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METAL CASTING PROCESS

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ABSTRACT OF THE DISCLOSURE

An improved refractory composition for coating ingot molds of the type comprising a refractory powder slurried into an aqueous silica-containing binder is afforded by incorporation with such refractory composition small amounts of chromium and/or vanadium and/or manganese containing salts.

INTRODUCTION

The instant invention relates to an improved metal casting process. More specifically, the present invention is concerned with a method of increasing the life of mold bottoms used to cast ingots, and prevent adherence of these mold bases to subsequently formed solidified ingots which must be removed from within the mold walls.

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 type 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, nonremovable 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 state 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 a 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 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.

The above described problems have been solved to a large extent by the introduction of refractory compositions which comprise a refractory powder slurried in an aqueous silica-containing binder and applying these compositions to at least the base memebr of an ingot mold and then allowing these compositions to dry. The thus treated mold is rendered immune to the erosion problem occasioned by the pouring of metal into such molds. The use of these refractory compositions are disclosed in the following U.S. patents, the disclosures of which are incorporated herein by reference: U.S. 3,184,815, U.S. 3,509,936 and U.S. 3,184,813.

While the compositions and methods disclosed in these patents have materially improved the erosion and sticking problems previously discussed, their use by the steel industry, for example, has indicated that certain characteristics of these formulas are not entirely satisfactory from the applicational standpoint.

For instance, it has been observed that when the refractory compositions are applied to molds whose temperature is in excess of 400° F. the coatings do not form a completely adherent bond to the mold surface. This means that the coatings, after metal is poured thereupon, tends to be loosened from the base or stool; thereby requiring complete retreatment when further pourings are to be made. In certain cases it has been found that coatings of the types described in the above listed patents tend to be removed from stools by contact with moisture such as heavy rains requiring application of additional coatings. This necessitates the use of more coating material to maintain a uniform film of the ceramic material on the base and other portions of the mold. If it were possible to improve the deficiencies discussed above when the refractory coatings described are used, it would be possible to provide better and more efficient ingot mold coatings.

OBJECTS OF THE INVENTION

The invention, therefore, has as an object the provision of the improved refractory coatings of the type described which may be applied to mold surfaces over a broad temperature range with a good ceramic bond being afforded.

Another object of the invention is to provide improved ceramic coatings of the type described which are adherent and are not subject to replacement due to contact with water.

Other objects will appear hereinafter.

THE INVENTION

In accordance with the invention it has been found that the erosion of ingot molds may be prevented by coating such molds with a refractory composition which comprises a refractory powder slurried in an aqueous silica-containing binder which refractory composition contains a chromium and/or vanadium and/or manganese salt in an amount to provide from 0.005 to 5% by weight expressed as CrO_4, V_2O_5 or Mn_2O_3 based on the SiO_2 content of the silica-containing binder. The chromium, vanadium or manganese salts in a preferred embodiment of the invention are employed in an amount ranging from 0.05 to 5% by weight and, most preferably, from 0.1 to 3% by weight.

THE REFRACTORY POWDER

The preferred refractories should include at least one refractory of the following types: vitreous silica, crystalline silica, magnesium silicate, aluminum silicate, alumina, graphite, zirconium silicate and clay. Chromium oxides may also be used. 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. The most preferred refractories, discussed in more detail hereinafter, are vitreous and crystalline silicas.

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.

Other 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, silicate glasses, silica glasses such as the well-known "Vycor" materials and fused silica glasses. With respect to all of these materials their thermal coefficients of expansion are relatively small in proportion to expansion properties of other refractories such as those of the soda-lime and lead glass types. Generally, the above preferred refractories have thermal expansion coefficients smaller than 5×10^{-6} cm./cm./° C. Also, the silica content of these granular siliceous refractory materials is generally greater than 96% silica expressed as SiO_2 and may range as high as 99.8% SiO_2. Thus, by the term "vitreous silica" is meant a refractory comprising a silica glass having a thermal coefficient of expansion and SiO_2 content within the above ranges.

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 silica-type refractories are those which have the highest silica content 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 97% silica expressed as SiO_2 and a thermal coefficient of expansion not greater than about 6×10^{-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 5×10^{-7} cm./cm./° C., has the following typical analysis:

Ingredients:	Percent by weight
SiO_2	97.3
Al_2O_3	1.7
Sub-oxides of silica	1.0

The above type silica products are readily prepared by grinding very pure fused silica glasses. Likewise, the boro-silicate glasses and "Vycor" silica glasses may also be ground to produce extremely useful refractories. Vitreous silica substances marketed under the trademark, "Nalcast" have been employed with much success in preventing erosion of stools and adherences of same to the formed ingots.

THE AQUEOUS SILICA-CONTAINING BINDER

(A) The alkali-metal silicates

The alkali metal silicates are a preferred 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, di-ethyl 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.

(B) Colloidal silica sols

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 I.

TABLE I

	Silica sol					
	I	II	III	IV	V	VI
Percent colloidal silica as SiO_2	15	30	35-36	21-22	49-50	35
pH	8.6	10.2	8.6	3.7	9.0	3.5
Viscosity at 77° F. cps	<5	<5	<5	<10	20-30	6.5
Specific gravity at 68° F	1.09	1.205	1.255	1.06	1.385	1.255
Average surface area M^2 per gram of SiO_2	330-430	190-270	135-190	135-190	120-150	135-190
Average particle size, millimicrons	7.9	11-16	16-22	16-22	20-25	16-22
Density, lbs./gallon at 68° F	9.1	10.0	10.5	8.8	11.6	10.5
Na_2O, percent	0.04	0.04	0.10	0.05	0.30	0.01

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. Pat. 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 .Pat. 2.574,902; Broge et al., U.S. Pat. 2,680,721; or Alexander et al., U.S. Pat. 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. Pat. 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 generally referred to as organo sols, and are typified by the sols described in Marshall U.S. Pat. 2,386,247. It is only necessary that the silica particles used can be dispersed colloidally 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 sole 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 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 organosols 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 colloidally 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. Pat. 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 available silica sols which may be deionized to produce "salt-free" silica sols are those which are described in Table I 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_2SO_4, of less than 0.01%.

APPLICATION OF THE REFRACTORY COMPOSITIONS

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.

Effecting 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 temperature 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" to 3" and most preferably from 0.01" to ⅛".

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 coatings, 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. However, it has found specially preferred use in coating cast iron metal base members for molds which are used in forming ingots of steel.

RATIO OF REFRACTORY POWDER TO AQUEOUS SILICA-CONTAINING BINDER

Regardless of the particular aqueous silica-containing binder used, the ratio of refractory powder to binder in making up the slurry may range from 2:1 to 1:50, the most preferred slurries containing refractory powder and more preferably crystalline or vitreous silica suspended in one or more of the above described binders in a ratio from 2:1 to 1:25.

THE CHROMIUM, VANADIUM AND MANGANESE SALTS

The salts used in a preferred practice of the invention are the water-soluble chromates and vanadates. The most preferred salts are the alkaline metal chromates such as, for instance, sodium chromate. While other salts such as the vanadium or chromium chlorides may be used, they are the least desirable since they are relatively expensive and are not compatible with the aqueous silica sols. Manganese salts such as sodium or potassium permanganate are also useful. Manganese chlorides may also be used.

The invention is most readily practiced by dissolving sodium chromate into a sodium silicate solution which is then admixed with the refractory oxide to form a finished binder composition. Where it is not possible to directly dissolve the chromium, vanadium or manganese salts into the aqueous silica-containing binder, the invention contemplates mixing the salts, which are usually in the form of dry crystals with the refractory oxide.

COMPOSITIONS OF THE INVENTION

To illustrate the typical compositions of the invention, Composition I is set forth below:

Composition I

Ingredients:	Percent by weight
Water ---------- gallons--	5
Sodium silicate solution containing 29% SiO_2 ---------- do----	1
Sodium chromate .$4H_2O$ ---------- grams--	100
Fused silica ---------- lbs--	52

The above composition was prepared by diluting the sodium silicate with the water and then adding the sodium chromate. Just prior to use, the fused silica was added and formed into a refractory slurry which had the consistency of house paint.

EXAMPLE I

Composition I described above was applied to small cast iron blocks which were 2½" thick, 6" long and 2" wide. One series of blocks was heated to 200° F., a second series to 400° F., and a third series to 700° F. In each case the coating was applied at these temperatures and allowed to cool at room temperature. They were then held under a water tap overnight. None of the slurry was removed.

Using the same test procedure, Composition I was prepared with the exception that the sodium chromate was omitted. The coatings applied to the 700° F. blocks were loosely adherent after cooling and partially removed by the stream of water.

EXAMPLE II

To further illustrate the advantages of the compositions of the invention, Composition I was used to coat 300 stools which were used to cast ingot molds in a steel mill. The thus coated stools received poured steel and none of the stools were shown to have any "stickers" occurring. The coating rate used in this particular coating test was 0.25#/ingot ton.

At the same mill a chromate-free Composition I was applied to 100 ingots at the same dosage level with the result that a "sticker" rate of 25% was evidenced.

In testing the compositions of the invention under field conditions it was found that steel could be teemed onto the coated molds at higher temperatures without destruction or displacement of the coatings occurring. This provides an additional advantage or object of the invention.

Having thus described my invention it is claimed as follows:

1. In a process of the type wherein the erosion of a metal mold used to cast ingots from molten metal is inhibited by coating at least the base member of said molds with a refractory composition which comprises a refractory powder slurried in an aqueous silica-containing bind-

er, the imprpovement which comprises adding to said refractory composition a metal salt from the group consisting of chromium, vanadium and manganese salts in an amount sufficient to provide from 0.005 to 5% by weight, expressed as CrO_4, V_2O_5, or Mn_2O_3 based on the SiO_2 content of the silica-containing binder.

2. In process of claim 1 wherein the refractory powder is from the group consisting of vitreous silica, crystalline silica, magnesium silicate, aluminum silicate, alumina, graphite, zirconium silicate and clay, the aqueous silica-containing binder is an alkali metal silicate and the chromium and vanadium salt is selected from the group consisting of alkali metal chromates and vanadates.

3. In a process of the type wherein the erosion of a metal mold used to case ingots from molten metal is inhibited by coating at least the base member of said molds with a refractory composition which comprises vitreous silica powder slurried into an aqueous sodium silicate solution, the improvement which comprises adding to said refractory composition a water-soluble chromate salt in an

amount sufficient to provide from 0.05 to 5% by weight, expressed as CrO_4, based on the SiO_2 content of the sodium silicate solution, with the ratio of vitreous silica to alkali metal silica-containing binder being in the range of from 2:1 to 1:50.

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