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REFRACTORY MOLD

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The present invention relates to the production of refractory molds for use, in particular, in the casting of high temperature fusing metals and alloys such as steel, stainless steels; non-ferrous alloys, such as stainless cobalt chromium alloy; and other high temperature fusing materials, such as platinum, platinum-iridium, platinum-rhodium alloys and the like.

While the invention is particularly adapted for the production of molds for casting dentures, denture parts or elements, bone surgery appliances, jewelry articles, and other similar devices or appliances, and for the precision casting of industrial castings, such as gear parts, turbine blades and the like, it is to be understood that the invention is not limited to these particular uses but may be employed for other fields as suitable and desired.

In the casting of high temperature fusing alloys, it is recognized that suitable refractory mold materials must be selected which will withstand the casting temperatures of the alloys. Silica has been one of the principal refractory constituents. Other refractory constituents have consisted of alumina, zirconia, ground silica-firebrick, ground magnesia-firebrick, fused magnesia, and many other materials already known to those familiar with this phase of the art of high temperature casting.

In addition to the proper selection of the refractory constituents to be used in making the molds, it is essential that a binder be present to bind together the refractory constituents.

Certain types of binders, such as the organic silicates, and more particularly tetra ethyl silicate and allied organic silicates, have been employed with varying degrees of success. While the use of such organic silicates as binders for refractory mold materials has advantages in the casting of small parts, it also has certain disadvantages from the standpoint of large scale mass production of high precision castings. In the use of these organic silicates it is necessary, for example, to utilize ethyl alcohol, or acetone, or other mutual solvent as a diluent. Where large volumes of investment are involved, as in mass scale production, the fire hazard is great. Certain other disadvantages are present under similar conditions of operation, as for example, the high basic cost of these organic silicates and the complicated technique required in formulating the processing of the necessary accessory ingredients along with the organic silicates in order to render them in

such a condition as to be considered suitable as a binder.

With the teachings of the present invention as will hereinafter be more fully set forth, I avoid the use of inflammable materials, complicated technique of formulation of the binder, and utilize a relatively inexpensive material as a binder.

A still further advantage results from the use of my proposed binder in conjunction with suitable refractory constituents. I have found, for example, a method of producing refractory molds of a given pattern which possess the maximum in detail and surface smoothness. With synthetic rubber-like materials, as an example Korogel, I can reproduce the maximum in detail of a given pattern. Having formed a Korogel mold around a given pattern, I can use this Korogel impression for forming one-half or an integral part of the ultimate refractory mold into which the high temperature fusing alloys will be cast. By utilizing the process of the present invention, castings of a high degree of accuracy are produced, representing the maximum in surface detail and smoothness.

It is an object of the invention to provide refractory molds capable of imparting a high degree of surface smoothness and fine detail to the finished castings.

It is another object of the invention to produce molds having the true surface and sharp definitions which it is desired to impart to the castings.

It is another object of the invention to provide a silica bond for comminuted refractory material which may comprise the major portion of the body of the mold.

It is an object of the invention to employ a so-called colloidal silica solution or sol, in the production of the desired molds.

Various other and ancillary objects and advantages of the invention will become apparent from the following description and explanation of the invention.

In the production of refractory molds heretofore, it has been customary to use a suitably comminuted refractory material such as silica, alumina, magnesia, titanium oxide, beryllium oxide, mullite, sillimanite, and zirconia, each alone according to its inertness to the conditions of use of the mold, or in mixtures thereof which are inert and non-fluxing under the conditions of use. Such materials, alone, or as suitable mixtures, are herein referred to as refractory filler,

of which silica in fine mesh of 80 to 300, for example, is suitable. The finer the mesh of the refractory filler, the more suitable it is for giving a polished-surface effect to the casting. The filler may be proportioned with various grain sizes to control the surface effect. The proportioning of the grain sizes may also be used to provide a mixture which can be packed efficiently on the vibrator, or to avoid shrinkage cracks.

A vibratory method is preferably employed for compacting the refractory mold mixture combined with the colloidal silica solution. Having mixed the refractory constituent with the colloidal silica to a near pouring consistency, the mixture is preferably vibrated around the patterns until the mold has been filled, said mold then being preferably placed on a second vibrator and allowed to remain there until complete packing has occurred. Through this vibration method, all entrapped air is removed and the refractory constituent is allowed to settle and compact to form a dense mold and a density at the surface of the pattern of such a degree as to be capable of imparting extreme surface smoothness and fine detail to the casting.

The vibration employed is for obtaining a packing effect rather than an agitating effect and, as illustrative of the extent of vibration preferably employed, I vibrate the material on the first vibrator until it is packed and most of the air removed. The vibration on the second vibrator is a relatively fine vertical vibration prolonged until the packing is completed; also preferably until all of the air is removed and until substantially no more liquid rises to the top.

It is also customary to use various binders to hold the refractory filler in permanent mold form. The choice of and amount of filler, and the choice of and amount of liquid used with the filler have their inherent effects upon the accuracy of the mold.

The present invention may provide silica as the ultimate surfacing substance or as body binder for the refractory filler, which may or may not be silica. But since silica is per se a refractory material and is insoluble, a liquid suspension of a form of silica is employed. Silica, for example "silica gel," is well known in various degrees of hydration and in various forms, such as a dry solid, an aqueous colloid gel, an aqueous colloid sol, an ethyl alcohol colloid gel, an ethyl alcohol colloid sol, an organo colloid gel, and an organo colloid sol. In these forms the silica is dispersed in water or other liquid and is capable of dilution, like other "solutions," with a liquid which is the same as the vehicle or with other suitable liquids. A characteristic of such solutions is that they are readily induced to gel, by loss of vehicle or by change in the composition. In gelling, the particles agglomerate and provide bond.

By using a refractory filler and a sufficient quantity of such a silica solution to produce a suitable mix which is adapted to be molded, and then inducing gelation, a clear cut solidified mold is produced. This is then dried to remove water or other liquid introduced with the sol. In drying a mold made from an aqueous colloid, silica may be left as a hydrated gel. The water of the gel may be removed by heat in amount comparable to the temperature imposed. Hydrated silica gel has a strong affinity for water and as the temperature to which it is subjected is increased, water is lost until at short of 300° F. the product is silica of the formula SiO_2 .

Where the term "silica" is used herein, it refers to the anhydrous form SiO_2 as well as to any hydrated forms generally of the formula $(\text{SiO}_2)_x(\text{H}_2\text{O})_y$, of which silicic acid $\text{Si}(\text{OH})_4$ is an example. The latter has been recognized as a probable form of silica in aqueous colloidal silica solutions, according to United States Patent No. 2,244,325.

Therefore, in the present invention molds so formed as to provide hydrated silica are not complete and stable with a refractory silica bond until they are exposed to a temperature of about 300° F. Before use of such air-dried molds for high temperature molten metal, as at a temperature of the order of 3000° F., the molds are heated for a time by exposure to a temperature in the range from 1700° to 2200° F., preferably 1900° F., at which temperature the mold may be cast, or it may be cooled to about 700° F. if desired. However, they may be cooled to room temperature. The molds are preferably used to receive the molten metal while the mold is heated, but this and the temperature depend upon conditions. Thereby, an expanded form of the mold resulting from a heated condition is used to compensate for the shrinkage of the casting on cooling. These compensating conditions are empirical and depend on the composition of the mold, upon the character of the metal cast, and upon other factors.

Aqueous colloidal silica solutions suitable for the present invention are available under the trade name of Nalcoag, marketed by the National Aluminate Company, of Chicago, Illinois. Other products of this general nature are also available, such as "Ethyl-sol" and "Aqua-sol" marketed by Monsanto Chemical Company of St. Louis, Missouri. United States Patent No. 2,244,325 is illustrative of methods of producing the colloid. In so far as I have been able to ascertain, the Nalcoag solutions are made by abstracting ammonium or metal base, such as Na_2O , from ammonium or metal silicate solutions, such as sodium silicate solutions, while keeping the residual form of silica in a sol form, the removal, in the case of sodium silicate, being to the extent that residual Na_2O in the solution, calculated as Na_2CO_3 is of the order of 0.2%, the balance being free water, and silica. Such solutions normally have about 3% of SiO_2 but by concentration may be made as high as 18% to 24% SiO_2 . "Aqua-sol" has been concentrated to 32% solids with still a stable solution.

The pH of the aqueous colloid solution has an effect upon the tendency to gel. The higher the pH of the solution above 7, the more stable is the sol. The lower the pH of the solution above 7, the more it tends to gel. Low pH solutions, either slightly above or slightly below 7, are avoided where a "shelf-life" to the solution is desired. The pH may vary as, I understand, from about 2 to 11, more or less, while the solution exhibits the sol form. Solutions of pH below 7 may be stable and, when carbonated by CO_2 , are more stable even at a pH of 2. Stabilizers to produce stable solutions at pH above 7 are sodium carbonate or ammonium compounds, such as the hydroxide, the carbonate and some other ammonium salts. It is to be understood that these stabilizers are effective in small amount, and, for example, in the case of sodium carbonate, the latter may or may not react with silica to form a sodium silicate, this being immaterial to the fact that by far the larger proportion of the silica remains as a colloidal form of silica.

Change of pH may induce the sol to go over to a gel in a short or long, but controllable, time. Also chemical reaction within the solution to produce focal points for gelation, by forming a precipitable substance, is one means of inducing gelation.

I have found that substances added in small amount are effective to induce or accelerate gelling, by one mechanism or another. These substances I term gel-accelerators.

In preparation for use of gel accelerators, acid may be added to stable alkaline solutions, and alkali to stable acid solutions, to lower or raise the pH, respectively to a condition of lower stability whereby a lesser quantity of accelerator becomes effective. A single substance may function to do this, and also function as an accelerator, but such substance does not exert an accelerator function until it is present beyond the point where stability is maintained. Thus in compounding a mass to make a mold, a stable solution of low stability may be mixed with refractory filler in which is incorporated accelerator material, whereby the process of gelation is set up to proceed as timed by choice of the materials.

It is not necessary to employ accelerators, since mere drying of liquid, such as water or other liquid vehicle derived from the silica sol, from a molded mix will induce gelling of highly stable solutions, by virtue of a concentration effect. Nevertheless, I prefer to accelerate gelling so that undried set molds may be quickly removed from the mold supporting form or pattern or the like, thereby facilitating more rapid handling of unit molds in production.

According to my experience, the setting of the molds without an accelerator is not as practical as where an accelerator is employed because it is very difficult to dry out the mold until after the set has taken place by formation of the gel without disrupting the mold through the formation of steam or without the formation of a sort of hard case caused by the migration of the binder to the surface, and the drying off of the water at the surface.

I also prefer to use accelerators in another usage to which the invention readily lends itself. By making a very fluid molding mix of refractory filler and colloidal silica solution, the same may be sprayed onto a pattern to build up an initial surface layer of the mold, assuring the proper detail in the mold surface. By incorporating an accelerator in such a mixture to be sprayed, and spraying it before gel-time has arrived, excellent reproduction of the pattern is assured.

Suitable accelerators for aqueous silica colloids are calcium carbonate, calcium chloride, magnesium oxide, magnesium carbonate, ammonium carbonate, sodium carbonate, carbonic acid, hydrochloric acid, sulphuric acid, and like materials which have an effect upon the pH of the colloidal solution, or are reactive therewith to form what may be mineral silicates. In the main, it appears that all electrolyte reactants are good accelerators, although experience has shown that some electrolyte reactants are more effective than others, and at the same time some accelerators are not electrolyte reactants at all, as for instance, magnesium oxide. Accelerators are normally found to be effective in percentages ranging from .01% to 1% based on the entire mix.

The amount of colloidal silica solution used as binder may vary over a wide range. It depends upon the fineness and character of the refractory filler, upon the concentration of silica in the so-

lution, and upon the degree of plasticity desired in the mold mix. For example, using silica of 80 mesh as the refractory filler, and using aqueous colloidal silica solution of 6% solids, and of pH 8.5, 100 parts by volume of silica filler may be mixed with from 22 to 26 parts by volume of silica solution, and workable mixtures result.

The gel-time varies with all the conditions employed, and also with the amount and kind of accelerator employed. These may be chosen to predetermine a gel-time.

The material may be used in many ways. While a mixture is at a pouring consistency, or near to it, the mix may be vibrated while it is around a pattern until the mold is filled and air is jiggled out. This tends to puddle a fraction of the mix adjacent the pattern giving a dense, smooth surface with excellent reproduction.

A sprayable mix may be sprayed onto a pattern and allowed to gel. Then the covered pattern, when set or dry, may be invested in another portion of the same or a different mixture. Thus, a layer about one millimeter thick may be applied using spraying pressures of from 30 to 80 pounds per square inch.

Patterns of fusible or volatile or volatilizable or combustible material may be completely invested and the pattern removed by melting or volatilizing. Fusible materials for such use are wax, tin, low melting alloys, or low or high melting metals. Resin patterns which will decompose and volatilize with heat may be employed, such as methyl methacrylate. Prolonged heating at suitable temperatures may be used to distill off the methyl methacrylate as a monomer and leave a minimum of residue. Polystyrene may be employed in fashion similar to methyl methacrylate. Cadmium as a metal for patterns may be melted or volatilized out of a mold investing it.

A plurality of molds or mold parts already set may be assembled and integrated into a complex mold by using more material for the integration.

One of the advantages of the aqueous colloid silica material as a bond is the inability of it to exert a solvent or swelling action on certain materials of which patterns may be made, such as resins or rubber-like masses which may be adversely affected by any alcohol or other organic solvent present or formed in making a mold. The absence of solid organic material, whereby heat may damage the mold, is particularly advantageous.

Another advantage of using a liquid binder containing silica, substantially all of which is present as a sol in the liquid, is the resulting substantial freedom from salt electrolyte in the mold, excepting such small amount as may be used as accelerator.

The following examples illustrate the invention:

Example I

Silica—80 mesh or finer	-----grams	100
Magnesium carbonate	-----do	.5
Colloidal silica solution 6% solids, SiO ₂ , pH 8.5	-----cc	26
Gel-time, at 37° C.	-----minutes	45

Example II

70 Silica (sea sand or coarser)	-----grams	23
Silica (80 mesh or finer)	-----do	77
Ammonium carbonate	-----do	.3
Colloidal silica (aqueous 12.6% solids SiO ₂ , pH of 8.6)	-----cc	26
75 Gel-time, at 37° C.	-----minutes	50

Example III

Silica (200 mesh or finer) -----	grams--	100
Ammonium carbonate -----	do--	2
Colloidal silica (aqueous 13.6% solids SiO ₂ , pH of 10.8) -----	cc--	26
Gel-time, at 37° C. -----	minutes--	75

Example IV—(For spraying)

Silica (300 mesh or finer) -----	grams--	100
Colloidal silica (aqueous 13.6% solids SiO ₂ , pH of 10.6) -----	cc--	26

Example V

Silica (sea sand or coarser) -----	grams--	23
Silica (80 mesh or finer) -----	do--	77
Magnesium oxide -----	do--	0.1
"Ethyl-sol" (18% SiO ₂) -----	cc--	13.5
Alcohol (ethyl) -----	cc--	13.5
Gel-time, at 35° C. -----	minutes--	45

The ethyl sol is a colloidal silica solution in ethyl alcohol vehicle.

Example VI

Silica (200 mesh or finer) -----	grams--	100
Magnesium oxide -----	do--	.01
"Aqua-sol" (32% silica) -----	do--	27

The above formula is suitable for spraying applications to obtain surface definition. Such a solution may be concentrated to at least 32% SiO₂ content and present a good shelf-life.

In one preferred use, a resilient mold material, such as the polymerized vinyl halide described in Semon Patent No. 1,929,453, is formed over or against a given pattern, and the plastic mix of the present invention is poured into this mold and vibrated. The vibration compacts the refractory mass, eliminates air, and provides the desired density and surface smoothness. The gelled mold is then air dried to remove free water of the mix, and leaving any "bound" water associated with the first-formed silica bond. Drying ovens of moderate temperature, such as 100° C. may be used in place of air drying. Then the dried molds are set aside if not needed immediately for casting. When they are to be used, the molds are heated to a high temperature as described, either to remove any bound water in the silica, or to expand the mold, and preferably employed immediately to receive the molten metal while they are so heated.

The molds may be large or small. Relatively small molds, such as employed for dentures, jewelry and the like, have been highly successful. Relatively small molds, such as employed for complicated parts, such as the turbine buckets of exhaust turbine superchargers and the like, are highly advantageous to produce accurate parts with a high degree of surface smoothness and fine detail and polished appearance, thus eliminating or reducing to a minimum machining, finishing, and polishing.

Large molds are equally useful, but of course such molds must be handled with more attention, especially in the heating, to avoid driving off any residual or bound water so fast that injury to the mold results.

The air-dried molds, made by spraying or by vibrating a mix, present hard smooth surfaces. They are hard to scratch and quite water resistant.

Molds made by other procedures, as for example with organic binders, have surfaces which may be rough and inferior compared to molds made as described above. Such molds may be

improved in their surface characteristics by applying to them a suitable quantity of the colloidal silica solution, preferably containing accelerator. Then such molds may be air-dried or heated to convert any resulting aqueous gel into a solid non-aqueous hydrated gel, and finally heated to form an anhydrous silica coat for the inferior mold. Refractory silica or other filler may be added to such surfacing composition to any desired extent. A paint-like composition may thus be made, and used to coat a rough surface of such an inferior mold.

Numerous modifications and applications of the formulas disclosed are contemplated as falling within the scope of the invention as defined by the appended claims.

I claim:

1. A plastic mix for making a refractory mold, said mix comprising a refractory filler, and a binder comprising a non-inflammable liquid which in its original condition and prior to mixing therewith of the refractory filler contains inorganic silica substantially all of which is present as silica in the form of an aqueous sol with a relatively small amount of alkali metal compound.

2. A plastic mix for making a refractory mold, said mix comprising a refractory filler, a binder comprising a non-inflammable liquid originally in the form of a fluid mixture of aqueous colloidal silica sol and in which substantially all the silicon is present as an inorganic silica with a relatively small amount of alkali metal compound, and a gel-inducer for said sol.

3. A composition for use in refractory molds, said composition comprising a refractory filler, and a binder comprising a non-inflammable liquid which at the time of mixing with the refractory filler is in the form of a substantially non-gelling fluid mixture of aqueous colloidal silica sol and in which substantially all the silicon is present as an inorganic silica with a relatively small amount of alkali metal compound, and a gel-inducer for said sol.

4. The method of making a refractory mold, which comprises mixing a refractory with a binder comprising a non-inflammable liquid which in its original condition and prior to mixing with the refractory contains silicon substantially all of which is present as an inorganic silica in the form of an aqueous sol with a relatively small amount of alkali metal compound, forming the resultant mix into mold form, inducing gelation of said sol, drying the mold-form thereby removing free water and providing a hydrous silica gel having only bound water, and heating said mold-form at an elevated temperature thereby removing said bound water and providing anhydrous silica bond for said refractory filler.

5. The method of making a refractory mold, which comprises mixing a refractory with a binder comprising a non-inflammable liquid which in its original condition and prior to mixing with the refractory is in the form of a non-inflammable aqueous colloidal silica sol and in which substantially all the silicon is present in the form of an inorganic silica with a relatively small amount of alkali metal compound, forming the resultant mix into mold form, inducing gelation of said sol thereby converting it to aqueous silica gel, drying the resulting mold-form thereby removing free water and providing a hydrous silica gel having only bound water, and heating said mold-form at an elevated temperature

thereby removing said bound water and providing anhydrous silica bond for said refractory filler.

6. The method of making a refractory mold, which comprises providing a refractory mold having a mold surface containing a binder in the form of a non-inflammable aqueous colloidal silica sol and in which substantially all of the silicon is present in the form of an inorganic silica with a relatively small amount of alkali

metal compound, inducing gelling of said sol thereby converting it to aqueous silica gel, drying free water from said gel thereby converting it to hydrous silica gel having only bound water, and heating said hydrous silica gel at an elevated temperature thereby removing said bound water and providing anhydrous silica bond at the mold surface.

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