METHOD OF INCORPORATING A REFRACTORY INSERT INTO THE BASE OF AN INGOT MOULD

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The following statement is a full description of this invention, including the best method of performing it known to us:

X670-77-1D-21P.C.
This invention relates to improvements in ingot molds and methods of making same, and more particularly, is directed to an improved base member for such molds and methods of forming same incorporating a refractory insert in its top surface.

All metal ingots are cast from molds. One popular type is a "big end down" mold. These molds rest on bases commonly known as "stools". The stools are merely large, normally rectangular, flat slabs of metal, commonly made of cast iron, which are used as support for the mold sides and also, of course, form the bottom portion of the mold. The mold sides generally taper up in diameter from bottom to top. Another types of mold is known as the "big end up" mold. These are ladle-like receivers for the molten metal, the bottom portion of which molds are integral, non-removable parts of the entire mold.

Various problems commonly occur in use of these molds and particularly with respect to the surface of their base portions. First, the unprotected metal surface quickly erodes and pits in the presence of molten metals which are cascaded upon their surface. Large gouges in the base portions are produced due to the force and high temperature developed by the flowing molten metal which contacts the surface of the stool. Since many molds are generally approximately 5-10 feet in height, the metal must be poured from a height at least equal to that distance and quite often is poured from even greater heights. A considerable pressure head is thereby developed. Thus, the hot molten metal easily gouges gaping depressions in the base members under such
force and at a temperature of at least the liquefaction temperature of the molten metal. Moreover, the problem of creation of pits or gouges in the base portions of the molds, caused by the above factors is aggravated due to the fact that the molten metal, especially near the bottom of the mold, remains in its erosive hot liquid states for a considerable amount of time subsequent to pouring.

The molten metal upon solidification to an ingot thereby has a bottom form conforming to the undesirable eroded surface configuration of the stool or base member of the mold. Thus, a considerable amount of the ingot, when withdrawn from the mold and subsequently processed into slabs or blooms, is lost through the cropping of the irregularly formed end of the slab. This, of course is highly undesirable, since it results in undue loss of usable metal and increase in scrap, which must be subsequently reprocessed.

Another extremely serious and costly problem results after the ingot in the mold has solidified to a point where it can be removed from both the mold sides and its base platform member or stool. In many cases, if the surface of the stool is unprotected, or inadequately protected, and erosion occurs as described above, the ingot has a greater tendency to remain tightly adherent to the stool. Thus, after the mold sides are removed from around the ingot, which process can normally be efficiently achieved with a minimal film of coating selected from a variety of coating agents, the ingot must be forcibly removed from the stool. This is normally achieved by raising both ingot and adherent stool, and thrusting them...
against some other larger object whereby the ingot is jarred loose. In many cases the stool and ingot are merely dropped on the floor from some suitable height. In such a situation, the stool is often broken into two or more smaller pieces and cannot be subsequently reused in casting other ingots. Again, replacement cost of these stools is high, making this aspect of the overall casting process somewhat disadvantageous. The same problem exists with respect to big end up molds wherein sticking exists with respect to big end up molds wherein sticking of ingots particularly occurs at their base portion. New molds of this type are especially vulnerable to sticking due to their smooth surface unprotected by any layers of metal oxides or scale. A tight metal-to-metal bond between mold bottoms and ingots then occurs.

Cracking of molds and particularly their base portions due to the above discussed rough handling occasioned by "stickers" between the base portions and ingots is also enhanced by thermal shock during ingot formation. Unprotected or inadequately protected bottom surfaces of mold are especially susceptible to such destructive shock.

Many solutions to alleviating the above described problems in connection with the erosion of base members of ingot molds have been proposed by the prior art. A number of refractory coatings have been suggested but these are not entirely satisfactory. An early solution to the erosion of ingot mold stools resided in the suggestion that refractory inserts could be placed into the bottom of the mold, which refractory would tend to minimize
erosion. Ceramic inserts have not met with any degree of commercial success. Their main drawback is that in use the molten metal works its way into the space between the insert and mold itself due to capillary action and tends to force the ceramic insert from its cavity. When this occurs the ceramic insert is above the top surface of the stool and tends to become entrained into the ingot. This entrainment produces metallic inclusions in the ingot which necessitates the expensive operation known as "butt cropping".

If it were possible to produce improved base members of ingot molds or to repair eroded stools whereby improved life could be achieved a substantial advance to the art would be afforded.

The present invention provides a method of mounting a refractory insert in the top surface of a base member of an ingot mold wherein the member is initially formed with a cavity in said surface or wherein said surface is worn in the shape of a cavity, said method including the step of fixedly arranging at least two irregularly-shaped metal anchor elements in the cavity, filling the cavity with a thermally-resistant plastic refractory composition and then applying to said top surface a slurry comprising a refractory suspended in a binder, said slurry being applied to form a coating of sufficient thickness to inhibit erosion and prevent adherence, and allowing said slurry to dry whereby a protective solid coating is formed upon said base member, said slurry comprising at least one of the refractories, vitreous silica, crys-
talline silica, aluminum silica, alumina graphite, zirconium silicate, magnesium silicate and clay suspended in at least one of the binders, aqueous alkali metal silicate, colloidal silica sol, liquid acidic aluminum phosphate and ethyl silicate, said binder binding the refractory particles together to thereby form a tightly adherent coating which is bonded to said surface.

Further features and advantages of the invention will be evident from the following description taken together with the accompanying drawings in which:

Figure I is a horizontal cross-sectional side view of an eroded mold which has been repaired by the method of the invention.

Figure II is a top view of an eroded base member of an ingot mold.

Figure III is a horizontal view of a cavity showing Z-shaped metal anchor bars fitted within the cavity.

With more specific reference to the drawings wherein like parts have like numbers, there is shown a base member of an ingot mold 10 of substantially rectangular dimension. This base member or stool is normally of large dimension and is constructed of cast iron. Typically such stools can have a thickness of 12 inches or more and a length of 4 to 6 feet. Badly eroded stools can be eroded to a diameter of as much as 3 feet and to a depth of as great as 10 inches. When such erosion occurs these stools are normally discarded as being unfit for service.

As shown to the best advantage in Figures I and II the stool 10 has a cavity 12 which is formed in the
The drawings show affixed to the side walls 16 of the cavity 12 two or more irregularly-shaped anchor element or bars 18, which are shown in the drawing in their preferred form as being of a Z-shaped configuration. The Z-bars shown in the drawing are anchored to the side walls 16 of the cavity 12 by means of threaded studs 20, which are shown in greater detail in Figure III. A convenient method of anchoring irregularly-shaped Z-bars resides in the use of a cartridge actuated nail-driving impact tool, which allows for rapid anchoring of the Z-bars into the cavity.

While the metal anchor bars are shown to be in the shape of a Z, it will be understood that other irregularly-shaped configurations of a general serpentine nature may be used. Thus, cork screw shapes, L-shapes, V-shapes, and the like may be used.

It is preferred that in anchoring the irregularly-shaped anchor bars that the base portion thereof which contacts the cavity of the stool be in the same plane as the surface rather than being perpendicular. Expressed in other words, threaded studs wherein a pointed end is affixed into a base member is not desirable since the end of the stud forms a heat transmission foci which would cause a hot spot or burning effect when the top portion of such a stud were contacted with molten metal. As seen in the drawings the base portion of the Z-bar contacts the cavity wall, thereby providing a greater heat transfer surface to minimize localized hot spotting of the mold.
After the irregularly-shaped metal anchor bars 18 are positioned in the mold cavity, the cavity is then filled with a ceramic material which is designated by the numeral 22. This plastic refractory material should be heat resistant and curable to provide a dense ceramic surface which is capable of receiving teemed molten metal such as liquid steel.

As indicated, the irregularly-shaped metal anchor bars 18 are preferably in the form of a Z. They may be positioned inside of the cavity 12 in a variety of configurations. They should be sufficient in number to allow a good anchoring effect to be achieved between the surfaces of the cavity 12 and the plastic refractory composition 22.

The plastic refractory compositions that have given outstanding results in the practice of the invention are composed predominantly of alumina and may contain other ingredients such as inorganic phosphates, minor amounts of water, clay and the like. These so-called high alumina ramming mixes are discussed and described in U.S. Patent No. 3,547,664, including certain of the references cited there against. A preferred ramming mix of the type described in this patent has the following composition:
Compositions of the above type are rammed by pneumatic means or the like into the mold cavity which has been previously fitted with the irregularly-shaped metal anchor bars. In addition to using ceramics of the type described, the invention contemplates using other ceramic materials as long as they are thermally resistant to contact with molten metal.

After the cavity 12 has been filled the plastic refractory composition 22 is thermally treated to bond the refractory into a unified shape. Molds thus treated have been put back into service and have exhibited a useful life which in many instances is far in excess of that achieved by the use of new cast iron stools.

It is apparent that the techniques thus described for repairing eroding stools may be adapted to the preparation of new stools. When it is desired to produce new stools, a cast iron stool is produced which has formed in its top a suitable cavity like the aforesaid cavity 12. Into the cavity is affixed the irregularly-shaped metal anchor bars 18 and the plastic refractory composition 22 is then placed into the cavity.
suitable casting facilities are available the preformed cavity may have incorporated therewith the irregularly-shaped metal anchor bars by means of the initial casting process rather than the use of a subsequent anchoring procedure.

In accordance with the present invention the stools produced with the foregoing methods are further improved in their ability to withstand erosion by placing thereupon certain stool coating compositions. These refractory compositions are disclosed in the following U.S. patents, which are incorporated herein by reference: U.S. 3,184,815, U.S. 3,509,936 and U.S. 3,184,813. These refractory compositions are applied in the form of slurries which contain vitreous silica, crystalline silica, magnesium silicate, aluminum silicate, alumina, graphite, zirconium silicate and clay. These materials are all well-known substances and are all commercially available. Typical aluminum silicates, for example, may include mica, a laminated type of aluminum silicate and mullite, an orthorhombic aluminum silicate available from the Island of Mull or artificially made by heating andalusite, sillimanite or cyanite. Excellent magnesium silicates are forsterite or talc, while a useful zirconium silicate is zircon. A typical crystalline silica is quartz. The most preferred refractory, discussed in more detail hereinafter, is vitreous silica. The binder used with any one or more of the above refractories may be colloidal silica sol, aluminum phosphate, i.e., liquid acidic aluminum phosphate, ethyl silicate or alkali metal silicate. Mixtures of these binders may also be employed. One of the
most preferred suspending mediums for the above refractories is colloidal silica sol, which also will be discussed more exhaustively in a later section.

The slurry is provided in an amount adequate to form a coating of sufficient thickness to prevent the above mentioned adherence and erosion from occurring. After the slurry is allowed to dry with or without application of heat, whereby the liquid phase is driven from the surface of the base member, leaving a thin film of solid refractory coating, the molten metal is thereafter poured into the mold and on top of the now coated base member. The liquid metal is allowed to solidify into an ingot and then removed from the coated base member and mold sides.

The liquid acidic aluminum phosphate binders are materials normally synthesized by chemical combination with sources of alumina and phosphoric acid. The resultant products take on a variety of molecular forms according to the ratios of the respective reactants. Thus, the aluminum phosphates are best defined in terms of ratio of $P_2O_5$ to $Al_2O_3$. Liquid aluminum phosphates preferred for use in practice of the invention have a ratio of $P_2O_5:Al_2O_3$ of from 1:1 to 5:1.

The aluminum phosphates are all substantially acidic in nature, and must be maintained in the acid form in order to remain as liquids. Generally, aluminum phosphates suitable as binders in the instant process have a pH of less than 3.0 as 1% aqueous solutions. The aluminum phosphate binder, at the time it is mixed with one or more of the above recited solid refractories to constitute
a slurry, is usually in the form of an aqueous solution. Preferred binder solutions contain 10 - 65% by weight of aluminum phosphate solids based on the total weight of an aqueous solution containing dissolved aluminum phosphate.

Excellent liquid aluminum phosphates useful as binders are available under the trademark "ALKOPHOS". Typical of these materials are "ALKOPHOS C" and "ALKOPHOS CE" which are clear or lightly colored aqueous solutions of mixtures of mono and dialuminum ortho phosphates. Analysis of representative samples of these two materials is set forth below in Table I.

TABLE I

<table>
<thead>
<tr>
<th></th>
<th>ALKOPHOS C</th>
<th>ALKOPHOS CE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>318</td>
<td>1110</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>33.1%</td>
<td>36.0%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.6%</td>
<td>11.0%</td>
</tr>
<tr>
<td>Viscosity at 25°C., cps.</td>
<td>35-90</td>
<td>500-2000</td>
</tr>
<tr>
<td>Sp.gr., 25/15.5°C.</td>
<td>1.47</td>
<td>1.60</td>
</tr>
<tr>
<td>pH, 1% solution</td>
<td>2.6</td>
<td>2.6</td>
</tr>
<tr>
<td>Free acidity (as H₃PO₄)</td>
<td>6.8%</td>
<td>0.03%</td>
</tr>
<tr>
<td>% Loss at 110°C.</td>
<td>48.0%</td>
<td>32.0%</td>
</tr>
<tr>
<td>Estimated solubility</td>
<td>50-70%</td>
<td>50-70%</td>
</tr>
<tr>
<td>Melting point of solids content</td>
<td>1500-1800°C</td>
<td>1500-1800°C</td>
</tr>
</tbody>
</table>

The alkali metal silicates are another class of binders. Preferred binders include sodium silicate and potassium silicate. Among these, the most preferred by virtue of availability and low cost is sodium silicate.

As set out above, the preferred source of silicate material is a sodium silicate. Commercial sources of this material range from about 25% to about 40% by
weight of solids of sodium silicate, generally supplied in aqueous form. More typically, they contain 30-40% by weight of solids. These commercially available silicates may be concentrated somewhat or diluted to any solids content as desired. Preferred alkali metal silicate binders for use in the invention are those materials containing 5-45% by weight of alkali metal silicate as a water solution.

While water alone may be used as the solubilizing agent for alkali metal silicate to form the liquid binders of the invention, it is understood that a binder may contain other solvents, polar in nature. It is only necessary that the organic solvents be compatible in water and do not deleteriously affect the alkali metal silicate, such by initiating polymerization of it to a solid, unusable, glassy mass.

Particularly preferred organic substances used in combination with water as solvents for the alkali metal silicate material are those which lower the freezing point of pure aqueous alkali metal silicates by their mixture with aqueous silicate solutions. Such products are especially useful during the colder months of the year when they must be stored and/or used at relatively low temperature. Amines such as morpholine, diethyl amine, etc., and polyhydroxy organics as ethylene glycol, glycerine, etc., are preferred materials in making up solutions of alkali metal silicate binder.

A preferred binder, "winterized" against freezing contains 5-45% by weight of alkali metal silicate, 10-95% of water and 5-50% by weight of a polyhydroxy water
compatible polar organic compound.

Regardless of whether the binder is a relatively pure aqueous solution of alkali metal silicate or a combination solvent system involving both water and water compatible organic solvents of the type described above or others, the ratio of refractory to binder in making up the slurry products of the invention ranges from 2:1 to 1:50. The more preferred slurries contain refractory and more preferably crystalline silica or vitreous silica suspended in one or more of the above described binders above in a ratio of from 2:1 to 1:25.

Another preferred binder used to form the slurries of the invention is a colloidal silica sol. These are well-known materials and are commercially available from several sources of supply. A typical group of commercially available silica sols that may be used in the practices of the invention are those silica sols sold under the name "Nalcoag". Silica sols of this type are described below in Table II.
<table>
<thead>
<tr>
<th>Silica Sol</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percent colloidal silica as SiO₂</td>
<td>15</td>
<td>30</td>
<td>35-36</td>
<td>21-22</td>
<td>49-50</td>
<td>35</td>
</tr>
<tr>
<td>pH</td>
<td>8.6</td>
<td>10.2</td>
<td>8.6</td>
<td>3.7</td>
<td>9.0</td>
<td>3.5</td>
</tr>
<tr>
<td>Viscosity at 77°F. cps.</td>
<td>Less than 5</td>
<td>Less than 5</td>
<td>Less than 5</td>
<td>Less than 10</td>
<td>20-30</td>
<td>6.5</td>
</tr>
<tr>
<td>Specific Gravity at 68°F.</td>
<td>1.09</td>
<td>1.205</td>
<td>1.255</td>
<td>1.06</td>
<td>1.385</td>
<td>1.255</td>
</tr>
<tr>
<td>Average Surface Area m² per gram of SiO₂</td>
<td>330-430</td>
<td>190-270</td>
<td>135-190</td>
<td>135-190</td>
<td>120-150</td>
<td>135-190</td>
</tr>
<tr>
<td>Average particle size millimicrons</td>
<td>7.9</td>
<td>11-16</td>
<td>16-22</td>
<td>16-22</td>
<td>20-25</td>
<td>16-22</td>
</tr>
<tr>
<td>Density pounds/gallon at 68°F.</td>
<td>9.1</td>
<td>10.0</td>
<td>10.5</td>
<td>8.8</td>
<td>11.6</td>
<td>10.5</td>
</tr>
<tr>
<td>Na₂O Percent</td>
<td>0.04</td>
<td>0.40</td>
<td>0.10</td>
<td>0.05</td>
<td>0.30</td>
<td>0.01</td>
</tr>
</tbody>
</table>
Other silica sols that may be used in addition to those above, may be prepared by using several well-known conventional techniques. In a preferred practice of the invention the silica sols are treated with a suitable base either at the time of manufacture, or just prior to use, to provide a pH of at least 11.0 and most preferably at least 11.5. These alkaline sols tend to promote adherence of the coating to the stools. Perhaps, the most convenient method of making aqueous colloidal silica sols is described in Bird, U.S. Patent 2,244,355, wherein a dilute solution of an alkali metal silicate is passed in contact with a cation exchange resin in hydrogen form, whereby the silicate is converted to a dilute aqueous colloidal silica sol. The dilute sol may be concentrated to solids concentrations which are more economically usable from the standpoint of shipping costs and ultimate process use, by employing the techniques described in either Bechtold, et al., U.S. Patent 2,574,902; Broge et al, U.S. Patent 2,680,721; or Alexander et al, U.S. Patent 2,601,235. Another type of silica sol which may be used in the practices of the invention is described in the specification of Reuter, U.S. Patent 2,856,302. While aqueous colloidal silica may be used it will be understood that other forms of colloidal silica may be employed, such as for instance, sols which contain a major portion of polar organic solvents. Said sols may be generically referred to as organo sols, and are typified by the sol described in Marshall U.S. Patent 2,386,247. It is only necessary that the silica particles used can be dispersed colloidal in a hydrophilic substance, such as
water or lower alkyl alcohols and other organic compounds possessing relatively high dielectric constants.

In some instances mixtures of water and organic substances compatible with water may be employed as suspending media for the colloidal silica particles. Particularly preferred organic substances are those which lower the freezing point of pure aqueous sols by their admixture with these aqueous silica sols. Such final product sols then are especially useful during the colder months of the year when they must be stored and/or used at relatively low temperature. Amines such as morpholine, diethyl amine, etc., and polyhydroxy organics as ethylene glycol, glycerine, etc., are preferred materials in making up silica sols containing these substances as sol silica suspending media or as a portion of a mixture additionally containing water. A preferred sol, "winterized" against freezing contains 5-50 parts by weight of polyhydroxy compound such as ethylene glycol, 20-85 parts by weight of water and 10-60 parts by weight of silica.

Regardless of the method employed to produce the colloidal silica sol containing water, polar organic liquids or mixtures of these substances as a continuous suspending phase, it is desirable that said sols contain silica particles which are dense, amorphous, and have an average particle diameter which does not exceed 150 millimicrons. As evidenced by a reading of Table I, all the silica sols contemplated as starting materials have an average particle size diameter well below 150 millimicrons. Preferably, the starting silica sols have an average particle size diameter of from 10-50 millimicrons. The
silica concentration in the sols may be between 0.1% and 60% by weight silica expressed as $\text{SiO}_2$. More preferred sols contain from 3.0 to 60% by weight of silica and most preferably 10-60% by weight.

Other sols which may be employed as binders for the silica refractory are those known as "salt-free" silica sols. These are particularly preferred when the suspension media of the silica particles in the binder itself is solely a polar organic liquid or a mixture of water and polar organic liquid. Since many of the above described sols usually contain alkali metal compounds as stabilizers, they are generally not compatible with organic systems due to the fact that the salts present in the aqueous sol cause gelation or precipitation of the silica particles when the aqueous phases are exchanged for polar organic solvents. This can be avoided by use of "salt-free" aqueous silica sols as starting materials in preparation of pure organo-sols or mixtures of water and organic as silica carriers. In order to avoid this gelation effect, it is necessary that the causative cations be removed from the surface of the colloidal dispersed silica particles and from the liquid phase of the sol. This may be readily accomplished by treating typical silica sols of the type described in Bechtold et al, U.S. Patent 2,574,902, with a cation exchange resin in the hydrogen form and a strong base anion exchange resin in hydroxide form. This treatment tends to produce a finished aqueous sol in which both the continuous aqueous phase of the sol and the particles of silica are considered "salt-free". Typical commercially avail-
able silica sols which may be deionized to produce "salt-free" silica sols are those which are described in Table II above. These aqueous "salt-free" silica sols may be either used as such in combination with one or more of the named refractories to constitute a slurry coating material or may be modified whereby the aqueous phase is completely or partially exchanged for a hydrophilic polar liquid such as an alcohol or the alcohol is mixed with aqueous sol in desired proportions. The "salt-free" pure alcohols or aqueous-alcoholic silica sols may then be easily combined with a refractory and the resultant slurry used to coat the stools.

When the particle sizes of the silica sols described above are within the ranges specified, the silica particles present in the starting aqueous or organic sol have specific surface areas of at least 20 m$^2$/g, and usually in excess of 100 m$^2$/g. Further, when deionized sols are employed as a binder, they generally have a salt content expressed as Na$_2$SO$_4$ of less than 0.01%.

The slurry is provided in an amount adequate to form a coating of sufficient thickness to prevent the above mentioned adherence and erosion from occurring. After the slurry is allowed to dry with or without application of heat, whereby the liquid phase is driven from the surface of the base member, leaving a thin film of solid refractory coating, the molten metal is thereafter poured into the mold and on top of the now coated base member. The liquid metal is allowed to solidify into an ingot and then removed from the coated base member and mold sides.
The slurry coating reagent is simply applied to the stool or bottom of the mold by a wide variety of methods. For example, the slurry may be applied by flowing it over the stools, by spray techniques, by coating the stool with some type of applicator, etc. Spray application is believed to be the most efficient and practical way of slurry application. The slurry is best applied to the stool portion of big end down molds before the metal mold sides are placed thereon.

Effective removal of the liquid phase of the slurry from the solid refractory material may likewise be carried out in a variety of methods. For example, the bottom portion of the mold may be coated with the slurry and allowed to dry gradually. Another method of laying down a thin protective coating is to apply the slurry to an already heated stool or mold having an integral base portion. This is particularly preferred in that the stools and their metal mold sides or big end up molds are generally already hot before introduction of the molten metal due to the residual heat from the previous casting run, and in such a method drying time is a very minimum period.

Another way of applying the protective film is to coat the base member, and then heat it as slowly or rapidly as desired to drive off the liquid portion of the slurry. In any event all that is necessary is that the coating be laid down in some manner after contact of the base member with the slurry.

In the most preferred method the coating slurry is applied to stools or mold base members having a temper-
ature ranging from that of room temperature to 1,000°F., and more preferably from 200°F. to 800°F. Best adherence of solid coating to stool is achieved by slurry application to the stools at a temperature range of 200-500°F. For best results, it has been determined that films should measure in thickness from 0.01 inch to 3 inches and most preferably from 0.01 inch to 1/8 inch.

It is believed that the excellent coating success achieved by use of the above described slurries is their ability to form a strong ceramic coating even when affixed to the base members of the mold at relatively low temperatures, at least under foundry conditions, of say about 500°F. or even lower. The coating becomes completely resistant to subsequent contact with water and stays tightly adherent to the base portions of the mold even under such washings.

After the coating has been formed preparation for casting is complete except when big end down molds are used. In those cases the mold sides should be placed on the base member following coating, if not already present during coating.

After coating operations, molten metal is poured into the mold, allowed to solidify into an ingot and the ingot is then separated from mold surfaces. The invention is not limited to use with specific mold sides or any particular metal mold bottom or to use with any particular molten metal.

As mentioned above, two refractories have shown extreme promise for coating. Both of these materials are well-known and need little further elaboration. The first...
is a crystalline silica refractory. Representative types include sand, crystalline silica flour, crystalline silica grains, etc.

The most preferred refractory materials are those generally referred to as vitreous silicas. These are glassy modifications of silica, obtained by the fusion of selected low temperature crystalline forms, and are frequently referred to as quartz glass or silica glass. Specific vitreous silicas include those particles made from fused quartz glasses, silicates glasses, silica glasses such as the well-known Vycor, registered trade mark, materials and fused silica glasses. With respect to all of these materials the thermal expansion coefficients are relatively small in proportion to other refractories such as those of the soda lime and lead glass types. Generally, they have thermal expansion coefficients smaller than \(5 \times 10^{-6}\) cm./°C. Also, the silica content of these granular siliceous refractory materials is generally greater than 96% silica expressed as \(\text{SiO}_2\) and may range as high as 99.8% \(\text{SiO}_2\). Thus, by the term "vitreous silica" is meant a refractory comprising a silica glass having a thermal coefficient of expansion and \(\text{SiO}_2\) content within the above range.

It has been determined that for best results in coating stools the refractory used in the silica slurry should be able to withstand severe heat shocks. Due to the extreme hot temperature of the molten metal as compared to that of the stool even when the latter is heated, an exceedingly abrupt change in temperature occurs when the metal contacts the stool. The coating must itself be able
to withstand this heat shock to impart necessary protection to the stool base. It has been theorized that failure of some prior art materials was due, at least in part, to their inability to withstand this sudden increase in heat, thereby resulting in cracking of the coating and subsequent exposure of the metal surface to the cascading molten metal poured into the mold.

In view of the above it is generally thought that the most preferred refractories are those which have the highest purities concomitant with the lowest thermal coefficient of expansion. These properties are particularly possessed by vitreous silicas and more particularly those of the fused silica types. The latter materials have a silica content greater than 95% and preferably greater than 97% silica expressed as SiO₂ and a thermal coefficient of expansion not greater than about 6 x 10⁻⁷ cm./cm./°C.

A typical fused silica of the type described above which is extremely useful in the practice of the invention, having a thermal coefficient of expansion of about 5 x 10⁻⁷ cm./cm./°C., has the following typical analysis:

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Percent by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>97.3</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.7</td>
</tr>
<tr>
<td>Sub-oxides of silica</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The above type silica products are readily prepared by grinding very pure fused silica glasses. Likewise, the borosilicate glasses and Vycor silica glasses
Another preferred refractory is alumina. This is a well-known material that needs a little elaboration by way of characterization. For example, crushed tabular aluminas may be employed with much success. An excellent alumina source is a calcined, low soda, finely ground alumina, having a particle size of minus 325 mesh.

The particle size of the refractory may vary over a wide range. It is preferred, however, that the refractory particles be sufficiently small so that a uniform dispersion of refractory and binder may be made. The smaller the particle size the longer a slurry made up of binder and refractory, remains in a homogeneous state.

It has been determined that particles ranging in size from 150-mesh to as low as a fraction of a micron may be employed. Preferred refractory materials have an average particle size ranging from 75 to 500 microns in particle diameter, with particles corresponding to the lower range diameters being most preferred. Specific vitreous silica substances, marketed under the name, "Nalcast" registered trade mark fall within the above preferred particle size range and have been employed with much success in preventing erosion of base portions of molds and adherence of same to the formed ingots.

The amount of binder making up a portion of the coating slurry must be such that it is present in an amount sufficient to bind the refractory particles together to thereby form a tightly adherent, continuous and unbroken coating which is securely bonded to the surface.
of the stool. Without proper amount of binder in relation to refractory, the resultant coating, after application and drying of slurry, exhibits a "pancake" effect with numerous undesirable holes appearing in the coating, thereby exposing portions of the stool or mold base surface. To achieve this, it has been determined that the slurry is preferably composed of from 10 to 70% by weight of refractory and from 30 to 90% by weight of binder. Most preferably the slurry contains from 20 to 60% by weight of refractory and from 40 to 80% by weight of binder.

The following examples show typical ways of carrying out the aims of the invention. It is understood, of course, that these examples are merely illustrative, and that the invention is not limited thereto.

The following examples show typical slurries which may be made in order to achieve a uniform coating surface upon the stool. The particular sodium silicate constituting a portion of the binder contained 37.5% solids, with the remainder being water. It is understood, of course, that these examples are merely illustrative and that the invention is not limited to use of these alone. The percentages expressed are percents by weight.

**EXAMPLE I**

50% sodium silicate
50% crystalline silicon flour

**EXAMPLE II**

25% sodium silicate
25% water
50% crystalline silicon flour
EXAMPLE III
10% sodium silicate
40% water
50% crystalline silicon flour

EXAMPLE IV
30% sodium silicate
30% water
40% crystalline silica flour

EXAMPLE V
20% sodium silicate
20% water
60% crystalline silica flour

EXAMPLE VI
20% sodium silicate
75% water
5% crystalline silica flour

The following example illustrates the efficacy of the invention in protecting stool bottom from erosion and subsequent sticking to formed ingots.

EXAMPLE VII
A coating slurry was made up having the following proportions:

<table>
<thead>
<tr>
<th>Material</th>
<th>Pounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>37.5% aqueous solution of sodium silicate</td>
<td>117</td>
</tr>
<tr>
<td>Water</td>
<td>28</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>31</td>
</tr>
<tr>
<td>Crystalline silica flour</td>
<td>140</td>
</tr>
<tr>
<td>Bentonite</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The bentonite, used as a dispersing agent, was 456,682
mixed with about 3 volumes of the crystalline silica powder and added slowly to the sodium silicate which had been further diluted with the water. Stirring was effected for 15 minutes, after which time the ethylene glycol was added. The remainder of the crystalline silica powder was then rapidly stirred until a smooth suspension was obtained.

Vitreous silica may be used in combination with sodium silicate to form a slurry having as good or better coating efficacy than the just discussed slurry. An excellent slurry combination comprises "Nalcast" material and sodium silicate.

The method of this invention for repairing eroded base members of metal ingot molds requires the application of a stool coating composition for the purposes of reducing erosion, preventing adherence of the ingot to the plastic ceramic insert and to fill in spaces that occur between the insert and the base member of the metal ingot mold to prevent metal penetration and to form a bond between the plastic insert and the eroded base member of the metal ingot mold.

EVALUATION OF THE INVENTION

EXAMPLE VIII

An eroded stool cavity had placed therein four Z-bars having the following dimensions: 2½ inches x 3 inches x 2½ inches. They were positioned as shown in Figure I of the drawing, then packing therein the specific ramming mix described herein. This composition was heat cured with a gas torch.

The thus repaired stool was then prepared with an application of a stool coating material to seal any
possible spaces and prevent metal penetration, to reduce erosion, and reduce or eliminate the possibility of the ingot adhering to the ceramic insert. The repaired stool went through 26 campaigns of steel pouring in which approximately 1200 tons of steel were poured.
The claims defining the invention are as follows:

1. A method of mounting a refractory insert in the top surface of a base member of an ingot mold wherein the member is initially formed with a cavity in said surface or wherein said surface is worn in the shape of a cavity, said method including the step of fixedly arranging at least two irregularly-shaped metal anchor elements in the cavity, filling the cavity with a thermally-resistant plastic refractory composition, heat-curing said plastic refractory composition and then applying to said top surface a slurry comprising a refractory suspended in a binder, said slurry being applied to form a coating of sufficient thickness to inhibit erosion and prevent adherence, and allowing said slurry to dry whereby a protective solid coating is formed upon said base member, said slurry comprising at least one of the refractories, vitreous silica, crystalline silica, aluminum silica, alumina graphite, zirconium silicate, magnesium silicate and clay suspended in at least one of the binders, aqueous alkali metal silicate, colloidal silica sol, liquid acidic aluminum phosphate and ethyl silicate, said binder binding the refractory particles together to thereby form a tightly adherent coating which is bonded to said surface.

2. The method of claim 1, wherein the irregularly-shaped metal anchor elements are Z-shaped and have the base portion of said Z-shaped element engaging the mold surface.

3. The method of claim 1 or 2, wherein the plastic refractory composition is an alumina-containing ramming mix.

4. The method of claim 1, 2 or 3 wherein the
refractory coating utilizes an aqueous colloidal silica sol as the binder and vitreous silica as the refractory.

5. A method of mounting refractory inserts in the base member, substantially as herein described.

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[Signature]

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