CASTABLE REFRACTORY DIE AND MODEL COMPOSITIONS

ABSTRACT: A dimensionally accurate, thermally stable, castable refractory composition having a controllable coefficient of thermal expansion, setting expansion and firing shrinkage which consists essentially of an admixture of magnesium oxide, calcium aluminate, ammonium dihydrogen phosphate, an alkali metal or alkaline earth fluoride compound and a colloidal silica solution. The refractory composition may be adjusted in its thermal expansion properties by variation in the fluoride content of the composition. The adjustment in coefficient of thermal expansion would coincide with that coefficient of porcelain employed in the coating of dental prosthetic restorations. The invention also includes a separating coating composition for the cast-fired composition above mentioned, which enables it to maintain separation between the refractory cast composition and an applied porcelain slurry which is spread over the cast and separating medium to construct the dental prosthesis. The separating coating is made up of a composition of potassium fluoride, stearic acid and a volatile organic solvent such as carbon tetrachloride.

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BACKGROUND OF THE INVENTION

In accord with prior practices, the construction of cast porcelain jacket crowns for dental prostheses requires the use of a metal substrate such as platinum foil which is prefabricated by shaping the substrate manually to a model composed of a gypsum-type of plaster or a plastic composition or the like. This plaster model is itself poured and set in the cavities of a wax, rubber or other soft impression taken by pressing the wax impression against the tooth to be covered by the porcelain restoration. The prior procedure involves a number of intermediate relatively expensive steps between the taking of the wax impression, the preparation of the plaster model therefrom, molding the platinum foil to the surface of the plaster cast model and finally pouring a slurry of porcelain over the surface of the metal substrate and firing the same at temperatures as high as 2,000° F. to cast the porcelain liquid slurry into a solid inlay.

Following the above procedure, it has not heretofore been possible to cast the porcelain liquid slurry directly on a die whose conformation is derived directly from a wax impression since plaster, which is presently used, breaks down long before temperatures between 1,500° and 2,000° F. required for casting, are approach. This material could not be used nor could various plastic material be used to replace it. As a result, the human error factor is necessarily interjected when first transposing the precise shape of the impression to a metal foil substrate which is shaped by hand onto the plaster model and then pulled off and separated therefrom before it is filled with a slurry of porcelain and placed in the casting furnace to be fused.

Furthermore, after the porcelain jacket has been formed, the platinum metal substrate must be removed and at this point, dimensional errors are introduced into the confirmation of the porcelain dental restoration. Stated in a general way, the principal difficulty has been that previously known materials for construction of dies to mold porcelain inlays are unable to withstand the thermal treatment necessary to glaze the porcelain and, without themselves losing either physical integrity or having a coefficient of thermal expansion such that, upon heating, the porcelain material being glazed in the die is subject to an unequal expansion pressure and is cracked either on heating or on cooling.

A still further difficulty with the use of a plaster metal or plastic die is that in the case of the plaster material, a reaction takes place between the fused porcelain and the die material itself which prevents subsequent separation of the die from the porcelain fused therein. With respect to the use of metal dies, the repeated heating necessary in the preparation of multiple restorations tends to warp and distort the metal die and such condition induces a creep or movement of the porcelain unless the casting is supported. Hitherto, no castable refractory die material has existed which can be individually adjusted to the porcelain material being fused therein so as to avoid all the problems of heating effects during the course of fusion of the porcelain and to prevent uneven thermal expansion or contraction leading to cracking or crazing of the porcelain inlay. The die composition of the present invention overcomes all of these problems of the prior art as will be illustrated in the following description and examples of the invention.

BRIEF STATEMENT OF THE INVENTION

According to the present invention, therefore, castable refractory compositions for the manufacture of ceramic dies have for the first time been made available. The dies manufactured from these compositions may be employed as dies or models for fusing thereon porcelain bridge work, without the difficulties enumerated above in the statement of prior practices. A particular feature of the invention involves the use of an alkali metal or alkaline earth metal fluoride in a predetermined amount which, when so adjusted to the amounts of thermal expansion of the porcelain, will cause the solid principal inorganic components of the composition to expand only to a degree which is commensurate with the coefficient of rate of the porcelain being fused. The principal ingredients of the refractory die composition are magnesium oxide which is present in from 4–5 parts by weight, calcium aluminate which is present from 1 to 2 parts by weight and ammonium dihydrogen phosphate which is present in from about 1 to 1.25 parts by weight and a silicate added as aqueous silicon dioxide of a 0.1 to 10μ particle size. It follows, therefore, that the fluoride component which is preferably magnesium or lithium fluoride is present in amounts of from about 4 to 1.75 parts by weight, which amount will fluctuate according to the curve set forth in the drawing as FIG. 1 for lithium fluoride or the curve for magnesium fluoride in FIG. 2. The shape of curve is determined by the coefficient of expansion taken from a sample of the porcelain to be fused in the die whose coefficient must be matched to the same. In general, the ratio of the other components such as the magnesium oxide to the calcium aluminate may be varied so as to conform to use requirements. The ratio of magnesium oxide to ammonium dihydrogen phosphate may be varied to provide further control setting expansion and firing shrinkage. The amount of fluoride is variable as indicated above so that it can be increased or decreased depending upon the particular porcelain being fused and is so selected that the coefficient of thermal expansion of the die is equal to or substantially the same as the coefficient of thermal expansion of the porcelain being fused. In other words, the amount of the fluoride salt component incorporated into the refractory mixture prior to fusing thereof, controls the coefficient of thermal expansion of the die which is formed, which die is ultimately used to mold a porcelain inlay. In general, the fluoride salt component will range from about 3.0 percent by weight to about 12.0 percent by weight of the total composition which has been found adequate to provide the die with workable coefficients for most porcelain mixes.

In terms of operation of the process for example, 5 parts by weight of the refractory composition of magnesium oxide, calcium aluminate, ammonium dihydrogen phosphate and fluoride salt are mixed with one part of colloidal silica (SiO₂) solution to give a thixotropic slurry which can be poured directly into a conventional impression material such as paraffin or polyethylene wax which has a cavity of the desired shape and size. Any nonaqueous impression material may be employed, for example, rubber, wax or other suitable plastic compound or material. However, the impression material from which the die is cast cannot be an aqueous impression material such plastic or a hydrocolloid. The refractory slurry may, however, be poured against such aqueous impression materials provided that the impression is first very thinly coated with a paraffin oil or varnish to provide a hydrophobic barrier between the impression and the refractory material. After the mixture of refractory composition and colloidal silica solution is cast in the impression materials, it is allowed to remain therein for about 20 minutes to enable it to set to a hard mass. This hard mass is then removed from the wax impression and fired at temperatures of about 1,900° to about 2,000° F. for maturation of the materials so as to yield a ceramic die having dimensions which are within tolerance of plus or minus 0.3 percent reproducibility of the original tooth preparation. The resulting die or model formed is not only dimensionally stable, but as hereinafter explained, makes it possible to construct porcelain jacket crowns from the other form of porcelain construction directly upon the cast and fired die or model, since the die itself has a capacity to withstand temperatures of the order of 2,000 F. which are required to fuse porcelain.

Prior to constructing or imposing the porcelain slurry on the fired model or die, the model is coated with a layer of a
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separating medium of thickness of about 0.05 to 0.1 millimeters. One separating medium which has been employed is composed of 50 parts by weight of potassium fluoride, 1 part by weight of stearic acid and 150 parts by weight of carbon tetrachloride. The carbon tetrachloride ingredient functions only as a volatile solvent for the stearic acid and as a carrier for the potassium fluoride and as such may be replaced by similar volatile solvents such as ethyl acetate, trichloroethylene and the like without deviating from the essence of the invention.

After the separating medium has been applied to the cast ceramic die, the solvent is eliminated from the separating medium by air drying during which period the solvent volatilizes and a porcelain slurry made in a known manner is applied to the die. The die with its content of porcelain is then inserted into the oven and fired at a temperature as high as 2,000°F. to fuse the porcelain which is then easily removed from the die and is ready for insertion as a dental prosthesis.

The invention may be illustrated by the following example which is not intended to limit the invention but merely to supply one preferred mode of operation thereof.

**EXAMPLE**

Porcelain jackets are prepared on a castable refractory composition composed of by weight:

- **Magnesium oxide** 51.18%
- **Calcium aluminate** 18.09%
- **Ammonium dihydrogen phosphate** 10.85%
- **Lithium fluoride** 3.25%
- **Colloidal silica (40% by weight Silasol 16-64)** in water (Ludox)

A dry mix of the magnesium oxide, calcium aluminate, ammonium dihydrogen phosphate and lithium fluoride is mixed with the colloidal silica which is in liquid form in the ratio of 5:1 to provide a semisolid slurry which is then poured into an impression in rubber, wax, etc., or into an "aqueous impression previously coated thinly with a hydrophilic material," and sets therein to a hard mass within 20 minutes. After setting and removal from the impression, the cast mass, on firing to 1,900°F., results in the final die having exceptional dimensional stability and accuracy within ± 0.3 percent.

After the maturation firing the die retains its coefficient of thermal expansion and its dimensional accuracy even after several subsequent firings at 1,800°F.

Before a porcelain jacket or other porcelain prosthesis is constructed on the die, it is necessary to treat the die with a separating medium which is a suspension of potassium fluoride in a solution of stearic acid in a volatile solvent having a composition for example of:

- **Potassium fluoride** 24.8%
- **Stearic acid** 0.36%
- **Carbon tetrachloride** 74.63%

When the separating medium is applied to the die and left to dry by volatilization of the carbon tetrachloride, a very thin film is left on the die which ensures clean and complete separation of the fired jacket from the die and thus the porcelain construction can be formed directly on the cast and fired die.

It must be understood that the foregoing illustrative example is merely intended to illustrate the preferred mode of practice of the invention and should not be taken as limiting thereof, and within the terms of the several appended claims modifications may be made without departing from the spirit or scope of the invention. For example, variations may be made in the ratio of magnesium oxide to ammonium dihydrogen phosphate to provide for greater or lesser expansion on setting, or conversely contraction on firing. Most specifically, variations may be made in the particular fluoride content as indicated by Fig. 1 and Fig. 2 of the drawing wherein the specific amount of fluoride present will be determined by the particular coefficient of linear expansion desired in the finished fused ceramic die. As has been pointed out earlier, it has been found that the heart of this invention comprises the amount of fluoride component present to control the coefficient of thermal expansion of the die and it is exceedingly important to have the coefficient of thermal expansion of the die adjustable to that of the porcelain constructed thereon. The coefficient of the expansions of the two materials must be substantially the same within very narrow limits which are described mathematically by the formula Δ/Δt, where Δ/Δt stands for coefficient of thermal expansion. The ideal relationship of coefficient of thermal expansion of the die can be expressed as: Δ/Δt = 0.75 since Δ/Δt = 3 Δ/Δt, where Δ/Δt for porcelain is 14.4 ± 17 ± 10°F. For example, Δ/Δt for the die = 10 ± 0.13 ± 0.6.

In general, the coefficient of thermal expansion of the die model ultimately obtained may be slightly less than that of the porcelain but not greater than the coefficient of thermal expansion of the same porcelain. The case die must have a high degree of dimensional accuracy and topographical reproduction, and it must be capable of repeated heatings at temperatures of the order of 1,800°F. without distortion or spalling, while at the same time maintaining a controllable coefficient of thermal expansion such that thermal stresses in the die will not be transposed or impressed in the porcelain jacket upon firing. Of course, the die should be readily separable.

The scope of the invention will be further defined by the following appended claims.

What is claimed is:

1. A castable refractory composition for the manufacture of dimensionally accurate and thermally stable ceramic dies at casting and firing temperatures which range from 1,500°F., which comprises 1 part by weight of an aqueous colloidal silica solution of 40 percent silicon dioxide and 5 parts by weight of a refractory powder comprising magnesium oxide in about 4 to 5 parts by weight, calcium aluminate in about 1 to 2 parts by weight, ammonium dihydrogen phosphate of from about 1.0 to 1.25 parts by weight and from about 3 to 12 percent by weight of the total composition of an alkali metal or alkaline earth metal fluoride wherein said amount is sufficient to provide a coefficient of linear expansion as shown by the curves described in FIG. 1 and FIG. 2 of the drawing.

2. A castable refractory composition according to claim 1 wherein the alkali metal fluoride is lithium fluoride.

3. A castable refractory composition according to claim 1 wherein the alkali metal fluoride is magnesium fluoride.

4. A castable refractory composition according to claim 1 wherein the compositions contain the following constituents in the following relative amounts expressed in percent by weight of the total composition:

   - **Potassium fluoride** 50 parts
   - **Stearic acid** 1 part
   - **Volatil organic solvent** 150 parts

5. A castable refractory die for the manufacture of a dimensionally ceramic porcelain inlay which die is composed of the fused composition of claim 1 which is coated with a separating layer composed of by weight:

   - **Potassium fluoride** 50 parts
   - **Stearic acid** 1 part
   - **Volatil organic solvent** 150 parts

6. A castable refractory die for the manufacture of dimensionally correct ceramic porcelain inlays of claim 5 wherein the volatile organic solvent for the separating layer employed is carbon tetrachloride.
7. A castable refractory composition for the manufacture of dimensionally accurate and thermally stable dies according to claim 1 wherein the fluoride component is lithium fluoride and the amount present therein is at least 3 percent of the weight of the total composition.

8. A castable refractory composition for the manufacture of dimensionally accurate and thermally stable dies according to claim 1 wherein the fluoride component is magnesium fluoride present in amount of at least 3 percent by weight of the weight of the total composition.

9. A dimensionally accurate and thermally stable ceramic die for the firing and casting of porcelain which die is formed from the materials set forth in claim 2.