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PREPARATION OF MOLDED ARTICLES

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The present invention relates to the field of precision casting of metals.

In recent years several methods have been devised for precision casting of metals. One of the most successful methods has been the so-called Croning process in which the face of the mold is composed of an aggregate bonded with an organic resin such as a phenolic resin. By using this method relatively good precision is obtained which minimizes the amount of machining necessary. However, for extremely high precision this method is inapplicable because the organic resin binder gases when the molten metal is poured into the mold. This gassing gives a defective metal surface which cannot be tolerated when extremely high precision is needed in the casting. Attempts have been made to avoid this difficulty by employing alkyl silicates. However, it has been found that these materials suffer from two serious disadvantages. The first is that the alkylsilicates produce gas on contact with the molten metal unless the mold has been previously heated to temperatures of 1800° F. or above. To fire at such temperatures is both expensive and time-consuming. Furthermore, it has been found that attempts to prepare silicate molds by the commonly employed ramming technique results in a cracking of the mold during curing. Consequently, alkyl silicates are not suitable.

Attempts have also been made to employ alkali metal silicates and alkali metal salts of silanols as the bonding agent for the aggregate. However, these materials suffer from the serious disadvantage of forming hard crusts on the surface of the metal. This is caused by the vitrification of the mold surface when in contact with the molten metal. As a result it is extremely difficult to remove the mold from the metal surface. Consequently, this is a time-consuming and expensive method.

It is the object of this invention to avoid the above difficulties. The process described below has the following advantages over the prior art methods:

(1) It employs a water soluble material.
(2) The molds can be formed by a simple ramming technique.
(3) The molded article can be cured without cracking and to the desired strength at or below 700° F. This means they can be used in the conventional ovens used in foundries.
(4) The molded articles will not gas in contact with molten metal.
(5) The mold is easily removed from the surface of the cast metal.

These advantages provide a cheaper method for precision casting of metals.

This invention relates to a method of preparing molded articles suitable for use as molds and cores in the forming of precision cast metal articles which comprises mixing an aqueous dispersion of a hydrolyzate of a silane of the formula $RSi(OR')_3$, where R is an alkyl radical of from 2 to 3 inclusive carbon atoms and R' is an alkyl radical of from 1 to 2 inclusive carbon atoms, with a foundry aggregate in amount (1) such that the water employed is sufficient to bond the latter into a non-crumbling and non-slumping article when the mixture is shaped by a ramming process and (2) in amount such that the residual silica after firing is at least 0.4 percent by weight based on the weight of the aggregate, thereafter forming the mixture into the desired shape by ram molding, drying the molded article to remove most of the water, and thereafter firing the shaped article at a temperature not greater than 700° F. until the hydrolyzate is reduced to silica whereby a unitary bonded article having a compressive strength of at least 400 p.s.i. is obtained.

In the practice of this invention the silane is mixed with water and agitated until it hydrolyzes to give a homogeneous solution. The solution is facilitated by employing a small amount of a mild acid such as acetic, propionic and the like. These solutions are stable for matters of several weeks and are ready for use in the process of this invention.

The aqueous dispersion thus formed is then mixed in any suitable manner with any desired foundry aggregate. The relative proportions of water and organosilicon compound employed should be such that the mixture is non-crumbling and non-slumping. This is to insure that the aggregate can be satisfactorily formed in a conventional ramming process. If the amount of water is too little, the formed article crumbles upon removal from the pattern. If the amount of water is too great, the aggregate will flow upon removal from the pattern. The precise amount of water varies with the degree of fineness of the aggregate and must be determined with each material.

The amount of organosilicon compound employed must be such that the residual silica after firing will be at least .4 percent by weight based on the weight of the aggregate. Here again the optimum amount of organosilicon compound varies with the particle size of the aggregate. For coarser particles less organosilicon compound is needed, and for more finely divided aggregate a larger proportion of organosilicon compound is needed. In all cases the amount used should be sufficient to produce a fired article of at least 400 p.s.i. compressive strength. The optimum proportions can readily be determined by observing the compressive strength of the fired objects. Obviously for reasons of economy the amount of silane should be kept as low as will give the desired strength. In general, the organosilicon compound will be in minor amount relative to the weight of the aggregate.

After the aqueous dispersion has been mixed with the aggregate, the mixture is formed by conventional ramming technique and the formed article is then allowed to dry to remove most of the water. If desired, the drying can be facilitated by heating at a temperature of 105° C. or above, however, they can also be allowed to air dry.

The dried articles are then fired at temperatures of below 700° F. until the organosilicon compound is reduced to silica. At that point the article stops losing weight. In general, heating at temperatures of 600° to 700° F. for 8 hours is sufficient. However, lower temperatures may be employed for longer times if desired.

Objects made in accordance with this invention have a compressive strength of 400 p.s.i. or above. These strengths are needed in order to prepare molds of sufficient durability to be satisfactory in the precision casting of metals.

For the purpose of this invention any foundry aggregate suitable for use in the formation of sand molds for precision casting can be employed. These include, for example, sand, zirconium silicate, kyanite, olivine and alumina. In short, any refractory material which is inactive toward the metal to be cast and which melts below the casting temperature can be employed herein as the aggregate.

The following examples are illustrative only and are not to be construed to limiting the invention which is properly set forth in the appended claims.

EXAMPLE 1

In each of the mixtures shown below the ethyltrimethoxysilane is hydrolyzed by mixing it with a .1 percent solution of acetic acid in water. The mixture was stirred until the solution was complete and the solution was then mixed with the zirconium silicate in a Kitchen Aid mixer. The resulting mixtures were then made into standard 2 inch cylinders on the Dietert sand rammer. The cylinders so formed were dried at 105° C. for 8 hours and then heated at 600° F. in air for 8 hours. This oxidized the ethyl groups in the residual ethyl siloxane to produce SiO_2. After cooling to room temperature, the compressive strength of each cylinder was determined. The results are shown below.

The zirconium silicate sand employed had a particle size distribution as follows:

None larger than 420 microns
4.06% larger than 250 microns
34.8% larger than 149 microns
50.6% larger than 105 microns
7.82% larger than 74 microns
.37% larger than 65 microns
.98% smaller than 65 microns

The zirconium silicate flour employed at a particle size as follows:

None larger than 250 microns
.013% larger than 149 microns
.005% larger than 105 microns
.075% larger than 74 microns
.400% larger than 65 microns
99.400% smaller than 65 microns

Table I

Mixture No.	Zirconium silicate sand, g.	Zirconium silicate flour, g.	Ethyltrimethoxysilane, g.	Water, g.
1	600	400	7.6	7.6
2	600	400	12.6	12.6
3	600	400	17.6	17.6
4	600	400	25.1	25.1
5	600	400	37.8	37.8

The SiO_2 content and the compressive strength of the articles made from each of these mixtures are shown in the table below:

Table II

Mixture No.	Percent by wt. SiO_2 based on wt. of silicate	Compressive strength, p.s.i.
1	.3	158
2	.5	488
3	.7	939
4	1.0	1,472
5	1.5	2,180

EXAMPLE 2

In each of the samples shown below ethyltrimethoxysilane was hydrolyzed by mixing it with an aqueous solution of .1 percent by weight acetic acid. The aqueous solution of the hydrolyzate so formed was then mixed with a mixture of 420 g. of No. 48 kyanite and 180 g. of No. 100 kyanite. The amount of the aqueous solution was varied so as to give the percent by weight silica based on the weight of the kyanite shown in the table below.

After mixing the solution with the kyanite the mixture was formed and 2 inch cores on a Dietert sand rammer. The cores were then dried for 8 hours at 105° C. and then fired in air for 8 hours at 660° F. to oxidize the ethylsiloxane to SiO_2. After cooling the cores were tested for compression strength. The results are shown in Table III below.

The particle size distribution of the No. 48 kyanite is as follows.

.45% larger than 420 microns
3.22% larger than 250 microns
10.55% larger than 149 microns
15.48% larger than 105 microns
16.95% larger than 74 microns
8.88% larger than 65 microns
44.35% smaller than 65 microns

The kyanite No. 100 had the following particle size distribution:

None larger than 420 microns
.4% larger than 250 microns
6.3% larger than 149 microns
15.6% larger than 105 microns
25.73% larger than 74 microns
11.5% larger than 65 microns
40.1% smaller than 65 microns

Table III

Percent by wt. SiO_2 after firing:	Compressive strength, p.s.i.
1.0	175
1.5	296
2.5	679
3.5	1037

EXAMPLE 3

25 g. of ethyltrimethoxysilane was mixed with 25 g. of an aqueous solution containing .1 percent by weight acetic acid. The mixture was shaken until a homogeneous solution was obtained and then mixed with a mixture of 600 g. of No. 70 olivine sand and 200 g. of No. 150 olivine sand. The mixture was formed in a ram mold and the molded article dried at 105° C. for 8 hours. The resulting article was then heated in air at 660° F. for 8 hours. The room temperature compressive strength was 502 p.s.i. and the article contained 1.25 percent SiO_2 based on the weight of the total olivine.

The experiment was repeated using 40 g. of ethyltrimethoxysilane, 40 g. of .1 percent aqueous acetic acid, 450 g. of No. 70 olivine sand and 350 g. of No. 150 olivine sand. The resulting fired article contained 2.0 percent by weight SiO_2 based upon the total weight of the olivine and had a compressive strength of 995 p.s.i.

The No. 70 olivine sand had the following particle size distribution:

3.7% larger than 420 microns
49.15% larger than 250 microns
33.4% larger than 149 microns
5.69% larger than 105 microns
2.8% larger than 74 microns
.9% larger than 65 microns
4.2% smaller than 65 microns

The olivine sand No. 150 had the following particle size:

None larger than 250 microns
1.7% larger than 149 microns
16.7% larger than 105 microns
62.1% larger than 74 microns
6.6% larger than 65 microns
12.6% smaller than 65 microns

EXAMPLE 4

Employing the procedure of Example 3 a fired article was prepared from a mixture of 700 g. of 100 mesh alumina, 200 g. of 325 mesh alumina, 25 g. of ethyltrimethoxysilane and 25 g. of .1 percent aqueous acetic acid. The resulting fired article had a compressive strength of 659 p.s.i. and contained 1.1 percent by weight SiO_2 based upon the weight of the total alumina.

This experiment was repeated employing 700 g. of 100 mesh alumina, 200 g. of 325 mesh alumina, 40 g. of ethyltrimethoxysilane and 40 g. of .1 percent aqueous acetic acid. The resulting fired article had a compressive strength of 1231 p.s.i. and contained 1.78 percent by weight SiO_2 based upon the weight of the alumina.

EXAMPLE 5

48.1 g. of ethyltriethoxysilane was mixed with 48.1 g. of a .1 aqueous acetic acid. The mixture was shaken overnight to give a homogeneous solution. This solution was then mixed with a mixture of 420 g. of No. 48 kyanite and 180 g. of No. 100 kyanite. The mixture was formed into a cylinder in the Dietert sand rammer and dried 8 hours at 105° C. and then fired in air 8 hours at 660° F. to give an article containing 2.5 percent SiO_2 based on the weight of the kyanite. The resulting article had a compressive strength of 636 p.s.i.

EXAMPLE 6

Equivalent results are obtained when 52.5 g. of propyltrimethoxysilane is employed in the process of Example 2. The resulting article would contain 3.15 percent by weight SiO_2 based upon the weight of the kyanite.

That which is claimed is:

1. A method of preparing articles suitable for use as molds and cores in the forming of cast metal articles to close tolerances which comprises mixing an aqueous dispersion of a hydrolyzate of a silane of the formula $RSi(OR')_3$ where R is an alkyl radical of from 2 to 3 inclusive carbon atoms and R' is an alkyl radical of from 1 to 2 inclusive carbon atoms with a foundry aggregate in amount such that (1) the amount of water in the aggregate is sufficient to bond the aggregate into a non-crumbling and non-slumping article when the mixture is shaped by a ramming process and (2) the amount of silane employed is such that the residual silica after firing is at least .4 percent by weight based on the weight of the aggregate, thereafter forming the mixture into the desired shape by ram molding, drying the molded article to remove most of the water and thereafter heating the shaped article at a temperature not greater than 700° F. until the hydrolyzate is reduced to silica, whereby a unitary bonded article having a compressive strength of at least 400 p.s.i. is obtained.

2. The method of claim 1 wherein the silane is ethyltrimethoxysilane.

3. The method according to claim 1 wherein the silane is ethyltriethoxysilane.

4. The method according to claim 1 wherein the silane is propyltrimethoxysilane.

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