



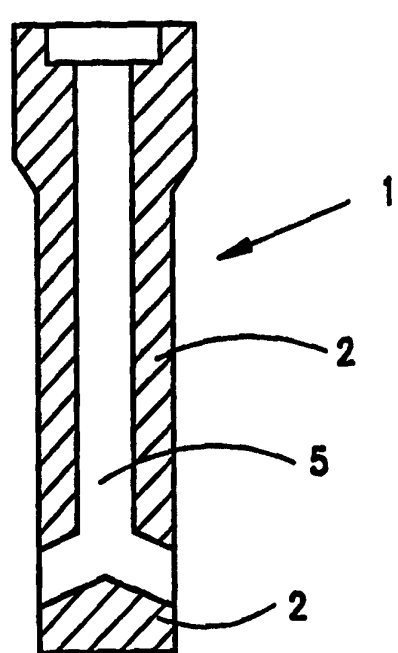
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(54) Title: APPARATUS FOR DISCHARGING MOLTEN METAL IN A CASTING DEVICE AND METHOD OF USE

(57) Abstract

A nozzle or tube (1) is useful for pouring molten metal, especially aluminum killed molten steel. The nozzle (1) is formed from a blend of dolomite and graphite which is bonded together in a carbonized matrix. Nozzles or tubes (1) made in accordance with this invention have enhanced thermal shock resistance. Furthermore, nozzles or tubes (1) of this invention resist the formation of aluminum oxide therein when they are used for pouring aluminum killed steel. Consequently, these tubes or nozzles (1) can be used in a continuous casting process for a long period of time without having to periodically stop the procedure and change the tubes (1) as they become blocked with aluminum oxide. As a result of the thermal shock resistance, the usual preheating step prior to contacting the nozzle (1) with the molten metal is greatly reduced.



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APPARATUS FOR DISCHARGING MOLTEN METAL IN A CASTING DEVICE AND METHOD OF USE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to the art of casting aluminum killed molten steel and related ferrous alloys. The invention is directed toward tubes such as casting shrouds, nozzles (including submerged entry nozzles and submerged entry shrouds) and the like through which the molten metal passes during a continuous casting process. Typically these tubes are used in a continuous casting process for pouring the molten metal from a ladle into a tundish or from a tundish into a casting mold. The tubes of the present invention are made from a composition which is effective in preventing the deposition of non-metallic inclusions, especially alumina (Al_2O_3), on the interior surface of the tube as the metal passes therethrough. In addition, the tubes made from this material also have a surprising thermal shock resistance. The invention is more particularly directed toward submerged entry nozzles and submerged entry shrouds which resist clogging caused by the deposition of aluminum oxide therein and which also have a surprising thermal shock resistance.

2. Background Information

It is well known that aluminum metal or alloys thereof may be added to molten steel in order to remove dissolved oxygen. The aluminum removes the oxygen from the steel by reacting with the oxygen to produce solid Al_2O_3 , most of which floats to the top of the molten steel where it can

be easily removed. However, a small amount of Al_2O_3 remains in the steel. The Al_2O_3 which remains in the steel is known to accumulate and form a deposit on the inner surface of casting shrouds and nozzles as the molten metal passes therethrough. Although the reasons for this phenomenon are not completely understood, it is believed that the deposition occurs due to the presence of alumina in the refractory material of the nozzle which comes in contact with the molten steel containing residual alumina from the aluminum killing process.

The deposition of alumina is particularly troublesome in the nozzles and shrouds associated with a tundish which is used in a continuous casting process. In this type of process, the molten steel is teemed from a ladle through a nozzle or shroud into a tundish. The tundish includes a plurality of holes in the bottom which are connected to nozzles for the flow of molten steel therethrough into the casting machine. In order to accomplish this objective, it is important that the nozzles be able to provide a regular flow of molten metal to the casting machine. Typically, such casting machines operate at a specific casting rate. Obviously, it is important that the supply of molten metal which flows through the nozzles to the casting machine must remain as constant as possible during the casting procedure. Thus, nozzles which become partially or wholly occluded due to the deposition of alumina within the bore of the nozzle will cause serious problems in the casting procedure.

Various techniques are known in the prior art for avoiding the above-noted clogging problems. However, none of these have been totally satisfactory for a variety of reasons. For example, it is known in the art to provide a nozzle with a plurality of openings in the internal surface for the passage of an inert gas into the bore while the metal is flowing therethrough. In operation, gas is injected through these openings into the bore and this gas minimizes contact between the molten metal and the

nozzle surface, thus preventing interaction between the metal and the nozzle which, in turn, prevents clogging from taking place. Typically, the openings constitute a highly porous surface which may be in the form of a porous sleeve within the bore of the nozzle. A nozzle of this type must
5 include a complex and costly internal structure in order for the inert gas to reach the openings or pores within the internal portion of the nozzle. Thus, the manufacturing steps and costs associated with such a nozzle make this type of nozzle undesirable. In addition, the use of such nozzles is known to produce defects such as pinholes in the steel product due to the large
10 amount of inert gas which is required to avoid the clogging problem.

Another approach to solve the clogging problem involves the fabrication of the nozzle from a material which inherently does not interact with the molten metal to form deposits of alumina. However, there are only a limited number of materials which are capable of functioning in this
15 manner and which have the refractory properties which are needed in the environment of the molten metal casting apparatus. In particular, it is difficult to find a material which has the required thermal shock resistance needed for nozzles and the like through which molten metal flows.

U.S. Patent Nos. 5,244,130; 5,046,647; 5,060,831 and 5,083,687
20 disclose various types of materials which are used to make nozzles and the like for casting molten metal. The specifications of each of the above-noted patents are incorporated herein by reference.

U.S. Patent No. 5,244,130 (Ozeki *et al.*) provides an improved nozzle which is said to overcome the problems associated with other prior art
25 nozzles. Ozeki *et al.* mention two types of prior art nozzles over which their invention is said to be an improvement. The first prior art nozzle is made from graphite and calcium zirconate (zirconia clinker) containing 23%-36% CaO. Ozeki *et al.* mention that the calcium oxide contained in the

calcium zirconate does not sufficiently move toward the surface of the nozzle bore through which the steel flows and consequently the calcium oxide does not come into sufficient contact with the non-metallic inclusions such as α -alumina, and for this reason, this prior art nozzle is not effective
5 in preventing the accumulation and deposition of alumina within the nozzle.

The second type of prior art nozzle discussed in U.S. Patent No. 5,244,130 is similar to the first, but additionally includes calcium metasilicate ($\text{CaO}\cdot\text{SiO}_2$). It is said that the presence of the calcium metasilicate in the second type of prior art nozzle overcomes the problems
10 noted with respect to the first type of prior art nozzle due to the combined effects of calcium zirconate and calcium metasilicate which allows the calcium oxide in each particle of zirconia clinker to move toward the surface. However, Ozeki *et al.* also note with respect to the second type of prior art nozzle that the calcium metasilicate has a low content of
15 calcium oxide which is insufficient to adequately replenish the calcium oxide which reacts with the alumina in the molten steel; thus making it impossible to prevent clogging of the nozzle for a long period of time. In order to overcome this problem, Ozeki *et al.* use crystal stabilized calcium silicate ($2\text{CaO}\cdot\text{SiO}_2$ and $3\text{CaO}\cdot\text{SiO}_2$).

20 The nozzles disclosed by Ozeki *et al.* include graphite in the amount of 10-35 wt.% which is added to improve oxide resistance, wetting resistance against molten steel and to increase thermal conductivity. Graphite in amounts which exceed 35% are avoided since such large amounts of graphite degrade corrosion resistance. There is no suggestion
25 for adding flake graphite to improve the thermal shock resistance which is not surprising since the zirconia clinker used by Ozeki *et al.* is said to have a low thermal expansion coefficient.

U.S. Patent No. 5,083,687 (Saito *et al.*) provides an improved nozzle for overcoming the above-noted clogging problem. Saito *et al.* mention that one type of prior art nozzle which was designed to avoid the clogging problem uses an inner lining made from a material containing 90-50 wt.% MgO and 10-50 wt.% C. However, it is noted in the specification that such materials containing graphite (C) and MgO suffer from cracking due to a large thermal expansion coefficient as compared to conventional nozzles made from alumina and graphite. Saito *et al.* also note that nozzles containing MgO and C exhibit inferior anti-spalling. In view of these undesirable features associated with refractories containing MgO and carbon, particularly the poor thermal shock resistance associated with the presence of MgO in the composition, Saito *et al.* concluded that nozzles which includes these ingredients would be unacceptable. Thus, Saito *et al.* avoid any material which contains MgO as a material for making the nozzle. Instead, they use a composition containing boron nitride, zirconium oxide and a sintering assistant containing SiC and B₄C.

U.S. Patent No. 5,046,647 (Kawai *et al.*) discloses two types of improved nozzles for dealing with the clogging problem. One nozzle is made from ZrO₂, C and SiO₂. Kawai *et al.* emphasize that CaO and MgO should be avoided, or at best, can be tolerated in small amounts so that the sum of CaO and MgO is less than 1%. Kawai *et al.* also describe a second type of nozzle containing CaO and SiO₂ in which the ratio of CaO to SiO₂ is limited to 0.18 to 1.86. No MgO is disclosed for use in this second type of nozzle which is not surprising in view of the lack of thermal shock resistance noted in the prior art when MgO is included in the composition of the nozzle.

Patent No. 5,060,831 (Fishler *et al.*) discloses a material for covering a casting shroud such as a tundish nozzle used for casting steel. The

composition includes CaO and a zirconium oxide carrier. There is no suggestion for including MgO in the composition.

SUMMARY OF THE INVENTION

5 It is an object of the present invention to provide a casting element such as a nozzle or the like which does not become clogged with alumina when used in a process for casting aluminum killed ferrous metal alloy, especially aluminum killed steel.

10 It is a further object of this invention to provide a casting element such as a nozzle or the like which combines the aforementioned clogging resistance with enhanced thermal shock resistance.

It is a further object of the present invention to provide a method for casting aluminum killed ferrous metal, especially aluminum killed steel which utilizes the casting element of the present invention.

15 These and other objectives are accomplished by providing a tubular casting element containing doloma (*i.e.*, doloma or CaO.MgO) and flake graphite in a carbon matrix or network derived from a binder resin by heating the resin under carbonizing conditions. It has been discovered that tubular casting elements such as a nozzle made from the above material avoids the clogging problem. In addition, it has also been discovered that
20 the selection of doloma as the refractory material for such casting elements combined with flake graphite results in a casting element having highly desirable thermal shock resistance so that the molten metal can flow through the casting element without cracking with a minimum or absence of preheating of the casting element being necessary. The thermal shock
25 resistance obtained with the doloma refractory is surprising in view of the prior art observation that nozzles which include MgO have an unacceptable

level of thermal shock resistance which causes them to crack when used in a casting process.

Although the present invention is more particularly directed to nozzles used in continuous casting procedures, the invention is not limited to such nozzles but is more generally applicable to any tube or the like through which molten metal flows and which is susceptible to clogging as described above. Thus, while the following descriptive material refers to nozzles used in casting procedures, it will be understood that the description applies equally well to related devices which are susceptible to the aforementioned clogging problem.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a sectional view illustrating an embodiment of the nozzle of the present invention.

Figure 2 is a vertical section illustrating another embodiment of the nozzle according to the present invention.

Figure 3 is a graph which illustrates the relationship between the parameter R_{cr} and the probability of failure.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The nozzles of the present invention are made by substituting doloma/graphite in place of the Al_2O_3 /graphite used in prior art nozzles. It has been discovered that the doloma avoids the clogging problem associated with alumina/graphite tubes because the doloma causes the production of soluble reaction products which do not clog the nozzle. Doloma is a well known and commercially available refractory material which is currently used for a variety of refractory applications due to its

heat resistant capability. It is made by calcining dolomite to convert the $MgCO_3$ to MgO and the $CaCO_3$ to CaO . Sintering is then performed on the calcined dolomite to densify the grain. Typically, the doloma is sold in pulverized form which can be shaped into a variety of structures.

5 The nozzles of the present invention are made by mixing doloma powder with graphite, preferably flake graphite, with sufficient liquid resin binder to form agglomerates. Generally, 9-13% by weight, preferably about 9½-10½% by weight of liquid resin binder (based on the weight of the solids blend) is sufficient to form agglomerates in the mixing process.

10 The agglomerates are pressed isostatically in a mold at ambient temperature to shape the material into the desired form. The shaped mass is baked in a curing oven where the temperature is gradually increased to harden (cure) the resin. Next the formed mass is carbonized (coked) in a furnace at a carbonizing temperature greater than 850°C (e.g., 1800-
15 2400°F) in an inert gaseous atmosphere which is unreactive with the resin (e.g., nitrogen or argon) to fully carbonize the resin and form a carbon network or matrix which holds the doloma and graphite together.

 Resins which have sufficient green strength to bind the refractory materials and which can be carbonized to form a carbon network are well
20 known to those skilled in the art. Many synthetic resins are known to be useful for forming refractory materials such as nozzles and can be used in the present invention. In general, it is known that these resins form a carbon network after the carbonizing or coking step. The carbon network holds the article together so that it resists breaking. Thus, the amount of
25 resin should be enough to provide a sufficient amount of carbon network to accomplish this well known objective. Excessive amounts of carbon network should be avoided. Thus, it is preferable that the amount of carbon network should be no more than the amount which is required to

hold the finished article together so that it resists breaking. Generally, the carbon network constitutes 4-7 wt.% of the finished nozzle, preferably about 5-6% (e.g., 6%).

5 If solid resin is used, it should be dissolved in a solvent to form a liquid binding resin composition. Typically, resins which are known for use in forming nozzles have a high coking value in the range of about 45%-50% to produce sufficient carbon network after carbonization. Also, curing the resin should avoid a condensation reaction since the water produced by such a reaction would be expected to react with the calcium oxide in the dolomite to produce the corresponding hydroxide which occupies a higher volume and thereby causes the structure to come apart. Thus, resins which are known for use with other calcium oxide containing refractory materials can be used in the present invention. The binding resin will produce a carbon network after the carbonizing or coking step which is sufficient so that the nozzle resists breaking. It is known that some weight loss of the resin occurs during the carbonization step. This weight loss results in some open porosity. Ideally, the weight loss which accompanies the thermal treatments does not result in an open porosity greater than 16%.

20 A preferred resin is phenol-formaldehyde resin. Such resins are well known and are produced by the reaction of phenol and formaldehyde. Preferably, the resin system contains formaldehyde and phenol in a ratio of 0.85 formaldehyde to phenol. The reaction between the phenol and formaldehyde is normally acid catalyzed so that the resulting resin must be buffered, dewatered and have the free phenol adjusted. The preferred levels are pH about 7.0, water below 0.1% and free phenol between 0.2-0.9%. The resin should then be put into solution with solvent. Suitable solvents include primary alcohols such as methyl, ethyl, isopropyl and furfuryl alcohol; glycol such as ethylene glycol; ketones such as methyl

ethyl ketone and methyl isobutyl ketone; aldehyde such as furfuraldehyde and acetaldehyde; dibasic esters and dimethyl formamide. Preferably the solvent is a furan compound, preferably furfuraldehyde or a solution of furfuryl alcohol and furfuraldehyde. In practice, the resin solution includes
5 a basic co-reactant such as triethylene tetramine, diethylene tetramine, ethylene diamine or tetraethylene pentamine. Other suitable co-reactants include diamines having an amine value of 1000 ± 100 and the equivalent molecular weight of 30 ± 2 .

As an alternative to the B staged phenolic novolak-furfural solution,
10 the invention may use a phenolic novolak dissolved in glycol and methyl alcohol but this resin is less desirable.

Another alternative binder system involves the use of furfural and a powdered phenolformaldehyde resin, mixed until the furfural picks up the solid, powdered resin and the resulting plasticized resin then causes the
15 raw materials to roll up into agglomerates. A tumble dryer is subsequently used to densify the agglomerates. This process results in agglomerates with excellent properties.

The graphite used is preferably natural flake graphite with a carbon content of not less than about 94%. Preferably the flake size should be
20 described by a normal distribution curve centering around 250 microns. Although minor amounts of impurities may be tolerated in the graphite, it is preferable to minimize such impurities. Preferably the graphite should be substantially free from contaminants and residual flotation compounds and the water content should be less than 0.5%. An analysis of a preferred
25 flake graphite is shown in Table 1.

Specie	Wt. %
Carbon	95 ± 1
CaO	0.15
MgO	0.06
Al ₂ O ₃	0.87
SiO ₂	2.7
Fe ₂ O ₃	1.0
Other	0.22

5

10 The graphite is in the form of a powder so that it can form agglomerates with the doloma powder and resin and so that these agglomerates can then be molded into a fixed shape for carbonization. Preferably the particles are 0.044-0.3mm in diameter.

15

The doloma is also in the form of a powder which can form agglomerates with the graphite and resin. Preferably the doloma is small enough to pass through a 14 mesh screen and large enough to be held on a 100 mesh screen (U.S. standard mesh). However, when screening the doloma to obtain the appropriate size range for this invention, it is not absolutely necessary to remove all of the material which would pass through the 100 mesh screen. For example, it is acceptable to include up to about 10 wt.% of the fines which would eventually pass through the 100 mesh screen if the screening process were continued for a very long period of time. In addition, doloma ball mill fines may also be included. Ball mill fines are small enough to pass through a 325 U.S. standard mesh and can be defined as particles having a surface area-to-weight ratio of 2300 Cm²/gm to 2800 Cm²/gm. A suitable doloma is a powder having particles ranging in size from 0.15mm to 1.4mm in diameter and which may further include dolomite ball mill fines. Minor amounts of impurities may be tolerated in the dolomite. However, it is preferable to minimize such

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impurities. Preferably, the doloma should contain a minimum of 56.5% CaO, 41.5% MgO and a maximum of 2% other impurities with a maximum of 1% Fe₂O₃. An analysis of a preferred doloma is shown below in Table 2.

5

Specie	Wt. %
CaO	56.7
MgO	41.2
Al ₂ O ₃	0.5
SiO ₂	0.4
Fe ₂ O ₃	1.2

10

Preferably the density of the doloma is from 3.25 to 3.28 grams/cubic centimeter. Thus, the doloma should be sintered until the bulk density of the grain is a minimum of 3.25 grams/cubic centimeter. Preferably the total porosity, open and closed, should not exceed 5%. The preferred particle size distribution of the doloma fraction contained in the nozzle is 150 microns - 1300 microns with the ball mill fines having a statistical mean particle diameter of 7.2 microns. In another preferred embodiment, the doloma includes a fraction having a particle size range from 0.15mm - 1.4mm in diameter (coarse fraction) and a ball mill fines fraction. In this preferred embodiment, the coarse fraction of doloma should be in the range from about 32 wt.% to about 43 wt.% with respect to the solids blend. The solids blend includes all the solid material (e.g., graphite and doloma) and excludes the resin, solvent and resin co-reactant. In this preferred embodiment, the ball mill fines fraction may range from 20-25 wt.% of the solids blend.

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The solids blend used in the present invention may further include other oxides which are compatible with CaO and MgO. Such oxides include silica (SiO₂), zirconia (ZrO₂), hafnia (HfO₂), ceria (CeO₂), titania

(TiO₂) and magnesia (MgO). These oxides should be below 25 wt. % of the solids blend, preferably no more than 10 wt. % and most preferably no more than 5 wt. %. The amount of MgO may exceed 1% (e.g., more than 1% up to 10% or more than 1% up to 5%). In addition, effective amounts of known antioxidants used in refractory nozzles may also be included in the solids blend. Suitable antioxidants can include the metal powders of aluminum, silicon, boron, calcium and magnesium or the carbides of silicon, calcium, zirconium, boron, tantalum and titanium. Some low melting oxides such as boric oxide, sodium borate or any combination of glass formers - aluminum, silicon, boron, phosphorous and zirconium oxides can be added to the body in order to form a protective layer on the surface to ban the ingress of oxygen into the body. This oxygen will destroy the bond carbon, and therefore, must be prevented from doing so by some barrier layer. The additions of metals or glass-forming oxides or carbides accomplish this. These materials are added in antioxidant effective amounts to protect the nozzle from oxidation particularly when the nozzle is hot.

The nozzles and related articles of this invention are made by conventional molding techniques. First, the solid blend containing the dolomite, graphite and optional metal oxide additives and optional antioxidant additives are mixed. Next, the resin is added to the dry solid blend and the ingredients are mixed in an agglomerating mixer to form agglomerates. Preferably the agglomerates have a normal size distribution centered around 400 microns with no agglomerates being greater than about 2000 microns and none being finer than about 150 microns. The agglomerates are formed in the mixing operation when the solids blend is wet blended with the resin. For example, in a preferred embodiment, the agglomerates are formed by wet mixing the solids blend with the resin solution along with the co-reactant. Densification of the agglomerates occurs during the mixing operation through viscosity enhancement of the resin which occurs when the volatile liquids evaporate and the resin and co-

reactant react with each other. Preferably, the bulk density of the agglomerates should not be less than 1.65 grams/cubic centimeter, more preferably from 1.9-2.1 grams/cubic centimeter. Such agglomerates, when pressed at 10000 PSI, will form an article having a bulk density of 2.37-
5 2.45 grams/cubic centimeter.

The agglomeration is best performed at ambient temperature with only a gradual and limited amount of warming which occurs due to the mixing and slight exothermic reaction which occurs as the resin cures. Preferably the material being agglomerated should not be allowed to exceed
10 a temperature more than about 140°F and the rate of temperature increase should be no more than about 3°F per minute.

The agglomerates are placed in a mold (*e.g.*, rubber mold) and formed at high pressure, *e.g.*, 8500 PSI (580 bar) to 25000 PSI (1700 bar) to form the shaped structure having a bulk density in the range of 2.35-
15 2.45 grams/cubic centimeter which is a preferred density for operation in a metal casting procedure. An isostatic press with rubber tooling may be used for the molding operation. After molding, the shaped structure is heated in the absence of oxygen (*e.g.*, in an atmosphere of nitrogen or argon) at a high temperature (*e.g.*, 975-1375°C) until the resin bond is
20 converted to a carbon bond. The articles in this coked state will have the required physical characteristics to permit successful use as nozzles and the like for casting molten metal.

There may be wide variation in the amount and proportion of the solid materials which are used to form the nozzles and similar articles of
25 this invention. Generally, the doloma (including ball mill fines) can vary from 30-70% based upon the weight of the solids blend. Unless otherwise stated, all percentages given herein are percentages by weight.

There should be at least about 25 wt.% graphite in the solids blend. There is no upper limit to the amount of graphite as long as there is sufficient dolomite to avoid the clogging problem. However, it is preferred to limit the graphite to no more than 45% to avoid excessive erosion associated with nozzles containing a large amount of graphite. Thus, a preferred embodiment of this invention, the graphite can vary from about 25 wt.% to about 45 wt.% based upon the weight of the solids blend, more preferably about 30% to about 45% by weight. However, in order to combine the anticlogging advantage with the desired thermal shock resistance required for adequate performance, the graphite content should be greater than 33% (*e.g.*, greater than 35%) to about 43%, preferably about 37-43% and most preferably about 38% and the dolomite should be in the range of 37-63 wt.% based upon the weight of the solids blend.

The thermal shock resistance property of the nozzles of this invention is very significant since it allows the nozzles to be used without having to undergo an extensive and time consuming pre-warming procedure.

When molten steel which can vary from 2850-3100°F depending on the grade, hits a cooler tube, the interior of the tube begins to expand at a faster rate than the outer parts of the tube. This generates a tensile "hoop stress" in the outer parts of the tube. The tube will crack if this stress exceeds the tensile fracture strength of the material. Air will be admitted to the steel stream when the tube cracks and this will result in unwanted oxidation.

A parameter which is used to evaluate thermal shock resistance is shown in the formula below:

$$R_{st} = \sqrt{\frac{G}{\sigma^2 E}}$$

In the above formula: G is the surface fracture energy; α is the linear coefficient of thermal expansion and E is Young's modulus which is the ratio of stress-to-strain in the elastic region of the stress-to-strain curve.

5 For the purposes of the present invention, adequate thermal shock resistance is achieved when the probability of failure (*i.e.*, cracking) is below an acceptable level. Figure 4 is a graph which shows the relationship between the probability of failure on the vertical axis and the R_{st} value on the horizontal axis. For practical purposes, an acceptable thermal shock resistance is obtained when the R_{st} value is about 25 or
10 higher, since such R_{st} values are associated with a probability of failure which is less than 10^{-2} . Such values begin to be achieved when the graphite content is more than about 33% since it has been observed that when the graphite content is 33% with 62% doloma, the R_{st} value is 24.6. There is a distinct improvement in the thermal shock resistance when the
15 graphite level is greater than 35 wt.% of the solids blend.

The nozzles of the present invention may be formed entirely of the above described composition like the embodiment shown in figure 1. Figure 1 shows a nozzle indicated generally by reference numeral 1. The entire nozzle is made from the refractory material of this invention which is
20 shown by reference numeral 2.

Figure 2 shows an alternative embodiment wherein only the inner portion of the nozzle is made from the refractory material of this invention. Thus, figure 2 includes an inner lining 3 made from the refractory material of this invention while the outer material 4 may be less expensive material
25 which does not come in contact with the molten metal. Figures 1 and 2 show an inner bore 5 within the nozzle for the passage of molten metal therethrough.

The following examples illustrate preferred embodiments of the invention which have acceptable thermal shock resistance values.

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	
5	Graphite 0.3mm- 0.15mm dia.	38	30	38	30	45	38
10	Graphite 0.15mm- 0.044mm	0	8	0	8	0	7
	Doloma 0.42mm- 0.15mm	7	7	37	37	0	12
15	Doloma 1.4mm- 0.15mm	30	30	0	0	37	25
20	Doloma Ball Mill Fines	25	25	25	25	25	25
	Liquid Resin	10	10	10	10	10	10
	Basic Coreactant	1	1	1	1	1	1

25 Examples 1-6 were made from the compositions shown in Table 3 which shows the parts by weight for each ingredient used therein. In examples 1-6, the dry ingredients (graphite, doloma and ball mill fines) are dry mixed to form a blend which is then wet mixed with the resin and co-reactant. Mixing is continued to form agglomerates of the cured resin and solid

30 particles. These agglomerates are placed in a rubber mold and formed at high pressure (e.g., 8500-25000 PSI). Next, these parts are then heated in the absence of oxygen until the resin is converted to a carbon bond. The parts in this coked state have desirable physical properties to permit successful use as pouring tubes. These properties are shown below in Table 4.

35

TABLE 4						
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Bulk Density	2.28 ± 0.05	2.29 ± 0.05	2.26 ± 0.06	2.26 ± 0.06	2.23 ± 0.05	2.20 ± 0.05
Apparent Porosity	15.4 ± 2%	15.1 ± 2%	16.1 ± 2%	16.0 ± 2.0%	16.3 ± 2.0%	16.7 ± 2.0%
Room Temp. MOR (psi)	700 ± 200	700 ± 200	600 ± 200	660 ± 200	600 ± 200	550 ± 100
Rst	38.1	36.4	36.4	35	41	40

5
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All of the above examples have R_{st} values well in excess of 25. However, lowering the amount of graphite from 38% of the solids blend to 33% of the solids blend results in an R_{st} value of only 24.6 compared to an R_{st} value of 38.5 when the amount of graphite is 38%. This distinction is illustrated by a comparison between the composites A and B formed by pressing and carbonizing the compositions shown below in Table 5 which indicates the parts by weight of each ingredient.

20

TABLE 5		
	Example A	Example B
Graphite 0.3mm-01.5mm dia.	38	33
Doloma 1.4mm-0.59mm	30	30
Doloma 0.42mm-0.15mm	7	12
Doloma BMF	25	25
Resin	10	10
Coreactant	1	1

25
30

The physical properties of the composites A and B are shown below in Table 6.

TABLE 6		
	Example A	Example B
5		
	$6.8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$	$8.7 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$
	1.65	2.33
10	119	107
	38.5	24.6

It can be seen from the R_{st} values in Table 6 and the graph of figure 3 that the probability of failure for composite A is very low at about 1 tube in 1428 tubes while the probability of failure for composite B is much higher at about 1 tube in 100 tubes.

While the present invention has been described in terms of certain preferred embodiments, one skilled in the art will readily appreciate that various modifications, changes, omissions and substitutions may be made without departing from the spirit thereof. It is intended, therefore, that the present invention be limited solely by the scope of the following claims:

WHAT IS CLAIMED IS:

1 1. A nozzle for pouring molten metal; said nozzle having an inner
2 portion which forms a bore extending therethrough for the passage of
3 molten metal through said nozzle wherein:

4 at least part of said inner portion of said nozzle is formed of a
5 refractory containing solids blend which comprises doloma and graphite and
6 said solids of said solids blend being bonded in a carbonized matrix.

1 2. The nozzle of claim 1 wherein the solids blend comprises 30-
2 70 wt.% of doloma and at least 25 wt.% of graphite based upon the
3 weight of said solids blend.

1 3. The nozzle of claim 2 wherein the solids blend comprises 37-
2 66 wt.% of doloma based upon the weight of said solids blend.

1 4. The nozzle of claim 3 wherein the solids blend contains at
2 least 33 wt.% of graphite based on the weight of said solids blend and said
3 dolomite is doloma having a density of at least 3.25 grams/cm³.

1 5. The nozzle of claim 4 wherein the solids blend contains at
2 least 35 wt.% of graphite based upon the weight of said solids blend.

1 6. The nozzle of claim 4 wherein the solids blend contains 33-45
2 wt.% of graphite based upon the weight of said solids blend.

1 7. The nozzle of claim 6 wherein the graphite is flake graphite.

1 8. The nozzle of claim 6 wherein the solids blend contains 35-45
2 wt.% of graphite based upon the weight of said solids blend.

1 9. The nozzle of claim 8 wherein the graphite is flake graphite.

1 10. The nozzle of claim 8 wherein the solids blend contains 35-43
2 wt.% of graphite based upon the weight of said solids blend.

1 11. The nozzle of claim 10 wherein the graphite is flake graphite.

1 12. The nozzle of claim 7 wherein the solids blend contains about
2 33 wt.% of graphite and about 62 wt.% of doloma based upon the weight
3 of said solids blend.

1 13. The nozzle of claim 11 wherein the solids blend contains about
2 38 wt.% of graphite based upon the weight of said solids blend.

1 14. The nozzle of claim 13 wherein the graphite is 0.044 mm to
2 0.3 mm in diameter and said doloma includes a ball mill fines fraction
3 having a surface to weight ratio of 2300 cm²/gm to 2800 cm²/gm and a
4 coarse fraction having a diameter of from 0.15 mm to 1.4 mm in diameter;
5 said coarse fraction being in the range of 32-43 wt.% based upon the
6 weight of said solids blend and said ball mill fines fraction being in the
7 range of 20-25 wt.% based upon the weight of said solids blend.

1 15. The nozzle of claim 14 wherein the total doloma content of
2 said solids blend is about 62 wt.%.

1 16. The nozzle of claim 15 wherein the amount of ball mill fines
2 constitutes about 25 wt.% of the solids blend and the coarse fraction of
3 doloma constitutes about 37 wt.% of the solids blend and said coarse
4 fraction includes a first subfraction having a diameter of 0.15 mm to 1.4
5 mm and a second subfraction having a diameter of 0.15 mm to 0.42 mm;

1 said first coarse subfraction being present in an amount of about 30 wt. %
2 based upon the weight of said solids blend and said second subfraction
3 being present in an amount of about 7 wt. % based upon the weight of said
4 solids blend.

1 17. The nozzle of claim 16 wherein the graphite has a diameter of
2 0.15 mm to 0.3 mm.

1 18. The nozzle of claim 9 wherein the solids blend further includes
2 an oxide selected from the group consisting of SiO_2 , ZrO_2 , HfO_2 , CeO_2 , TiO_2
3 and MgO_2 ; said oxide being present in an amount below 25 wt. % based
4 upon the weight of said solids blend.

1 19. The nozzle of claim 9 wherein said solids blend further includes
2 an antioxidant selected from the group consisting of aluminum, silicon,
3 boron, calcium, magnesium, silicon carbide, calcium carbide, zirconium
4 carbide, boron carbide, tantalum carbide and titanium carbide.

1 20. The nozzle of claim 9 which further includes an oxidation
2 barrier layer to prevent ingress of oxygen into the carbonized matrix; said
3 barrier layer comprising a low melting oxide selected from the group
4 consisting of boric oxide and sodium borate and glass forming compounds
5 selected from the group consisting of aluminum oxide, silicon oxide, boron
6 oxide, phosphorous oxide, zirconium oxide, aluminum carbide, silicon
7 carbide, boron carbide, phosphorous carbide and zirconium carbide.

1 21. The nozzle of claim 6 wherein the entire inner portion of said
2 nozzle is formed from a refractory containing solids blend which comprises
3 doloma and graphite and said solids of said solids blend being bonded in a
4 carbonized matrix.

1 22. The nozzle of claim 11 wherein the whole of said nozzle is
2 formed from a refractory containing solids blend which comprises doloma
3 and graphite and said solids of said solids blend being bonded in a
4 carbonized matrix.

1 23. A method for casting molten aluminum killed ferrous metal
2 which comprises pouring said molten metal through a nozzle into a mold
3 and then solidifying said metal wherein said nozzle has an inner portion
4 which forms a bore extending therethrough for the passage of molten metal
5 through said nozzle and wherein at least a part of said inner portion of said
6 nozzle is formed of a refractory containing solids blend which comprises
7 doloma and graphite and said solids of said solids blend being bonded in a
8 carbonized matrix.

9
10 24. A method for pouring molten aluminum killed ferrous metal
11 which comprises pouring said molten metal through a nozzle having an
12 inner portion which forms a bore extending therethrough for the passage
13 of molten metal through said nozzle wherein at least a part of said inner
14 portion of said nozzle is formed of a refractory containing solids blend
15 which comprises doloma and graphite and said solids of said solids blend
16 being bonded in a carbonized matrix.

17

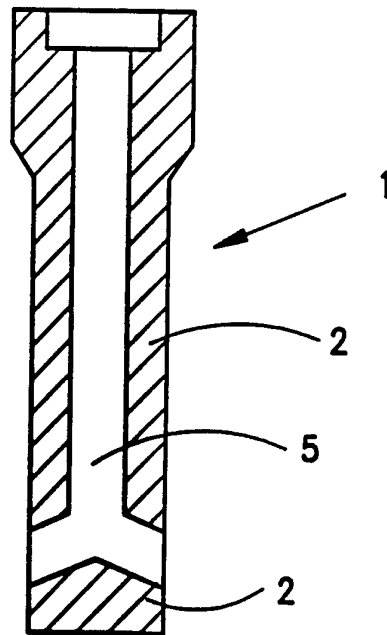


FIG. 1

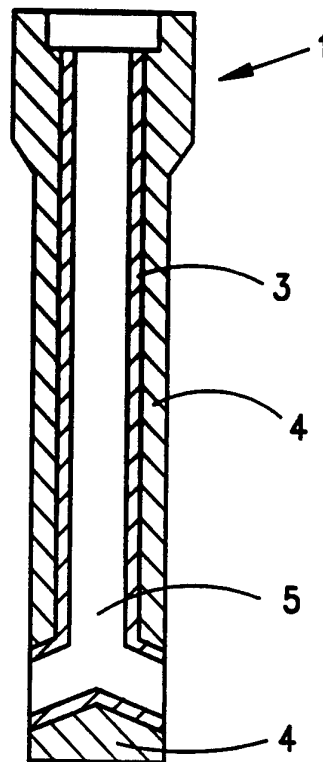


FIG. 2

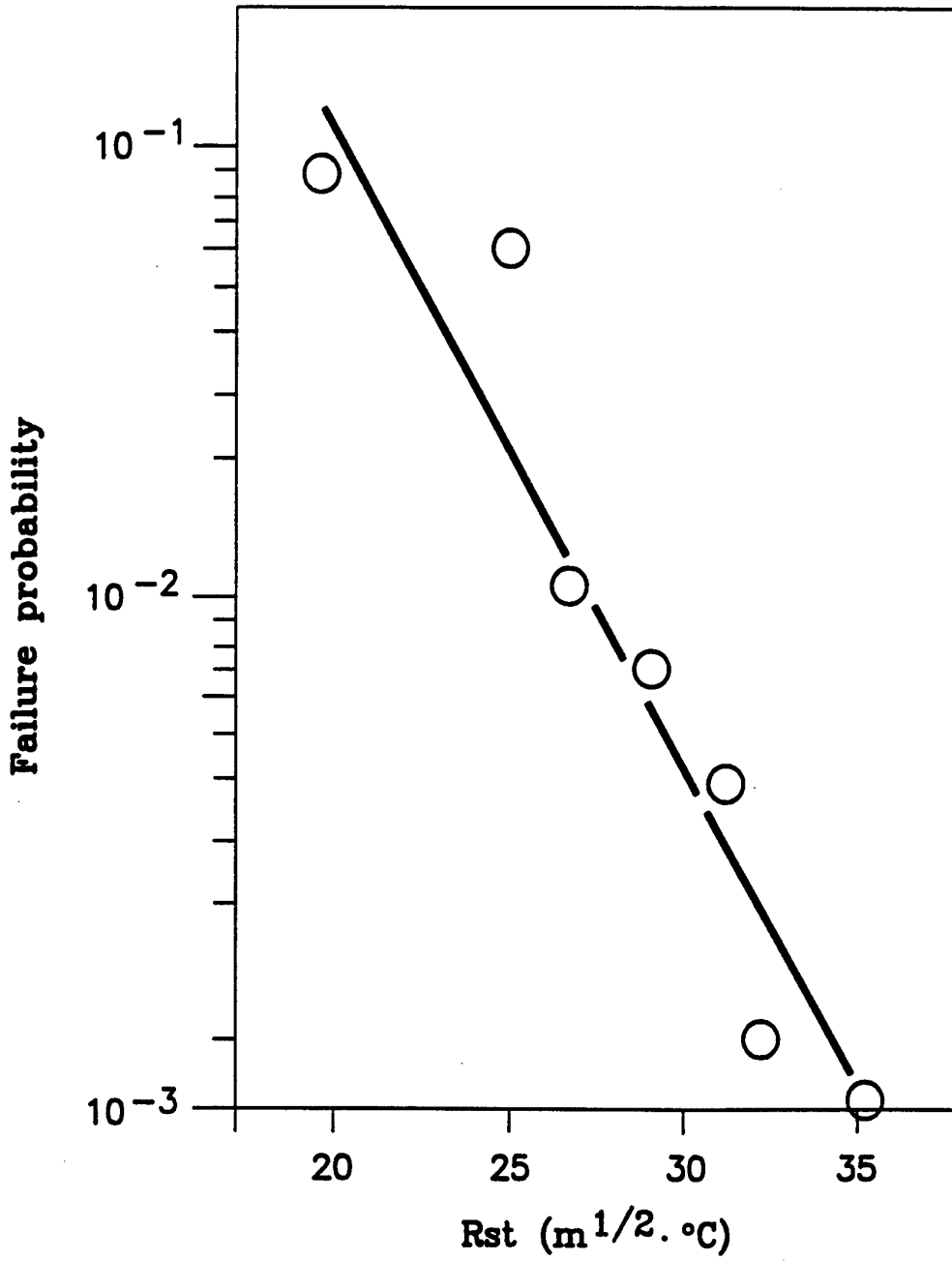


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05654

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C04B 35/04

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 266/236; 222/606, 607; 501/108, 121, 122

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,407,972 (BREZNY) 04 October 1983, col. 3, lines 3-14 and 40-44.	1-24
A	US, A, 4,730,754 (BUHR ET AL) 15 March 1988, fig. 1.	1-24
A	US, A, 5,369,066 (FURUTA ET AL) 29 November 1994, col. 4 lines 16-27.	1-24

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

08 JULY 1996

Date of mailing of the international search report

07 AUG 1996

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/05654

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

266/236; 222/606, 607; 501/108, 121, 122