturability of crack-
free castings, an occasional very minor amount of ran-
domly dispersed islands of crystalline fluoride phase ap-
pears between the periclase and intergranular spinel
grains.

In analyzing the relative proportions of all the chrome-
containing spinel in the above noted as-manufactured
microstructure, the intergranular spinel is found to con-
stitute more than 60 wt. percent of all the spinel and the
intragranular spinel makes up the remaining minor por-
tion. The intergranular spinel is mostly euhedral and/or
subhedral crystals or grains of primary spinel, but also
includes minor amounts of anhedral coating spinel that
appears as film or layer-like crystal portions forming thin
coating bonds or layers between periclase grains. Prob-
ably at least some of the anhedral coating spinel results
from precipitation or exsolution from the periclase to the
surface of the periclase grains. The ratio of anhedral coat-
ing spinel to euhedral-subhedral spinel is usually less
than 0.45.

After numerous heats of steel have been made in a fur-
nace having a roof and/or walls made of the above de-
scribed brick castings and the temperatures to which the
latter have been exposed has varied during each heat gen-
erally from about 1250° C. to about 1650° C. and even
as high as 1800° C. and back to about 1250° C., our
studies of the hot face areas and spalled areas (usually 2
to 4 inches from the original hot face) of these bricks have
found a considerable change in microstructure, main-
ly with respect to the relative proportions of the three
types of spinel: euhedral-subhedral intergranular spinel,
anhedral coating intergranular spinel and intragranular
spinel. The quantity of intragranular spinel relative to the
total spinel in the casting has markedly increased to well
over 50 wt. percent with a corresponding decrease in the
amount of total intergranular spinel. The decrease in
euhedral-subhedral intergranular spinel, in many cases, is
even more notable because of an actual increase in the
amount of anhedral coating intergranular spinel. Other
minor observable changes in many cases are a very slight
decrease in the amount of periclase and a decrease in the
amount of any free iron metal originally present.

We have now discovered that the above noted continued
spalling problem is directly related to, and made possible
by, the change in microstructure as described above for
refractory casting compositions that form the large
amounts of intergranular spinel by conventional or known
practices of their production. Moreover, we have now dis-
covered that this spalling problem in these fused cast
magnesia-chrome ore refractory castings can be greatly
reduced to a very low level of occurrence heretofore un-
obtainable by providing the refractory castings with an
as-manufactured microstructure similar to that resulting
in the prior art bricks after being subjected to thermal
fluctuations as described above. We have found that the
latter microstructure is much more thermally stable and
subject, at most, to only insubstantial or insignificant
change or transformation that leads to very little or neg-
ligible spalling of the castings in furnace service. Coin-
cidentally, we have found that the more thermally stable
microstructure exhibits substantially improved resistance
to corrosion-erosion by basic ferruginous slags and slag
vapors.

As a part of our discovery, we have found a distinct
and improved change that is necessary in the prior process
of melting, casting and solidifying magnesia-chrome ore
raw material of a composition that previously produced
the thermally unstable microstructure with the large
amounts of intergranular spinel and particularly of euhe-
dral-subhedral intergranular spinel. That change involves
the step of solidifying the melted and cast material at an
increased rate over that employed heretofore and suffi-

ciently rapid to develop the microstructure as defined below. The more rapid rates of solidification have been found to suppress the formation of intergranular spinel and to increase the formation of intragranular spinel.

The improved thermally stable as-manufactured microstructure according to this invention consists essentially of at least 20 weight percent periclase grains, intragranular chrome-containing spinel grains within the periclase grains, intergranular chrome-containing spinel grains between the periclase grains, which intergranular spinel grains comprise, in part, euhedral-subhedral spinel crystals and the remainder anhedral coating spinel, the intragranular spinel being greater than 40 weight percent of all the chrome-containing spinel, nor more than 8 weight percent total of crystalline silicate phase plus crystalline fluoride phase when present, provided that the silicate phase does not exceed 6 weight percent, and the majority of the crystalline grains of the casting having a grain size of 15 to 1000 microns. As a further beneficial feature for this microstructure, the sum of the intragranular spinel plus the anhedral coating spinel should be greater than 55 weight percent of all the chrome-containing spinel and the ratio of weight percent anhedral coating spinel to weight percent euhedral-subhedral spinel should be not less than 0.5.

Although the preceding paragraph defines the as-manufactured microstructure of the invention in a broad sense, the most important microstructures of our discovery for excellent thermal stability are more specifically characterized further by having at least 25 weight percent of the periclase grains and a ratio of weight percent intragranular spinel to weight percent intergranular spinel being greater than 1. Preferably, for optimum thermal stability and spalling resistance, these most important microstructures are also characterized by the sum of the intragranular spinel plus the anhedral coating spinel being not less than 70 weight percent of all chrome-containing spinel, the ratio of weight percent anhedral coating spinel to weight percent euhedral-subhedral spinel being not less than 1, and the majority of the crystalline grains of the casting having a grain size in the range of 100 to 500 microns.

The general analytical composition of the castings of our invention, which under the slower solidification rates of previous manufacturing processes gave the undesirably larger amounts of intergranular spinel, consists essentially of, by weight, 40 to 78% MgO, 10 to 55% Cr_2O_3, 4 to 30% Al_2O_3, 1 up to less than 25% FeO where all iron content is calculated as FeO, 0 up to less than 5% CaO, 0 to 20% TiO_2, 0 up to less than 5% SiO_2, 0 up to less than 5% fluorine, the total of the above named constituents amounting to at least 95%, and the ratio of the moles of RO oxides to the sum of the moles of R_2O_3 oxides plus one half the moles of SiO_2 being at least 2.4.

However, the presently preferred analytical composition for basic steelmaking furnace refractories consists essentially of, by weight, 45 to 65% MgO, 10 to 30% Cr_2O_3, 5 to 25% Al_2O_3, 5 to 16% FeO where all iron content is calculated as FeO, 0 to 2% CaO, 0 to 10% TiO_2 where all titanium content is calculated as TiO_2, 0 to 3% SiO_2, 0 to 2% fluorine, the total of the above named constituents amounting to at least 98%, and the ratio of the moles of RO oxides to the sum of the moles of R_2O_3 oxides plus one half the moles of SiO_2 being at least 3.5.

As will be appreciated from the following detailed disclosure, there is no precise minimum value for the increased solidification rate that will produce castings according to our invention because of such variables as the size of casting desired and the particular composition desired. However, this detailed disclosure will provide adequate guidelines and examples to enable those skilled in this art to understand and carry out the invention with little difficulty, although a small amount of experimentation may be necessary to determine the suitable rapid solidification conditions for any particular size of casting or composition within this invention.

The rate of solidification is governed by four principal factors.

The first factor involves Chvorinov's rule which states that solidification time=K (volume/surface area)^2 where K is a constant for the particular composition and mold material employed. Thus for any particular composition and mold material, decreasing the ratio of the volume of a mass of melted material to its surface area will increase the rate of solidification. By changing the dimensions of the cavity of molds previously employed, castings can be produced at greater solidification rates than obtained heretofore. Where, as is often the case, the size and shape desired for a particular casting makes it impracticable to sufficiently decrease the volume/surface area ratio for an adequately rapid solidification rate to produce the microstructure of this invention, it will be necessary to additionally employ one or more of the other three factors.

The second factor involves the amount of dissolved gases in the melted material during solidification, which are derived from the raw materials and/or atmosphere around them during melting. Increased amounts of dissolved gases slow down the solidification rate. This results because the dissolved gases lower the liquidus temperature, which extends the solidification range. Thus, the solidification rate can be increased by reducing the amount of dissolved gases in the melted material. One way of reducing the amount of dissolved gases is to hold the melted material molten for longer periods of time whereby these gases have sufficient time to rise to the upper surface of the melted material and escape therefrom. Another way is to add solid fining agents to the molten bath of material, which agents at the temperature of the bath are caused to decompose and/or vaporize thereby producing gaseous bubbles that rise through the bath. As these bubbles rise, they coalesce with the dissolved gases and carry them along to the surface of the bath more rapidly. When it is deemed practical, suitable gases can be bubbled up through the bath to effect the same function as the fining agents. From our experience, this factor of reducing the amount of dissolved gases is not sufficient by itself to produce the necessary increase in solidification rate to yield the above described stable microstructure; therefore, one or more of the other factors must be employed in conjunction with this factor.

The third factor governing solidification rate is the temperature of the molten material at the time of pouring into a mold, commonly referred to as the stream temperature. Lower stream temperatures increase the rate of solidification. Ordinarily, heretofore stream temperatures were superheated by about 100–200° C. or so to assure greater ease in pouring and casting. However, somewhat lower stream temperatures can be suitably employed without serious difficulty to assist in increasing the solidification rate. But this factor alone appears insufficient to obtain the necessary increased rate for this invention, and some of the other factors must be employed in conjunction with it for obtaining the present invention.

The fourth factor involves the thickness of the graphite mold structure and the thickness of the insulating or annealing powder surrounding the graphite mold. Graphite molds have been employed because of the high temperatures of the melted magnesia-chrome compositions. Increasing the thickness of the graphite mold and decreasing the thickness of the annealing powder will provide increased solidification rates. It appears that this factor alone, within limits necessary to prevent cracking of the casting during cooling, is not adequate to produce the necessary sufficiently rapid solidification rate for this invention, and one or more of the other three factors must also be employed.

The invention will be illustrated and better understood by the examples given below. The raw materials used in their batch compositions in Table I are as follows (in weight percent).

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Magnesite (A)—calcined:
 98.51% MgO, 0.86% CaO, 0.28% SiO_2, 0.22% Fe_2O_3, 0.13% loss on ignition.

Magnesite (B)—calcined:
 95.2% MgO, 3.0% SiO_2, 1.0% CaO, 0.8% R_2O_3 (Fe_2O_3, Al_2O_3).

Chrome-ore—Transvaal:
 45% Cr_2O_3, 25% FeO, 14.7% Al_2O_3, 11.2% MgO, 2.2% SiO_2, 0.7% TiO_2, 0.13% CaO, 1.07% other plus loss on ignition.

Epsom salt—technical crystal:
 Substantially pure $MgSO_4 \cdot 7H_2O$.

Brucite—$Mg(OH)_2$:
 60.1% MgO, 4.3% SiO_2, 2.6% CaO, 1% R_2O_3, 32% loss on ignition (mostly H_2O).

Rutile:
 96–98% TiO_2, 1% max. Fe_2O_3, 0.3% ZrO_2, 0.3% Al_2O_3, 0.25% SiO_2, 0.1% Cr_2O_3, 0.29% V_2O_5, 0.025–0.05% P_2O_5, 0.01% S.

AlF_3—high purity:
 99+% AlF_3

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dition before pouring into the mold, which allowed more dissolved gases to escape. The latter fact was further indicated by an approximately 30 lbs./ft.³ greater density for Example No. 1 in comparison to Example No. 2. Notably, Example No. 2 did not have the stable microstructure despite the somewhat lower stream temperature and the inclusion of brucite. In both cases, the graphite molds used were two inches thick and the annealing powder was of similarly equal thickness.

Example Numbers 3 and 4 illustrate that similar differences in microstructure are obtained even when the condition of the melted materials are more reducing. Example No. 3 is a product according to this invention, and while it was melted with an open batch cover, coal was added to the pouring stream to effect more reducing conditions, as is evidenced by the presence of substantial free metal in the casting. Nevertheless, the shorter mold cavity, the smaller volume/surface area ratio and the longer holding time gave a satisfactory increased solidification rate that yielded the stable microstructure. Example No. 4 is a prior product melted by the older

TABLE I

Example No.	1	2	3	4
Batch composition (in parts by weight):				
Magnesite	(A) 53.13	(B) 53.0	(A) 55	(A) 55
Chrome Ore	43.87	44.4	45	45
Epsom salt	3.00			
Brucite		1.0	[1] 3	
Rutile		1.18	[1]	
AlF_3		0.81	[1]	0.6
Casting Chemical Analysis (calculated in weight percent):				
MgO	59.6	56.7	59.6	59.2
FeO	11.4	11.7	11.4	11.4
CaO	0.5	0.6	0.5	0.5
Cr_2O_3	20.3	20.2	20.4	20.2
Al_2O_3	6.7	6.6	6.7	6.9
TiO_2	0.3	1.5	0.3	0.3
SiO_2	1.2	2.7	1.1	1.1
F_2				0.4
Mole ratio	8.2	6.9	8.2	8.2
Casting Crystal Modal Analysis (in weight percent):				
Periclase, s.s.[2]	54.8	60.6	62.7	54.9
Intragranular Spinel (A)	34.2	11.7	23.9	14.4
Euhedral-Subhedral Spinel (B)	3.3	16.8	3.8	21.7
Anhedral Coating Spinel (C)	6.0	7.3	4.9	3.2
Silicate plus Fluoride	1.7	3.6	2.1	5.0
Free Metal			2.6	0.8
A=percent (A+B+C)	78.6	32.7	73.3	36.7
A+C=percent (A+B+C)	92.4	53.1	88.3	44.8
C/B	1.82	0.43	1.29	0.1
Majority Grain Size, microns	100–500	100–500	50–250	100–700
Casting size	6 x 13½ x 21	6 x 13½ x 72	6 x 13½ x 72	6 x 13½ x 72
(V/A)²	2.99	3.84	2.99	3.84
Holding time, minutes	30	5	30	5
Stream Temp., ° C	2,500	2,450–2,475	2,580	2,450–2,475

[1] Coal added to stream. [2] Solid solution.

A comparison of Example Numbers 1 and 2 indicates the difference between a product according to this invention (Example No. 1) and a prior product with the unstable microstructure (Example No. 2). Both of these examples were electrically arc melted by the more recent practice for obtaining more oxidizing conditions, which is evident by the substantial absence of free metal in the castings. This practice involves maintaining an opening in the batch cover or crust above the bath to allow substantial contact of air with the bath surface while arc melting with the electrodes held above the bath surface after an initial small pool is melted. Epsom salt as a fining agent (giving off SO_3 gas and water vapor) was included in the batch of Example No. 1 while brucite (giving off water vapor) was included in the batch of Example No. 2. A more rapid solidification rate was obtained in Example No. 1 by using a mold having a shorter cavity length, which gave a smaller volume surface area ratio as indicated by the (V/A)² values. Also contributing to the increased solidification rate of Example No. 1 was the longer time of holding the melted material in molten con-

conventional procedure of having the melted bath covered with batch and/or crust and having the graphite electrodes somewhat submerged in the bath. The thicknesses of the graphite molds and annealing powders in both these examples were substantially the same as in the first two examples.

After numerous thermal fluctuation tests, we have found that the castings of the present invention will undergo a minimum average of about 350 fluctuation cycles before they have an amount of spalling equivalent to the old castings, with the unstable microstructure, that have been subjected to only about 250 cycles. Moreover, the castings of our invention had much less change in microstructure as a result of these thermal fluctuations.

The instability of the microstructure of Example No. 2 can be seen by the data in Table II, which shows the original microstructure as well as the radically changed microstructures at the original hot face and in the spall area (approximately 3 inches inward from the hot face) after the casting was thermally cycled 248 times between 1250° C. and 1700° C.

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TABLE II

	Original	Hot Face	Spall Area
Periclase	54.9	51.3	48.0
Intragranular Spinel (A)	14.4	35.5	30.7
Euhedral-Subhedral Spinel (B)	21.7	8.0	8.6
Anhedral Coating Spinel (C)	3.2	1.8	7.3
Silicate Plus Fluoride	5.0	3.4	5.4
Free Metal	0.8		
A=Percent (A+B+C)	36.7	78.4	65.9
A+B=Percent (A+B+C)	44.8	82.4	81.6
C/B	0.1	0.2	0.9

We have also found that the grain size range of 15 to 1000 microns, as measured along the crystal axes, for a majority of the crystalline grains to also contribute beneficial effects in this invention. Such grain size is readily obtained by our more rapid solidification procedure. When the majority grain size is in excess of 1000 microns, there is a distinct tendency for microcracking of many periclase crystals or grains. Substantial amounts of microcracked periclase grains appear to permit greater ease of penetration by basic slag and slag vapors, thereby reducing the corrosion resistance of the castings. If the majority grain size is too small, it is unstable and tends to recrystallize into larger grain size in service. Also our noted grain size range appears to contribute to greater strength, e.g. modulus of rupture values (as determined in flexure with bars ¼" x ½" x 2–4") usually between 2000–6000 p.s.i.

As noted previously, castings of this invention were coincidently found to have better basic slag corrosion resistance. This has been determined to be the result of very little microcracked periclase grains. In prior products with the larger amount of intergranular spinel, it has been found that the intergranular spinel contributes to a substantial amount of microcracking of the periclase grains with which they interlock, apparently due to the difference in their respective coefficients of thermal expansion. With less intergranular spinel, the microcracking greatly decreases and the slag corrosion resistance improves significantly, as has been noted from photomicrographs showing much less slag penetration of the castings.

While the major characteristic of this invention is to maximize the amount of intragranular spinel while minimizing total intergranular spinel, especially euhedral-subhedral spinel, it is beneficial to maintain some intergranular spinel in those castings containing the permitted amounts of silica. It has been found that the presence of some intergranular spinel will retard the formation of continuous silicate film or matrix around the periclase grains, which film decreases the high temperature strength and the spall resistance of the castings. Also, the silicate phase content (and the corresponding analytical SiO₂ content) must be limited as previously noted because larger amounts adversely increase the amount of euhedral-subhedral spinel. Other factors found to enhance the major characteristic of this invention are the maximation of the weight percent ratios $Cr_2O_3:Al_2O_3$ and $MgO:R_2O_3$.

Certain terms used in this specification and the appended claims are intended to be defined as follows:

Periclase.—The cubic crystal phase normally formed by MgO, but may include other oxides in solid solution in the periclase lattice; for example, these other oxides include most of the FeO (which may actually form magnesiowustite (Mg, Fe)O with the higher FeO contents) and minor amounts of Cr_2O_3, Al_2O_3, Fe_2O_3, etc.

Chrome-containing spinel.—A complex magnesia-base spinel that can be represented, for example, as (Mg, Fe)O·(Cr, Al, Fe, Ti)₂O₃.

Intragranular spinel.—Chrome-containing spinel grains or crystals that occur wholly within the periclase grains as a result of exsolution from the periclase lattice to form inclusions of precipitated spinel.

Euhedral spinel.—Chrome-containing spinel crystals

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with almost all crystal faces well developed and occurring intergranularly between the periclase grains.

Subhedral spinel.—Chrome-containing spinel crystals with only a few well developed crystal faces and occurring intergranularly between the periclase grains.

Anhedral coating spinel.—Chrome-containing spinel with no well developed crystal faces and occurring intergranularly between the periclase grains in a layer-like coating or bond with a length-to-breadth ratio greater than 3.

Crystal modal analysis.—Microscopically observing the phase present at numerous uniformly spaced specific points over a specimen area traversed in a grid pattern, counting the number of times each phase was observed to provide a quantitative analysis in percent by weight by taking into account the specific gravity of each phase.

We claim:

1. A spall-resistant fused cast magnesia-chrome ore refractory casting having: (1) an as-manufactured microstructure of good thermal stability and consisting essentially of at least 20 weight percent periclase grains, intragranular chrome-containing spinel grains within said periclase grains, intergranular chrome-containing spinel grains between said periclase grains, said intergranular spinel grains comprising, in part, euhedral-subhedral spinel crystals and the remainder anhedral coating spinel, said intragranular spinel being greater than 40 weight percent of all the chrome-containing spinel, not more than 8 weight percent total of crystalline silicate phase plus crystalline fluoride phase when present, provided, however, that said silicate phase never exceeds 6 weight percent, and the majority of the crystalline grains of said casting having a grain size of 15 to 1000 microns, and (2) an analytical composition consisting essentially of, by weight, 40 to 78% MgO, 10 to 55% Cr_2O_3, 4 to 30% Al_2O_3, 1 up to less than 25% FeO where all iron content is calculated as FeO, 0 up to less than 5% CaO, 0 to 20% TiO₂, 0 up to less than 5% SiO₂, 0 up to less than 5% fluorine, the total of the above-named constituents amounting to at least 95%, and the ratio of the moles of RO oxides to the sum of the moles of R_2O_3 oxides plus one half the moles of SiO₂ being at least 2.4.

2. The casting of claim 1 further having the sum of said intragranular spinel plus said anhedral coating spinel greater than 55 weight percent of all said chrome-containing spinel and the ratio of weight percent anhedral coating spinel to weight percent euhedral-subhedral spinel not less than 0.5.

3. The casting of claim 1 wherein said periclase grains are at least 25 weight percent and the ratio of weight percent intragranular spinel to weight percent intergranular spinel is greater than 1.

4. The casting of claim 3 further having the sum of said intragranular spinel plus said anhedral coating spinel not less than 70 weight percent of all chrome-containing spinel, the ratio of weight percent anhedral coating spinel to weight percent euhedral-subhedral spinel not less than 1, and the majority of the crystalline grains of said casting have a grain size in the range of 100 to 500 microns.

5. The casting of claim 4 further having an analytical composition consisting essentially of, by weight, 45 to 65% MgO, 10 to 30% Cr_2O_3, 5 to 25% Al_2O_3, 5 to 16% FeO where all iron content is calculated as FeO, 0 to 2% CaO, 0 to 10% TiO₂ where all titanium content is calculated as TiO₂, 0 to 3% SiO₂, 0 to 2% fluorine, the total of the above-named constituents amounting to at least 98%, and the ratio of the moles of RO oxides to the sum of the moles R_2O_3 oxides plus one half the moles of SiO₂ being at least 3.5.

6. In a process of melting, casting and solidifying magnesia-chrome ore raw material proportioned to produce a fused cast refractory casting having an analytical composition consisting essentially of, by weight, 40 to 78% MgO, 10 to 55% Cr_2O_3, 4 to 30% Al_2O_3, 1 up to less than 25% FeO where all iron content is calculated as

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FeO, 0 up to less than 5% CaO, 0 to 20% TiO_2 where all titanium content is calculated as TiO_2, 0 up to less than 5% SiO_2, 0 up to less than 5% fluorine, the total of the above-named constituents amounting to at least 95%, and the ratio of the moles of RO oxides to the sum of the moles of R_2O_3 oxides plus one half the moles of SiO_2 being at least 2.4, and to further provide said casting with an as-manufactured microstructure of good thermal stability yielding improved resistance to spalling and corrosion, the improvement which consists of the step of solidifying said melted and cast material at an increased rate sufficient to develop a microstructure consisting essentially of at least 20 weight percent periclase grains, intragranular chrome-containing spinel grains within said periclase grains, intergranular chrome-containing spinel grains between said periclase grains, said intergranular spinel grains comprising, in part, euhedral-subhedral spinel crystals and the remainder anhedral coating spinel, said intergranular spinel being greater than 40 weight percent of all the chrome-containing spinel, not more than 8 weight percent total of crystalline silicate phase plus crystalline fluoride phase when present, provided, however, that said silicate phase does not exceed 6 weight percent, and the majority of the crystalline grains of said casting having a grain size of 15 to 1000 microns.

7. The process of claim **6** in which said increased solidification rate is further sufficient to develop in said microstructure the sum of said intragranular spinel plus said anhedral coating spinel greater than 55 weight percent of all said chrome-containing spinel and the ratio of

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weight percent anhedral coating spinel to weight percent euhedral-subhedral spinel not less than 0.5.

8. The process of claim **6** in which said increased solidification rate is further sufficient to develop in said microstructure at least 25 weight percent of said periclase grains and a ratio of weight percent intragranular spinel to weight percent intergranular spinel greater than 1.

9. The process of claim **8** in which said increased solidification rate is further sufficient to develop in said microstructure the sum of said intragranular spinel plus said anhedral coating spinel not less than 70 weight percent of all chrome-containing spinel, the ratio of weight percent anhedral coating spinel to weight percent euhedral-subhedral spinel not less than 1, and a majority of the crystalline grains of said casting having a grain size of 100 to 500 microns.

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