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METHOD OF MAKING A CASTING MOLD

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The invention relates to a method of making casting molds by means of expendable patterns for investment casting. In this process, the pattern used to make the mold is destroyed after the mold has been made, the actual casting cavity remaining in the mold. Thus patterns of wax or thermoplastics are destroyed, for example by being melted out of the mold, any pattern residues burning when the mold is subsequently fired. It has also already been proposed to dissolve the patterns out of the mold by means of a solvent, for example organic solvent vapors being used for wax patterns and water for urea patterns.

As compared with the melting method, the method in which the patterns are destroyed by being dissolved out of the mold has the advantage that there is no damage due to different thermal expansion of the pattern material and the mold material. On the other hand, the solvent used to dissolve the patterns out of the mold may occasionally enter into undesirable reactions with the binder in the molding material used for making the mold. This is the case, for example, where aqueous solvents are used in conjunction with molding materials containing a conventional silicate compound as binding agent. To obviate this disadvantage, it was necessary to use a different solvent, but this restricted the selection of possible pattern materials quite apart from the possibly higher price of organic solvents as compared with cheap aqueous solvents.

Nor was it possible heretofore to use one of the conventional aqueous binders in the molding material in conjunction with a pattern made from a water-soluble material. For example, the use of urea patterns precludes the use of waterglass-like binders or of colloidal aqueous silica as binder unless the mold is made waterproof by complicated additional treatment.

The invention enables the said disadvantages to be eliminated and also ensures a rational economic production process in the manufacture of investment casting molds. The method according to the invention is characterized in that the pattern is molded in a molding material containing a refractory granular molding substance and a substance active as a preliminary binder, and that the pattern in the resultant mold is at least partially destroyed by being melted out, burned or dissolved out, and that then the mold is impregnated with a liquid which contains or constitutes a material which can act as a secondary binder or be subsequently converted into the same.

In the method according to the invention the actual binder for the mold does not come into contact with the solvent for the pattern. Thus, in particular, solvents and pattern materials and binders can be used which in the previous method would enter into harmful reaction with one another. It is also possible to use cheap aqueous solvents in conjunction with the well-tried silicate-containing binders, provided, of course, that the pattern can be destroyed by an aqueous solvent, as is the case, for example, with urea patterns, which are particularly advantageous because of their crystalline structure. The substance active as the preliminary binder is intended mainly only to give the mold obtained by means of the pattern a strength sufficient for handling. It is unim-

portant whether the preliminary binder is destroyed during further treatment of the mold—for example, drying and firing. Therefore, for the purposes of this invention, any binder, as well known in the art, may be used as the preliminary binder so long as it imparts a sufficient binding of the finely divided refractory material for handling purposes.

The preliminary binder is advantageously a synthetic resin, for example an epoxy resin which is dissolved in an organic solvent and to which, if required, a substance can be added to accelerate curing. The preliminary binder may alternatively be a self-curing oily binder, for example of the conventional kernel oil type used in foundries. The oils involved have conjugate double-bonds.

The method according to the invention is very suitable for forming the mold by repeated dipping of the pattern into a pasty mold material, the preliminary binder giving improved strength properties to the various mold layers, particularly if drying is carried out after each dipping operation. The liquid used to impregnate the mold may advantageously be a solution or suspension of the binder. The substance contained in the impregnating liquid may be converted by a special treatment to an active binder form after the mold has been impregnated. Such a substance would, for the purposes of this invention, be considered a binder. For example, a silica ester can be used, in which case this substance is introduced into the mold and then may be hydrolyzed in order to convert it to the form active as a secondary binder. The substance used in the impregnating liquid may advantageously be a metallic salt from which the metallic hydroxide active as binder is precipitated under the action of an acid. The metallic salt may be a salt of one of the following metals: e.g. titanium, aluminum, zirconium, or silicon. An aqueous solution of phosphoric or boric acid may be used as a secondary binder.

A particularly advantageous embodiment of the invention is characterized in that where an organic binder is used the mold is subjected to a firing treatment before being impregnated with the liquid. This gives better binding of the completed mold by the secondary binder. Without such firing treatment prior to impregnation with the liquid, the organic preliminary binder would coat an appreciable part of the surface of the fine-grain refractory substances contained in the molding material, and thus block the access of binder liquid to the mold surface parts during the subsequent impregnation of the mold. If a firing treatment is carried out to convert the preliminary binder into a skeleton-like framework consisting of carbonized binder, the porosity of the mold is increased while the access of binders to the fine-grain refractory substance is facilitated, and this greatly improves the strength of the completed mold after firing. In such conditions the preliminary binder carbonized by the firing treatment gives the mold sufficient strength during handling for the subsequent impregnation with the liquid used for the introduction of the secondary binder.

The firing treatment may advantageously be performed in a reducing or inert atmosphere; this prevents any burning of the preliminary binder. The same effect can be obtained if the firing treatment is carried out with the exclusion of air or in air at a pressure of less than 1 Torr. Finally, it is advisable to carry out the firing treatment at temperatures in the range from 200 to 900° C. Higher or lower temperatures may be used depending upon the particular materials being employed.

The invention will be described in detail with reference to the following examples, for illustrative purposes.

Example I

12 kg. of finely ground mullite— $(Al_2O_3)_3(SiO_2)_2$ —are mixed with a solution of 0.5 kg. of polystyrene (molecu-

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lar weight approximately 20,000 to 40,000) in 5 litres of benzene. This solution of a thermoplastic is used as the preliminary binder and forms a pasty mold material with the refractory mullite.

A pattern of the required casting, for example the runner of a turbine together with those parts which form the subsequent downgates, is dipped into the pasty molding material and the thin mold layer adhering to the surface of the pattern is advantageously dried for 15 minutes by irradiation with infrared lamps. This process is repeated six to ten times, so that a shell-like mold built up from the corresponding number of layers forms around the pattern. This mold element forms the subsequent casting mold and its wall thickness may, for example, be 5 mm. The coating formed after each dipping operation is advantageously dried. The polystyrene solution gives the mold element sufficient strength for handling.

The pattern is then destroyed by the action of a liquid solvent. We will assume that the pattern has been made from a urea material. This pattern material is water-soluble, and the mold element together with the pattern contained therein is therefore placed in a water bath. The water can pass to the surface of the pattern through the mold element pores and dissolves the pattern. The pattern can be completely dissolved by means of the solvent, or else just partially so that the pattern residue is destroyed on subsequent firing of the mold element.

The mold element from which the pattern has been completely or partially eliminated is placed in methyl silicate (50% SiO_2) for a period of about two minutes. The methyl silicate impregnates the mold so that the pores between the refractory mullite particles are filled by liquid methyl silicate. The mold is then exposed to a saturated water vapor atmosphere. The water particles coming into contact with the methyl silicate effect hydrolysis and hence splitting of colloidal silica and liberation of alcohol. The colloidal silica, or silica hydrogel, is the actual secondary binder which on the subsequent firing of the mold element gives the latter the strength required for the casting operation. For firing, the mold is heated for four hours at about 800° C. in an oven. After removal, the mold element is ready for pouring as a casting mold. The casting obtained is distinguished by high precision and very good surface quality. Although a temperature of 800° C. is used, lower temperatures, or higher temperatures, such as 1200° C. or higher, may be employed.

In some cases it is advisable to use an acid of suitable concentration, for example, 1% hydrochloric acid, as a catalyst for hydrolysis of the methyl silicate. This acid can be sprayed on the mold element. Instead of a water vapor atmosphere, water may be sprayed onto the mold element, the water having previously been provided with an addition of acid.

Example II

12 kg. of finely ground sillimanite are mixed with 8 kg. of Chinese wood oil to form a paste. This oil has a conjugate double-bond and is conventionally used as a core binder in foundry practice.

As in Example I, this molding material is used to make a mold element and the pattern is then destroyed in one of the above-described ways. The mold element from which the pattern has been completely or partially eliminated is then placed in an aqueous solution of sodium titanate (12%) for at least 15 minutes. The mold element is thus impregnated with the aqueous solution which to a varying degree fills in the pores which are formed in the molding material during the drying of the latter.

The impregnated mold element is then placed in a carbon dioxide atmosphere, for example, such gas being blown onto the mold. Titanic acid and sodium carbonate form the resultant chemical reaction. The titanic acid forms the actual secondary binder. The casting mold ready for casting is obtained by firing at 900° the mold

element treated in this way. The mold is distinguished by very good strength and casting properties.

Example III

1000 grams of finely ground quartz sand are mixed with a solution of 400 grams of epoxy resin in 100 cc. of acetone to form a molding material for the production of the mold element containing the preliminary binder. The casting pattern is repeatedly dipped into this molding material as in Example I so as to form a shell-like mold element from which the pattern is then removed in the appropriate way. It is advantageous for the molding material used for the mold to be given a suitable hardener and an accelerator for the epoxy resin; conventional products may be used for this purpose.

The mold element is then impregnated with a 10% aqueous solution of sodium silicate. The mold is then treated with gaseous CO_2 as in Example II, colloidal silica being precipitated as the actual secondary binder.

Example IV

The procedure is the same as in Example III, but the sodium silicate is replaced by an 18% aqueous solution of sodium aluminate. By the action of carbon dioxide gas this is converted to $\text{Al}(\text{OH})_3$, which acts as a binder on firing of the mold element.

Example V

A mold element obtained from water-soluble urea by means of a pattern as in Examples I and II is impregnated with colloidal silica (18% SiO_2) and then dried. Silica precipitates at a degree of drying corresponding to about 40% of SiO_2 , and then acts as the actual binder during firing of the mold, while the preliminary organic binder is destroyed.

Example VI

A mold element obtained in accordance with Examples I or II is impregnated with an aqueous solution of phosphoric acid (60%) which constitutes the secondary binder. After firing (900° C.) the mold has very good strength properties and casting cavity surface quality. Instead of phosphoric acid, an aqueous solution of boric acid (3%) can be used.

Example VII

12 kg. of finely ground mullite— $(\text{Al}_2\text{O}_3)_3(\text{SiO}_2)_2$ —are mixed with a solution of 3.5 kg. of polystyrene (molecular weight about 20,000 to 40,000) in 5 litres of benzene. This solution of a thermoplastic serves as the preliminary binder and forms a pasty molding material with the refractory mullite.

A pattern of the required casting, for example the runner of a turbine together with those parts which form the subsequent downgates, is dipped into the pasty molding material and the thin mold layer adhering to the surface of the pattern is advantageously dried for 15 minutes by irradiation with infrared lamps. This process is repeated six to ten times, so that a shell-like mold built up from the corresponding number of layers forms around the pattern. This mold element forms the subsequent casting mold and its wall thickness may, for example, be 5 mm. The coating formed after each dipping operation is advantageously dried. The polystyrene solution gives the mold element sufficient strength for handling.

The pattern is then destroyed by the action of a liquid solvent. We will assume that the pattern has been made from a urea material. This pattern material is water-soluble and the mold element together with the pattern contained therein is therefore placed in a water bath. The water can pass to the surface of the pattern through the mold element pores and dissolves the pattern. The pattern can be completely dissolved by means of the solvent, or else just partially so that the pattern residue is destroyed on subsequent firing of the mold element.

The mold element from which the pattern has been completely or partly removed is then placed in an oven

and fired at a temperature of about 500° C. for six hours in a reducing atmosphere. A hydrogen atmosphere is used for this purpose. This treatment causes the polystyrene used as preliminary binder to carbonize and form a skeleton-like lattice which consists mainly of coke-like residues. The strength of the mold element after this firing treatment is quite sufficient for further handling until the secondary binder comes into operation. During this first firing treatment, any pattern residues can melt and provided the mold element is suitably stored, can flow out through the subsequent ingate.

The mold element obtained in this way is then placed in methyl silicate (50% SiO₂) for a period of about two minutes. The methyl silicate impregnates the mold so that the pores between the refractory mullite particles are filled by liquid methyl silicate. The mold is then exposed to a saturated water vapor atmosphere. The water particles coming into contact with the methyl silicate effect hydrolysis and hence splitting of colloidal silica and liberation of alcohol. The colloidal silica is the actual secondary binder which on the subsequent firing of the mold element gives the latter the strength required for the casting operation. For firing, the mold is heated for four hours at about 800° C. in an oven. After removal, the mold element is ready for pouring as a casting mold. The casting obtained is distinguished by high precision and very good surface quality.

As stated in connection with Example I, it is again in some cases advisable to use an acid of suitable concentration, for example, 1% hydrochloric acid, as a catalyst for hydrolysis of the methyl silicate. This acid can be sprayed on the mold element. Instead of a water vapor atmosphere, water may be sprayed onto the mold element, the water having previously been provided with an addition of acid.

Example VIII

12 kg. of finely ground sillimanite are mixed with 8 kg. of Chinese wood oil to form a paste. This oil has a conjugate double-bond and is conventionally used in foundries as a core binder.

This molding material is used as in Example VII to make a mold element and the pattern is then destroyed in one of the said ways. The mold from which the pattern has been completely or partly eliminated is then fired for four hours at a temperature of 650° C. in an inert nitrogen atmosphere so that the preliminary binder is converted to a binder skeleton consisting mainly of coke residues.

The mold element bound in this way is then impregnated with colloidal silica (18% SiO₂) and then dried. Silica precipitates at a degree of drying corresponding to about 40% of SiO and then on the subsequent second firing of the mold acts as the actual binder, while the skeleton-like structure formed by the preliminary binder is completely destroyed by burning.

Example IX

To produce the mold element provided with the preliminary binder 1000 grams of finely ground quartz sand are mixed with a solution of 400 grams of epoxy resin in 100 cc. of acetone to form a molding material. The pattern of the casting is repeatedly dipped into this molding material as in Example VII so as to form a shell-like mold element from which the pattern is removed approximately. A suitable hardener and an accelerator for condensation of the epoxy resin are advantageously added to the molding material used to make the mold and they may be conventional products.

The mold element is then subjected to a first firing treatment at a pressure of less than 1 Torr in a vacuum furnace at temperatures of about 800° C. for a period of about 2 hours.

The mold element is then impregnated with a 10% aqueous solution of sodium silicate and then treated with gaseous CO₂, this gas being blown onto the mold, for example,

The resultant chemical reaction causes silica to precipitate as the actual secondary binder and becomes active during the second firing treatment at temperatures of about 900° C.

The invention is not limited to the exemplified embodiments described. The mold element may be produced in some way other than by dipping the same into a pasty molding material, for example, by the use of flasks. In such cases a pattern of the required casting together with the parts forming the downgates and runner is backed with the pasty molding material in a flask and the pattern is destroyed preferably by being melted out or burnt. The mold element in the flask is then impregnated with the liquid which contains, for example, a substance active as the secondary binder. For this purpose the entire flask can be placed in an appropriate bath or else the liquid can be introduced into the mold elements through the casting cavity. The flask is then removed from the bath and/or the excess liquid is discharged. The flask with the impregnated mold element is then dried and fired. The mold element in the flask can undergo a first firing treatment in accordance with Example VII after the introduction of the pattern, the preliminary binder being converted during this treatment to a binder framework consisting of coke residues. After firing, the flask can be placed in a bath containing the substance active as the secondary binder. The flask with the impregnated mold element is then conventionally dried and fired. The firing treatment for carbonization of the preliminary binder may also be carried out with the exclusion of air; the firing temperatures are generally between 200 and 900° C.

Molding materials or pattern materials other than those mentioned in the examples may also be used. Impregnation of the mold element with the liquid may be carried out by spraying the liquid onto the mold element. Finally, the substance introduced into the mold element by impregnation with the liquid need not necessarily constitute the actual binder as in Example VI; the substance may be such that it is not converted into its active binder form until a suitable further treatment has been carried out after its introduction, for example, by a physical treatment or a chemical reaction.

The preliminary binders which may be used according to the invention may be any of the well-known binders customarily used in producing foundry molds, such as polystyrene, epoxy resins, such as epoxy resins on the basis of 2,2-bis-(4-oxyphenyl)-propane (Example III) or on the basis of dihydroxynaphthalene (Example IX). Suitable solvents for these resins include benzene, ketones and esters, e.g. acetone or acetylbutylate. Hardeners, respectively curing agents which may advantageously be used with the epoxy resins are well-known and include triethanolamine and n-amino ethylpiperazine. A suitable accelerator for the epoxy resins includes such a well-known accelerator as furfuryl alcohol.

The various oils which may be used as preliminary binders, and which contain conjugate double bonds, include the well-known binders such as kernel oils, especially Chinese wood oil and linseed-oil.

The secondary binders which may be used according to the invention are many of the well-known binders such as colloidal silica which may be prepared by the hydrolysis of a silica ester such as methyl silicate, ethyl silicate, propylsilicate, etc. (or by the destabilization of any suitable aqueous silicate solution). These esters are advantageously hydrolyzed in the presence of acids such as hydrochloric acid, sulfuric acid or phosphoric acid. Other binders which may be used include phosphoric acid or boric acid, as well as the reaction product of sodium titanate and carbon dioxide or the reaction product of sodium aluminate plus carbon dioxide.

The refractory materials which may be used according to this invention include any of the well-known refractory materials employed in precision casting, such as zirconium

powder, china clays, mullite, sillimanite, quartz, fused quartz and olivine.

I claim:

1. The process of producing a casting mold which comprises forming an admixture of a finely-divided refractory material and a preliminary low temperature binder capable of being carbonized in response to heat, contacting said admixture with a pattern material to form a molded admixture, heating the resulting molded admixture to a temperature sufficiently high to at least partially carbonize said preliminary binder, impregnating the molded admixture with a high temperature secondary binder, and heating the impregnated molded admixture to a temperature sufficiently high to bind the secondary binder with the finely-divided refractory material to form a casting mold.

2. The process of claim 1 in which the molded admixture is heated in an inert atmosphere.

3. The process of claim 1 in which the molded admixture is heated in a reducing atmosphere.

4. The process of claim 1 in which the molded admixture is heated in an atmosphere which is free from oxygen.

5. The process of producing a casting mold which comprises forming an admixture of a finely-divided refractory material and a resin, contacting the admixture with a pattern material to form a molded admixture, heating the molded admixture to a temperature sufficiently high and

in a suitable atmosphere to carbonize the resin, impregnating the molded admixture with colloidal silica, and heating the impregnated molded admixture to a temperature sufficiently high to bind the colloidal silica with the finely-divided refractory material to form a casting mold.

6. The process of claim 5 in which the molded admixture is heated to a temperature between about 200° C. and 900° C.

7. The process of claim 5 in which the resin is a polystyrene resin.

8. The process of claim 5 in which the resin is an epoxy resin.

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