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2,948,627

## MOLDING COMPOSITION AND PROCESS FOR PRODUCING SAME

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This invention relates to a molding composition and a process for preparing expendable molds to be used for casting titanium, titanium alloys, or other refractory metals and alloys which are normally subject to excessive surface reaction or internal contamination during casting.

The high melting metals of group IV of the periodic table, specifically titanium, zirconium and hafnium, and alloys containing major amounts of these metals, are highly reactive in their molten state. Because of this reactivity, serious difficulties have been encountered in obtaining suitable crucibles and molds for melting and casting operations. At the present time, there are melting operations which make available a source of the liquid metal for casting purposes. This invention provides new and improved molding compositions for these casting operations, and a method for making the same.

Problems associated with the casting process deal first with the mold composition and secondly with the method of preparing the mold. Prior attempts to solve these problems have been deficient in either or both of these categories. Machined graphite molds have been used for casting molten titanium. This method, however, is limited to relatively simple shapes, and it is expensive because of machining costs. The best results with machined molds have been obtained by vacuum baking the mold at a high temperature after it is machined into shape. It has been found that castings formed in machined molds have a contaminated surface layer but that they are otherwise free of excessive impurities. However, in addition to the difficulty in shaping the molding material by machining, the castings are often marred by cold shuts and seams since the heat conductivity and heat capacity of the mold can cause rapid surface chilling.

Molds made of refractory compositions containing high melting oxides, silica, alumina, zircon, zirconia, magnesia, thoria, etc., have caused excessive contamination because of the reduction of the oxides by the liquid refractory metal. Mold binders of various types such as clays and organic resin binders have been tried, but results have been poor because of excessive contamination from both the binder and the refractory oxide.

Cooled metal molds, for instance water-cooled copper molds, have been tried with moderate success, but this method is very expensive and limited as to the shapes which can be cast. Furthermore, the cooling of the mold will often result in cold shuts, seams, and other undesirable effects.

The objects of this invention are to develop a molding composition and process which permits the preparation of satisfactory molds for casting refractory metals at eco-

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nomical rates and with a minimum outlay for raw materials, equipment and labor. Further objects of this invention are to develop a molding composition and process for the production of quality castings of the refractory metals and their alloys, especially titanium, without being limited by size, shape, surface finish, or mechanical properties.

The above and other objects are realized by this invention which concerns a composition adapted to be mixed with water and be formed into a mold suitable for casting refractory metals. This composition comprises a mixture of starch, powdered bituminous pitch, sugar, an organic surface-active agent and powdered graphite. The starch serves as the temporary binder and is used in an amount sufficient to provide the necessary green strength in the fresh or unfired mold. The powdered pitch provides the high temperature binding action which is enhanced by the sugar in that a smooth, stable mold surface is retained during firing and use. The surface-active agent improves the wettability of the solids, thus reducing the amount of water required to form a moldable mixture. It is essential that all of the ingredients are substantially ashless so that the fired mold is composed of substantially pure carbon, a significant portion of which is in the form of graphite. The presence of any appreciable amount of ash in the molding composition will cause the mold to contaminate the casting and increase its porosity to an unacceptable degree.

A more specific composition comprises about 5–20% of starch, about 6–20% of powdered pitch, about 2–9% of a sugar, an organic surface-active agent in an amount sufficient to improve the water-dispersibility of the mixture, the remainder consisting essentially of graphite.

This invention also encompasses the above novel composition when admixed with water to form a moldable composition useful, for example, as a foundry ramming mixture. It also includes improved molds prepared from the water admixture.

The improved mold has a unique combination of properties. The moderate thermal conductivity gives better castings than machined dense graphite. The porosity, which is controlled by selection of certain particle sizes and proportions of the critical components of the mold mixture, makes possible the elimination of more difficult mold-venting procedures.

A typical procedure for preparing the composition which is later to be mixed with water involves compounding about 6–20% of powdered pitch, about 5–20% of powdered starch, about 0.2–7% of a water-soluble organic surface-active agent, about 2–9% of a sugar, and from about 44–86% of graphite. This is a stable mixture which is convenient for handling, storage and shipping. Use in a foundry merely requires admixing with water.

In the ultimate mixture used for forming the mold, the water content may range from about 5–25%, and preferably from about 5–10%. Thus, the composition of the water-containing molding mixture will comprise about 5–15% of starch, about 6–15% of powdered pitch, about 5–25% of water, about 2–7% of a sugar, about .2–5% of a water-soluble organic surface-active agent, with the remainder being essentially powdered graphite.

The invention also includes a process for preparing a mold suitable for casting refractory metals. The process comprises compounding a mixture of: about 5–20% of



starch, about 6–20% of powdered pitch, about 2–9% of a sugar, an organic surface-active agent in an amount sufficient to improve the water-dispersibility of the mixture, the remainder of the mixture consisting essentially of graphite. In compounding the above ingredients, enough water is added to form a moldable mixture which is then shaped into a mold and gradually heated to temperatures sufficient to carbonize the organic constituents. The order of mixing of the ingredients for this process is not at all critical. For instance, one may compound all of the non-aqueous ingredients and later, for example just prior to forming the mold, incorporate the water. It will be noted from a further reading of this specification that other sequences may be employed.

In a preferred procedure, the proper amounts of powdered graphite, ground pitch, and dry cornstarch are placed in a cone blender and allowed to mix thoroughly. The weight percentages of these in the typical final molding composition are about 63% graphite, about 10% pitch, and about 10% dry cornstarch. While this dry portion of the final mixture is being blended, the liquid portion may be prepared by mixing about 8% of an 80% sugar solution in water and water to total about 9% based on the weight of the final mixture. Then about 1% by weight of the surface-active agent (based on the final mixture) is incorporated. The dry mixed ingredients from the cone blender are placed in the sand muller, with the mixing equipment being operated at medium speed, and the liquid portion is then slowly added to the dry portion. After all of the liquid has been added, about 15 minutes of mixing will suffice to produce a molding mixture of the proper damp consistency. The pattern which in the foregoing illustration is a split mold type, and core boxes if any are used, should have been previously prepared for use. Metal, or lacquered wood patterns, or other suitable pattern materials may be used. All surfaces of the pattern coming in contact with the mold mixture should be given a light coating of a parting compound. Petroleum jelly, non-sticking silicone surface finishes and fluorinated finishes are suitable for this purpose.

The molding box, or flask, and the pattern within are assembled, and the molding mix is then added to the box and lightly tamped over all surfaces of the pattern to an even depth. A steel pressure plate, made to fit inside of the mold box, is then put in place. The retaining walls of the mold box can be made of removable angle iron or equivalent structural materials that will not buckle under the load here applied. C clamps or pins may be used to hold the enclosing sides in place during the molding operation. A very satisfactory green mold is obtained by placing the whole assembly on the table of a mechanical or hydraulic press and applying a load to the pressure plate until a total force of from about 60 to 100 lbs. per sq. in. exists on the mold mixture. The amount of pressure will depend on the dampness of the mix, the particle size of the refractory material used and many other factors, but it should not be great enough to cause extrusion of the mixture, or to distort the pattern. The length of time at this pressure does not seem critical, and short times of a minute or less have been found satisfactory. After pressure is removed, the pattern and the mold box assembly should be disassembled. The mold may then be stripped from the pattern by means commonly utilized in foundry practice.

The mold is allowed to dry at room temperature until it becomes fairly hard and can be handled without sagging or breaking. If the molds are small, about six hours is usually sufficient to reach this stage. The mold is then dried to remove the free moisture. Gradual heating is used to prevent crumbling. It has been found that for small molds heating for 16 hours at 60° C., after which time the temperature was raised to 80° C. for another 8

hours, and then a final bakeout at 100° C.–125° C. for a period of 16 hours, was sufficient.

The mold is now ready for firing to dehydrate and carbonize the temporary agents and fix the permanent binder to place the mold in condition for contact with the molten refractory metal such as titanium. The firing must be done in a protective atmosphere to prevent excessive oxidation of the graphite which would destroy the dimension and detail of the mold. With small molds which could be handled in the laboratory, it has been found that a steel box with a graphite bottom insert and a thick graphite lid to contain the mold and exclude oxygen was quite a satisfactory apparatus. The mold and box are then placed in the furnace, preheated to about 700–900° C., and fired at that temperature from one to two hours. The box is then removed from the furnace and allowed to cool without disturbing the graphite lid. After cooling to room temperature the mold is removed from the steel box, and it is ready to be assembled and used for casting.

While the above procedure outlines a typical operation for preparing split-mold halves, other types of mold forms may also be prepared by the process of this invention. Molds which do not have the parting line in a horizontal plane, multisection molds for casting complex objects, investment type molds wherein the pattern is destroyed during the mold hardening operation, and solid and hollow cores are examples of some of the types which can be made. While the drying and firing operation may be carried out, as indicated above, in several steps, a gradual continuous heating is fully as effective.

The mold-halves, prepared as above, are joined in a suitable manner by the use of alignment pins, wires or clamps, and then they are placed in the casting booth of the furnace. Optimum results are obtained with the refractory metal castings when vacuum casting procedures are used, since gases are more easily removed from the mold cavity.

After the casting operation, the mold and casting are removed from the furnace, and the mold is broken away with a hammer and a chisel. The mold material fractures rather easily and does not adhere to the metal of the casting. The casting can then be cleaned by conventional procedures.

The following examples are presented to illustrate my invention, but they are not meant to be in limitation thereof. Unless otherwise specified all percentages in the specification and claims refer to percentages by weight.

#### Example I

A mixture of the following composition was prepared using above-described procedure:

	Percent by weight
400 g. graphite refractory powder	64.0
56 g. electrode joint cement (45:40:15 mixture of —200 mesh graphite powder, sugar and water)	7.3
80 g. ground coal tar pitch, M.P. 250–350° F.	10.4
80 g. instant cornstarch	10.4
6 g. N,N diethyl cyclohexylamine salt of sulfated lauryl alcohol	.78
146 g. tap water	19.0
	99.88

The graphite powder had the following size distribution:

	Percent
—200	20
+200–150	7
+150–100	9
+100–65	10
+65–35	22
+35–20	31
+20	1

The mixture molded excellently at 2000 lbs. total pressure on an area of about 20 square inches using a small



hydraulic press and a steel pattern. The pattern and the retaining flask were lightly coated with petroleum jelly before the pressing operation to prevent sticking of the mold to the pattern. The mold was allowed to air dry 5 hrs. at room temperature, and then it was placed in an oven heated to 60° C. for 16 hrs., then to 80° C. for 8 hours with a final bakeout at 120° C. for 16 hrs. The dried mold was placed in a graphite-lined steel box having a graphite lid and fired at 700° C. for 1 hour in an electric muffle furnace. There was no buckling or distortion and shrinkage was about  $\frac{1}{64}$ " per linear inch. The mold was hard, abrasion resistant, strong, and fairly light in weight with good surface characteristics.

About one pound of molten titanium was cast in this mold using a research casting furnace similar to that described in "A Bottom-pour Arc-Type Furnace for Melting and Casting of Titanium," by O. W. Simmons, H. R. McCurdy and R. E. Edelman, 1954 American Foundrymen's Society, Preprint No. 54-36, 1954 Annual Meeting. The resulting casting had a smooth surface and no internal porosity. A thin surface layer  $\frac{1}{4}$  mm. thick showed increased hardness over the base metal stock but the balance of the cross-section was of original hardness. Data are as follows:

	Before Casting	After Casting
Brinell Hardness Number (BHN).....	245	248.
Contaminated Layer Depth.....		$\frac{1}{4}$ mm.
Max. Hardness of Contaminated Layer.....		400 BHN.
Carbon.....		.017% by weight.
Hydrogen.....		96 p.p.m.
Nitrogen.....		.043% by weight.

It should also be noted that carbon and hydrogen values are of an acceptable level for the majority of casting applications. The thin hard surface layer can be removed by pickling with acid solutions or sand-blasting with appropriate grits. The dark color existing on the surface of the casting when it is removed from the mold can be removed by ordinary descaling treatments for titanium.

#### Example II

A mixture of the following composition was prepared using the above-described procedure:

	Percent by weight
1600 g. graphite refractory powder .....	52.4
224 g. electrode joint cement (45:40:15 mixture of —200 mesh graphite powder, sugar and water) ..	6.96
320 g. ground pitch M.P. 250–350° F. ....	10.4
320 g. instant cornstarch .....	10.4
24 g. N,N diethyl cyclohexylamine salt of sulfated lauryl alcohol .....	.78
584 g. tap water .....	19.0

The mixture was molded over a steel pattern plate using only hand ramming. Petroleum jelly was again used as the parting agent on pattern parts and retaining flask. The mold was allowed to partially dry on the pattern and was then stripped without difficulty. The mold halves measured 7" x 14" x  $\frac{7}{8}$ " in size. They were allowed to dry at room temperature for 24 hours, and then they were baked out at 60° C. for 18 hrs. and 80° C. for 16 hrs., with a final bakeout at 120° C. for 8 hrs. Firing was done in a graphite covered steel box at 800° C. for 1 hr. Linear shrinkage was again about  $\frac{1}{64}$ " per linear inch.

Approximately 5 lbs. of molten titanium was cast into this mold using a bottom-pour casting furnace. This casting exhibited a smooth surface similar to the casting in Example I, and it showed no internal porosity.

Data are as follows:

	Casting
BHN .....	198
Contaminated layer depth .....	$\frac{1}{4}$ – $\frac{1}{2}$ mm.
5 Max. hardness of contaminated layer .....	490 BHN.
Carbon .....	.03 by wt.
Nitrogen .....	.02 do.
Hydrogen .....	146 p.p.m.

#### Example III

A mold-forming mixture was made of the following constituents:

130 gms. ground synthetic graphite having a sieve analysis of 1% plus 30 mesh, 70% minus 30 plus 200, and 29% minus 200; 20 gms. asphaltite ground to pass 100 mesh; 24 gms. potato starch powder; 10 gms. corn syrup of 80% solids and having a dextrose equivalent of 25; 4 gms. sodium lignin sulfonate and 12 gms. of water.

The graphite, asphaltite, starch and wetting agent were thoroughly mixed in a high-speed mixer (Waring Blendor). The corn syrup and water were mixed and added to the mixing solids. The mass developed cohesion and became crumbly. It was transferred to a muller and worked into a smooth mixture and shaped by ramming into a test mold pattern. The mold, separated from the pattern, was placed in a cold muffle furnace and allowed to stand at room temperature with the door open for 3 hrs. The door was closed and nitrogen purge gas supplied to the furnace chamber. The heat was turned on and the temperature slowly raised over a period of 16 hrs. to 950° C. and held at this temperature for a half hour. After cooling in the protective atmosphere of the furnace, the mold was removed and found to be strong and smooth-surfaced. A satisfactory small tantalum casting was made in it under an atmosphere of argon.

#### Example IV

The following ingredients were used in compounding a molding mixture:

1635 g. synthetic graphite powder.....	62.6
320 g. ground pitch, M.P. 250–350° F.....	12.23
320 g. instant cornstarch .....	12.23
150 g. water .....	5.72
115 g. corn syrup (22% water).....	4.40
50 g. graphite powder —325 mesh.....	1.91
24 g. Triton X-100 .....	0.92
2614 g.	100.01

The first portion of graphite, pitch and cornstarch was dry mixed in a cone blender and the corn syrup, water, fine graphite and wetting agent separately combined to form an aqueous solution. This solution was then milled into the dry mixture to form a ramming mix.

In the above examples, the carbonaceous refractory powder utilized in preparing the molds was a commercial product, having a specific particle size distribution. Coarser or finer grades of graphite may be used, depending upon the desired degree of porosity of the mold and the smoothness of the casting surface. It has been found that the smoothness of the product and the porosity is influenced by the particle size of the carbonaceous refractory grain and that the porosity is also influenced by the particle size distribution of the powder. The graphite powder used should be substantially pure and especially free from mineral ash content such as silica, alkalis, lime, etc. which are attacked by the molten metal. The very best natural graphite may be beneficiated to 99% or more in carbon content by grinding and leaching. This material is satisfactory but expensive. The more available, purer and cheaper synthetic graphites are much preferred. A major portion of the grains should be within the U.S. Standard Sieve size range of —20 plus 200 mesh (0.074 to 0.82 mm. dia.). While a major portion of the graphite is in the —20 +200 range, it is desirable to have from 5–45% of it in the —200 mesh range and usually including fines in the sub-sieve range even to colloidal graphite. Preferably a portion of



about 5–20% of the finer graphite is dispersed in the sugar-water solution as in Example IV. The fineness characteristics of the refractory powder should be governed by the same consideration governing the use of sand as a molding material and consequently selected sizes within the above range may be employed. A good base material is a graphite powder having an aggregate grain size approximating an AFS 70 (gfn).

The starch component in the mixture provides green strength and is readily carbonized to leave only carbon in the final mold after firing. Various forms of such water-swellable, finely divided carbohydrates may be used. Cornstarch is most readily available and cheap but potato, rice, wheat, barley and other starches are suitable. Also the prepared or modified starches, such as instant laundry starch, have been found entirely satisfactory. The amount used is determined experimentally and relates to the size of the mold being made and to the particle size of the graphite used. Variation in the proportion of starch in relation to the amount of graphite may also be employed as a means of regulating the thermal characteristics of the mold. The amount used generally lies in the range of from 5 to 20% by weight of the dry mixture or from 5 to 15% of the final moistened ramming composition.

Another essential ingredient is a sugar or sugars. This differs in its function from the starch in that it enhances the formation of a smooth mold surface during the firing step. These sugars are of the class of highly water-soluble carbohydrates. In contrast to the starches, they form true solutions or syrups rather than colloidal dispersions and gels. The amount used is also determined by practice but usually lies in the range of 2–9% of the solids in the mixture and from 2–7% of the final moist mix.

Various sugars may be used. Of the various saccharides which may be used, the disaccharides are preferred. Low cost is a factor; hence, the more common sugars such as sucrose, maltose, fructose and lactose are sought. The various useful commercial forms or products containing these sugars include commercial table sugar, brown sugar, maple syrup, etc. Sugars obtained by conversion of other material such as starch or cellulose are useful. One particularly useful source is corn syrup.

Both the water-swellable, finely divided carbohydrates (starch) and the water-soluble sugar are essential and appear to perform substantially different functions in the mold manufacture. The sugar seems to function to improve the high temperature bonding of the mold and preserve a smooth surface. The sugar is preferably dissolved in water, as in the syrup, where, by virtue of the increased viscosity it may help to disperse the graphite. Its exact behavior is not thoroughly understood but it appears essential to the composition. One should preferably make provision to have the sugar in a dissolved condition in the mold composition, either by presolution or by allowing time during the mixing for its solution in the water component. Commercial preparations, sometimes known as electrode joint cements, comprising sugar, water, and fine graphite are available and may be used in this composition.

The bituminous component is preferably utilized in the powdered state, a typical product being a pitch core compound type. Flake bitumens may be utilized as raw material if they are ground to sufficient fineness in such comminuting means as ball mills or grinders. The bitumen of the preferred type has a melting point of not less than 250° F. and not more than 350° F. The bituminous component may be coal tar, asphalt, asphaltite, gilsonite or a vegetable oil pitch.

Preferred surface-active agents which are the amine salts of sulfated aliphatic alcohols containing from 8–20 carbon atoms are disclosed in U.S. Patent 2,139,277. Other types of wetting agents are suitable although it has been found that larger quantities must be used and that

mixing is not as easily accomplished as with the preferred agents.

The following agents have also been tried and found to work; many others are available:

Trade Name	Composition
Darvan #2.....	Condensation product of formaldehyde with naphthalene sulfonic acid.
Daxad #21.....	Calcium salt of polymerized alkylaryl sulfonic acid.
Marasperse N.....	Sodium lignin sulfonate.
Daxad #11.....	Sodium salts of a polymerized alkylaryl sulfonic acid.
Triton X-100.....	Alkylaryl polyether alcohol.

15 Anionic surface-active or wetting agents such as the alkali and alkaline earth salts of dinaphthylmethane mono and disulfonic acids, for example sodium dinaphthyl methane disulfonate and calcium dinaphthyl methane disulfonate, have been found to be suitable. Cationic agents such as amines, amine salts and quaternary ammonia compounds have been found to be useful. Non-ionic compounds such as products obtained by condensation of phenolic compounds having lateral chains with ethylene oxide are also suitable. For example, 206 parts

20 by weight of p-isooctyl phenol are melted and reacted with 2 parts by weight of 40% caustic soda solution. During agitation at a temperature of 120° C. to 130° C., ethylene oxide is passed into the mass until ten molecules of ethylene oxide are absorbed for each molecule of the phenol, i.e., until a total of 644 parts by weight is obtained. The product is soluble in cold water and is useful as a wetting agent in this invention.

25 The useful surface-active agents are water soluble and are preferably non-ashing, or at least very low in ash content. The alkali silicates for example are not desired. The sodium and calcium salts of the organic sulfates and sulfonates have a very low ash content and may be used, but the completely mineral-free agents are preferred.

30 The wetting agent, whether liquid or powder, may be added to the liquid portion of the mix. If it is a powder, the dry portion of the mix can be made up using the carbon refractory powder, the carbohydrates, the bitumen and the wetting agent. This composition would require only the addition of water to produce the molding composition.

35 It has been found that the preferred water-containing composition utilizes starch in quantity of about 10% by weight of the total composition, but amounts may range from 5–15%. About 10% by weight of pitch in the molding composition is preferred, but usable molds have been produced with from about 6–15% of this material. About 2–7% by weight of sugar serves to aid in creating a stable high temperature bond, especially at the mold surface. About 1% by weight of the wetting agent is preferred, but satisfactory castings have been made with as little as .2% and up to about 5%. The preferred mold mix has about 7% by weight water, but from about 5–20% water has been utilized in preparing molds. The remainder of the composition comprises

40 the carbonaceous refractory powder, such as highly purified, ground natural graphite or synthetic graphite. Graphite containing at least 99% carbon is desired.

45 Usually core compositions are designed to be slightly weaker than the main mold. Modification of the molding mix to utilize slightly greater amounts of temporary binder and water, and smaller amounts of permanent binder will yield core mixes which are suitable.

50 In the preparation of the molds, the molding composition was preferably pressed around the pattern by the use of a force plate activated by a hydraulic press. This method of operation is preferred when split-half pattern plates are utilized because it serves to produce a mold which is strong and self-supporting. One may also utilize a hand-ramming method of compacting. Furthermore, this may be required in some types of molds

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especially where the parting line is not in a flat position. Separation of mold sections which have uneven parting lines may be accomplished by lightly dusting one mold surface with graphite powder while compacting and pressing another mold section onto it. This produces a parting line where the mold sections may be separated.

The time of drying the initial mold to produce a strong green mold is variable because of differences in the porosity of various molds, the amount of temporary binder used, and the amount of water utilized in the mix. One skilled in the art can properly regulate the drying cycle to obtain good green strength without cracking or disintegration of the mold. It is preferred to have the final drying temperature in excess of the boiling point of water since this will prevent any gassing or surface disruption when the mold is baked. The baking, or firing, destroys and carbonizes the green binder components and fixes the components of the permanent binder. If desired, a reducing atmosphere type furnace may replace the graphite enclosure utilized in the example for the firing operation. Firing temperatures usually range from about 700° C. to about 1100° C. It has been found that higher firing temperatures cause the mold to be less reactive towards the molten refractory metal. Maximum advantages may be obtained by vacuum firing the mold to temperatures in excess of the melting point of the refractory metal just prior to casting. With this procedure the mold composition is completely outgassed at the maximum service temperature.

The theory and action of my mold composition illustrate some of the advantages which may be obtained by utilizing my invention. Molten titanium metal reacts with all refractory materials to greater or lesser extent, but graphite seems to be the least reactive of available materials. Castings have been made in machined graphite that are quite satisfactory, but machined graphite is expensive and the molds for unusual shapes are extremely complex and must be made in many parts. Furthermore, because the machined graphite is relatively non-porous, extensive venting of machined graphite molds is required.

Refractory graphite powder and pitch are relatively cheap and abundant. The object of this invention is to utilize this cheap excellent refractory to produce a mold having the desirable non-contaminating properties of the machined graphite molds, while eliminating their limitations in respect to shape, size and complexity of production. To do this, a two-stage binder action is utilized. One binder allows room temperature molding and setting, and the other binder forms cohesion at elevated firing temperatures. In addition, an aid to the high temperature binder is used. The firing is considered to reduce substantially all of the raw materials to carbon, and this prevents subsequent reaction between the mold constituents and the molten refractory metal, such as titanium. It has been found that the surface-active agent contributes some unexpected and unique properties to the invention. Experience has shown that this component prevents mold breakdown, excessive shrinking and cracking. When it is omitted from the composition, the amount of water necessary for the process is much greater, and a number of the unique properties are lost.

The fired molds produced by these procedures are hard, durable and undistorted. The degree of reaction is about the same order as with machined graphite, and it has been far superior to other materials such as the refractory oxides which have been suggested. It has been found that the shrinkage of the molds is usually in the range of  $\frac{1}{64}$  to  $\frac{1}{16}$  of an inch per linear inch depending upon the composition utilized.

It is contemplated that the refractory metals in general, especially those of groups IV, V and VI, titanium, zirconium, hafnium, molybdenum, vanadium, tantalum, columbium, tungsten, and chromium, as well as uranium, thorium, and other high melters, including various al-

loys of these metals, may be suitably cast using molds produced by the process of this invention. The molds can be made without special, expensive equipment or time-consuming procedures. The shape of the object cast is not limited as with the machined graphite method. The process seems to be economical with the molds being expendable and with some of the material being reclaimable at little expense. Different degrees of thermal conductivity in the mold may be obtained by making changes in the particle size and minor changes in the proportion of graphite employed. The porosity of the mold, which is important in allowing trapped gases to escape, can be varied by varying the particle size of the carbonaceous refractory powder, the amount of water, and the temporary binder utilized. Thus, the mold prepared from this new composition provides good porosity and an optimum heat conductivity for solidifying the metal rapidly, thus minimizing contamination from the mold, and at the same time avoiding the chilling defects encountered with heavy-walled, high-conductivity, machined graphite molds.

This application is a continuation-in-part of my co-pending application Ser. No. 541,544, filed October 19, 1955, now abandoned.

I claim:

1. A composition for forming molds to be used in casting refractory metals comprising about 5-15% of starch, about 6-15% of pitch, about 2-7% of a sugar, water in an amount sufficient to form a moldable composition, an organic surface-active agent in an amount sufficient to improve the water-dispersibility of the mixture, the remainder consisting essentially of graphite.

2. A composition for forming molds to be used in casting refractory metals comprising about 5-15% of starch, about 6-15% of pitch, about 2-7% of a sugar, about 5-15% of water, about 0.2-5% of an organic surface-active agent, the remainder consisting essentially of graphite.

3. The composition of claim 2 in which the sugar is sucrose and the water content is about 5-10%.

4. The composition of claim 3 in which the organic surface-active agent is the amine salt of a sulfated aliphatic alcohol containing from 8-20 carbon atoms.

5. A composition for forming molds to be used in casting refractory metals comprising about 5-15% of starch, about 6-15% of pitch, about 1-7% of sugar, about 5-15% of water, about 0.2-5% of an organic surface-active agent, the remainder consisting essentially of graphite of -20 mesh particle size, from 5-45% of said graphite being of -200 mesh particle size.

6. A composition for forming molds to be used in casting refractory metals comprising about 5-15% of cornstarch, about 6-15% of powdered coaltar pitch, about 2-7% of sucrose, about 5-10% of water, about 0.2-5% of an amine salt of a sulfated aliphatic alcohol containing from 8-20 carbon atoms, the remainder consisting essentially of graphite of -20 mesh particle size, 5-45% of said graphite being of -200 mesh particle size.

7. A composition capable of being admixed with water and formed into molds to be used in casting refractory metals comprising about 5-20% of starch, about 6-20% of pitch, about 2-9% of a sugar, an organic surface-active agent in an amount sufficient to improve the water-dispersibility of the mixture, the remainder consisting essentially of graphite.

8. A composition capable of being admixed with water and formed into molds to be used in casting refractory metals comprising about 5-20% of cornstarch, about 6-20% of powdered coaltar pitch, about 2-9% of sucrose, about 0.2-7% of an amine salt of a sulfated aliphatic alcohol containing from 8-20 carbon atoms, the remainder consisting essentially of graphite of -20 mesh



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particle size, 5-45% of said graphite being of -200 mesh particle size.

9. A process for preparing a mold for casting refractory metals which comprises mixing by weight about 5-15% of starch, about 6-15% of pitch, about 2-7% of sugar, water in an amount sufficient to form a moldable composition, an organic surface-active agent in an amount sufficient to improve the water-dispersibility of the mixture, the remainder consisting essentially of graphite to form a molding composition, shaping said molding composition into a mold, and then gradually heating the mold to temperatures sufficient to carbonize the organic materials in the mold.

10. A composition adapted to be admixed with water to form a moldable mixture suitable for making casting molds for refractory metals consisting essentially of

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powdered graphite as a major constituent, 6%-20% powdered bituminous pitch, 5%-20% starch, 2%-9% sugar, and a water-soluble, organic surface-active agent in an amount sufficient to improve the water dispersibility of the mixture.

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UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 2,948,627

August 9, 1960

Alexander L. Feild, Jr.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 10, line 46, for "1-7%" read -- 2-7% --.

Signed and sealed this 31st day of January 1961.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON  
Commissioner of Patents