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PROCESS OF CASTING REFRACTORY MATERIALS

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This invention relates to a method of forming articles composed of sintered refractory materials and more particularly pertains to a process for casting refractory materials in a manner permitting the casting to be of complex shape and permitting close control of the dimensions of the casting without necessitating machining of the article while it is in the "green" state.

Many methods of casting and sintering refractory materials have been employed in the past to produce ceramic and metallic articles. Conventional casting methods have proved to be adequate for producing the bulk of commercial ceramic ware as that ware is usually simple in shape, is not required to have highly precise dimensions, and is made of materials that are relatively easy to work. In the past, casting of refractory materials was done by causing a fine powder of the refractory material to be consolidated into a coherent mass of putty-like consistency, pressing the material into a form or die to cause the material to be molded into an approximation of the desired finished shape, causing the piece to harden to a state where it could be ground or otherwise machined to its final configuration, and heating the "green" piece at a high temperature to cause the grains of powder to fuse together. Machining of the green piece is required to obtain complex shapes as conventional methods do not permit intricate configurations to be obtained directly by casting. Further, due to wear of the die or form and because of uncertain shrinkage of the green piece during the process, castings of highly precise dimensions cannot be produced by conventional methods. To obtain precise dimensions, the casting produced by conventional methods is usually deliberately made oversize and is then ground to the desired size. Grinding of the casting is expensive and difficult as sintered refractory materials tend to be extremely hard and brittle. In attempting, by conventional methods, to produce castings of shapes having sharp corners or having portions of small cross-section, it was found that strains are introduced in the green piece during drying which cause cracks to appear when the casting is fired into its final form. To produce articles having irregular contours, undercuts, internal holes, sharp corners, or severe bends, machining operations upon the "green" piece had to be performed.

The present invention resides in a process for forming objects of refractory materials which, without machining of the green or finished piece, permits intricately shaped articles of highly precise dimensions to be produced. In the novel process, the refractory material, in the form of a fine powder, is mixed with a binder and a deflocculating agent to form a slurry. The deflocculant may be oleic acid and the binder is a material, such as paraffin, having a volume just sufficient to fill the interstices of the loosely-packed powdered refractory material when the binder is solidified and the grains of the refractory material are in contact with one another. In order to maintain the mixture as a slurry, it is kept at a temperature where the binder is liquid. In the slurry the powdered refractory material is dispersed by the deflocculant so that the grains are distributed homogeneously throughout the binder. The slurry is cast into a mold of the desired shape and the binder is permitted to solidify so that a green piece is formed having a uniform density. The slurry, being a

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liquid suspension, conforms closely to the configuration of the mold so that the green piece can have intricate shapes, corners, and sharp bends. The green piece, after removal from the mold, is packed in an inert refractory powder, such as alumina, and is then heated slowly to a temperature at which the binder vaporizes and is driven off through a vent. A low rate of increase of temperature is employed to prevent the binder from vaporizing so rapidly as to weaken or rupture the casting. After a length of time sufficient to drive off all the binder, the temperature is raised to a level where partial sintering occurs. Partial sintering affords sufficient strength in the casting to permit it to be removed from the alumina packing and the alumina to be dusted from the presintered casting. Subsequently, the casting is heated to sintering temperature and there maintained for a period of time determined by the desired density of the finished article.

Castings having intricate shapes may be made by the process here described and irregular contours, undercuts, internal bores, and threads can be produced. Virtually any shape and size can be reproduced, depending principally upon the skill of the die maker. Further, because the powder is homogeneously dispersed in the binder the resultant "green" casting is of uniform density, and its shrinkage from the green state to the size of the finished casting does not result in stresses which crack the casting and permits the final size of the finished product to be known with a large degree of certainty. The shrinkage of the sintered casting is, in many instances, less than 1% of its volume in the green state.

This process may also be adapted to other forming methods. For example, hollow bodies such as beakers or thermocouple housing may be produced by using a form whose exterior dimensions conform to desired interior dimensions of the final product, coating the form with a parting agent such as silicone grease and slipping the form into the molten slurry. To build up a significant thickness of material on the surface of the form, the form should be cooled below the melting point of the slurry. After a sufficient thickness of the solidified slurry is built up on the exterior of the form, it is removed and handled as previously described.

The amount of paraffin or other binder used in the slurry is such as to fill the interstices of the powdered refractory material and the volume ratio of powder to binder is of major importance. The ideal ratio is one where when the particles of powder are in contact with each other and the binder is just sufficient to occupy the interstitial spaces. If the ratio is too low, then movement of the powder grains will occur when the binder is driven off, causing the piece to distort and lose its dimensions. If the ratio of powder to binder is too high, not enough binder will be present to completely fill the interstices so that when the slurry within the die solidifies, the green piece is not of uniform density. Furthermore, the slurry tends, when the ratio of powder is too high, to be viscous and, therefore, may not conform to the shape of the die.

When the binder is driven off, the green piece has no strength and cannot be handled. It is necessary, therefore, prior to driving off the binder, to put the green piece in an inert packing. A packing powder is used which does not react with the casting and which is composed of grains of such size as to give a good surface finish to the casting. Further, the packing powder must have a sintering temperature above that of the material of the casting because the casting is partially sintered immediately after all the binder has been driven off.

Specific examples of the process as applied to various materials are set forth below. It should be understood that the examples which are given illustrate the capabilities of the process and are not intended as limitations upon the scope of the invention.

Example I

A granular powder of tungsten is uniformly dispersed in a binder treated with a deflocculant. The binder is a material that is a solid at room temperature and is characterized by a low melting point, a low viscosity when molten, and a vaporization point below the presintering temperature of the powder used. The binder is preferably chosen from the waxes or paraffins and wherever "paraffin" is employed in the specification, a binder having the foregoing characteristics is intended. The deflocculant may be any dispersing agent that is miscible with the binder and which acts to provide complete and uniform wetting of the powder grains.

One thousand eight hundred and eighty grams (1880) grams of tungsten powder, milled to a fineness permitting it to pass through a screen of three hundred and twenty-five (325) mesh, is mixed in a molten solution of one hundred (100) grams of a paraffin binder and fourteen and two tenths (14.2) grams of oleic acid to form a slurry. Where a greater or lesser amount of the slurry is required, the quantities are determined by measuring the volume of the powdered tungsten, ascertaining the amount of paraffin which in its solid state is equal to about 45% of the powder's volume, and using about 1% by weight of oleic acid. It has been found that if the volume of binder is less than this, the viscosity of the slurry at the melting point of the paraffin is too high for easy flow and if the volume of binder is significantly higher than this proportion, large shrinkage occurs upon driving off the binder. The volume of binder in its solid form should be equal to the volume of the interstices of the granular tungsten. When in the molten state, the volume of binder should be sufficient to permit dispersing the grains sufficiently so that the viscosity of the mixture is such that the slurry can be poured freely. The temperature of the slurry is kept between 250° and 300° C. and the slurry is constantly agitated so as to maintain turbulence for a time sufficient for the slurry to "outgas." A period of thirty minutes was found to be adequate for outgassing the slurry. The temperature should not be allowed to exceed the 300° C. at which vaporization of the paraffin begins. Following outgassing of the slurry, it may be permitted to solidify in ingots or bars until needed for casting.

For casting, the ingot material is heated until it again becomes a slurry and the slurry is then poured into a mold which has been coated with silicone grease or some other parting agent. The material in the mold is permitted to cool and solidify. The solid casting is removed from the mold and packed in alumina powder that has been passed through a screen of at least 100 mesh. The package is heated slowly to a temperature of 400° C. to drive off the binder and the deflocculant. It should be noted that binder and the deflocculant vaporize without leaving any appreciable residue. The package is vented to permit the vapors to escape and the temperature is raised slowly so that rapid vaporization does not occur. A rate of temperature increase of 1.5° C. per minute is satisfactory. After all the binder and deflocculant are driven off, the temperature is increased to about 1700° C. and there maintained for a period of about three hours. The presintering, at about 1700° C., is performed in order to impart enough rigidity to the casting to permit it to be handled.

Subsequent to presintering, the casting is removed from the packing and, after being dusted to remove any adherent alumina particles, is fired at sintering temperature for a time determined by the desired density of the finished casting. In this example, a density of 72% is obtained by firing the casting at 2200° C. for one hour.

Example II

A ceramic casting was made by the procedure described hereinafter. Granules of zirconium dioxide (ZrO_2) which had passed through a screen of 325 mesh were

employed. To a melt consisting of 50 grams of paraffin and 2.8 grams of oleic acid was added 448 grams of screened zirconium dioxide. As described in the previous example, the melt was prepared by heating the paraffin until it was liquid and the oleic acid was thoroughly mixed with it. The powdered zirconium dioxide was put into the melt and the slurry was heated for a time sufficient to permit the temperature to stabilize somewhere between 250° and 300° C. and for all the air that was entrained in the mixture to escape. During this time, the slurry was agitated by stirring to assure that the powder was dispersed in the melt. The slurry was then poured into a mold that had been treated with silicone grease to insure that the casting could be easily parted from the mold. The slurry was permitted to cool and solidify. Following the solidification of the mixture, the casting was removed from the mold and packed in a refractory powder, again alumina, and raised very slowly from 25° C. to 1100° C. over a 24-hour period. Following the cooling of the casting, which has now been dewaxed, the casting was removed from the alumina and reheated from 25° C. to 1500° C. and maintained at that temperature for 18 hours whereupon a 72% density and 1.7% shrinkage was achieved.

Other materials have also been used for producing castings: for example, magnorite, forsterite, mullite and fused silica are just a few of the many types of materials that may be used following this disclosed process. Densities and shrinkage of the final product have varied, the following of which are typical examples:

Magnesium oxide devices have been built in which 68% of the theoretical density has been achieved with an .8% firing shrinkage, while mixtures of aluminum trioxide and silicon dioxide have been fired together with theoretical densities of 60% and a firing shrinkage of only .7%.

It should be understood although both examples described a granular powder sufficient to pass through a three hundred and twenty-five (325) mesh, the coarser or finer powders may be used.

Although this invention has been described in connection with specific examples, it can be readily recognized that the invention is capable of a wide variety of modifications and variations and should be limited in scope only by the appended claims.

What is claimed is:

1. A process for forming an object of precise predetermined configuration comprising the steps of: mixing a refractory granular material capable of being sintered with a meltable binder in sufficient quantities so that the volume of said binder when in a solid state is equal to the volume of the interstices of said material forming said mixture in a molten state into said configuration, allowing said mixture to solidify thereby forming a solid object having said predetermined configuration, packing said object into a non-reactive refractory powder, heating said packed object to a temperature sufficiently high enough to drive off said binder while leaving said granular material, raising the temperature of said object to a level for presintering to unify said material and thereafter removing said object from the powder and heating said object to a temperature for sufficient time for said object to reach a desired density.

2. A process of forming an object of predetermined configuration comprising the steps of: mixing a paraffin and a suspending agent with a refractory granular material capable of being sintered in sufficient amounts so that the volume of the paraffin and the suspending agent are equal to the volume of interstices of said granular material when the mixture is at room temperature heating the mixture to a viscosity level at which the mixture will freely pour, pouring said mixture into a mold having the predetermined configuration, allowing the mixture to solidify in said mold, removing the solid mixture from the mold, packing the solid in a nonreactive material, heating the

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casting to a temperature sufficient to volatilize said paraffin and said suspending agent but not sufficient to affect the granular material, maintaining said temperature until the paraffin and said suspending agent is driven off, increasing the temperature to a presintering level, allowing said solid to cool, and thereafter removing the object from the non-active material, heating the casting to a temperature for a sufficient time to sinter said object.

3. A process of making ceramic bodies of a predetermined configuration consisting of the steps of: preparing a solution of paraffin and oleic acid, heating said solution to a temperature of greater than 250° C. but less than 300° C. to place said solution in a molten state, forming a mixture by adding a ceramic material in granular form to said molten solution, agitating said mixture to create turbulence therein, maintaining said turbulence in said mixture for a period of time sufficient to homogenize and stabilize the temperature of said mixture and to free entrapped gas from said mixture, coating a mold of said configuration with a parting agent, pouring said mixture into said mold while said mixture is in a molten state, allowing said mixture to assume the shape of said mold and to solidify therein with said solidified solution just filling the interstices of said ceramic granules, removing said solid mixture from said mold, placing the molded object in a packing of a nonreactive, refractory, granular material to support said solid mixture, heating to a presintering temperature sufficient to dewax said object and to impart structural rigidity to the object, causing the temperature of the object to cool to 25° C., removing

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said solid from said packing, and heating said solid at sintering temperature to achieve a desired density.

4. A material suitable for molding with a shrinkage rate of less than 10% comprising:

a refractory granular material capable of being sintered, and a binder,

said granular material being dispersed throughout said binder, the relative amounts of said binder and said granular material being such that the volume of said binder in a solid state is equal to the volume of the interstices of said granular material at room temperature and wherein said binder has as its major constituent, paraffin.

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