A composition and method for preparing model bases in the manufacture of dental prostheses, in which the model base is made of a castable-refractory composition that is stable at high temperatures and is compatible with commercially available dental porcelains and gold alloys, as well as with the impaled dies and dowels. The castable-refractory composition of the invention is made by a dry blend consisting essentially of 40–50 weight percent of a refractory oxide, 6–8 percent by weight of an alkali phosphate, and 42–47 percent by weight of an alkaline-earth fluoride, and then mixing that dry blend with a colloidal silica sol of 40 weight percent content, using a ratio of 4 to 5 parts of blend to 1 part of sol.

4 Claims, 4 Drawing Figures
DENTAL PROSTHESIS MODEL BASE COMPOSITION CONTAINING CALCIUM FLUORIDE

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to castable-refractory compositions that exhibit excellent dimensional stability after being fired at temperatures as high as about 2,000°F., together with a high coefficient of thermal expansion, on the order of 12 or more microinches per inch per °C., and other properties suiting them for use in the manufacture of dental prostheses. It relates further to methods of making dental prostheses wherein such a castable-refractory composition is used as a model base.

2. Description of the Prior Art

Until recently, the construction of porcelain jacket crowns for dental prostheses has required the use of a fabricated metal substrate or matrix. The technician, having received from a dentist an impression of teeth in wax, rubber or the like, poured into it dental stone comprising unfirable glassy-type materials to provide a model of a tooth. He then constructed on the model a platinum foil matrix comprising a thimble-shaped cone having a thickness of about 0.001 to 0.002 inch. The porcelain is fabricated on this cone and the whole assembly is slowly removed from the stone die and fired. After firing, the platinum matrix is painstakingly removed from the internal surface of the jacket before cementation in the mouth. This procedure, besides being tedious, provides for an inaccurate fit—the thickness of the platinum foil insuring that the jacket is oversize. Also, the forces necessary to remove the porcelain and platinum from the die before firing will damage the weak, unfired structure.

Similarly, when porcelain is being applied and fired to a cast gold structure, unless the metal strip is adequately supported, and geometrically restricted, warpage and sagging of the total structure can and do occur on heating.

Many of the aforesaid difficulties are eliminated if the porcelain restoration is constructed directly on a fireable stone model or die. However, until recently, materials which were employed for making models or dies could not be used for direct construction of porcelain jacket crowns and the like since the material used for the die or model was unable to withstand the thermal treatment necessary to glaze the porcelain without loss of its physical integrity. Furthermore, the coefficients of thermal expansion of such materials were such that any porcelain surmounting the die would crack on firing and cooling.

Recently, refractory die compositions have been devised upon which dental prostheses can be directly fabricated and fired. These include, as essential constituents, magnesium oxide and ammonium dihydrogen phosphate, with or without additions of aluminum oxide and a soda-lime silicate glass. With this type of composition, all of the intermediate and expensive steps between the initial model and the formation of the metal substrate or matrix are eliminated, and the porcelain restoration can be constructed directly on the stone model or die material.

In forming a porcelain jacket crown, inlay or the like, a thickness of the tooth structure is first removed by a dentist. Thereafter, a wax, rubber or similar impression is made of the tooth so prepared. In this process, the impression of more than a single tooth is formed. That is, a reproduction of a group of teeth is formed in the wax impression, and, thereafter, a model of the entire group is cast. While the model of an entire group of teeth possibly can be used directly as a base for the fabrication of porcelain jackets on individual teeth, problems of bulk usually require that individual tooth dies be extractable from a gross model. This is accomplished by inserting a brass or other metal pin or dowel into the surrounding material before it sets, then pouring further stone to provide a "model base." The individual tooth die with the dowel attached is then cut away from the gross model, whereupon the dentist can use the cutaway die as a basis for the metal matrix on which the porcelain is constructed, without interference from adjacent tooth dies.

When the material used to form the model or die is of the ceramic type containing magnesium oxide and ammonium dihydrogen phosphate, it is not satisfactory to use for the above-mentioned "model base," which is cast around the dowels, etc., the same material that is used to form the above-mentioned die or model. The model base is, of necessity, a piece of material considerably more massive than any of the small, individual tooth dies. Moreover, the die material has a high specific heat and a low coefficient of thermal conductivity, as well as a low coefficient of thermal expansion. If an attempt were made to fire in an oven, at temperatures up to about 1,800°F., an assemblage of dies and dowels resting in a model base, with the model base being made of the same material as the dies, cracking or misalignment would develop.

The small, individual tooth dies would rapidly be heated to a temperature approaching that of the furnace, whereas the more massive "model base" piece would reach only a substantially lower temperature, such as about 1,000°F. at the most. Accordingly, it has hitherto been necessary, in firing the castable-refractory die pieces that are used in the making of dental prostheses to remove the die pieces from the model base employed and place them into the furnace individually. This is undesirable, not only from the standpoint of the labor required in the removal of the die pieces from the model base before firing and the replacement of these in the model base after firing, but also from the standpoint that the pieces involved are deprived of support during the firing operation, increasing the chances of warpage or misalignment.

It has not been obvious to those skilled in the art how to produce a castable-refractory composition that possesses the desired, high coefficient of thermal expansion that is required for the making of relatively massive model base pieces for use in the manufacture of dental prostheses and, at the same time, is sufficiently cohesive and also resistant to the development of components in the refractory composition that would, upon repeated firing, cause rupture of the model base in view of the thermally induced stresses that occur in it in the course of such repeated firing. Indeed, those skilled in the art have, for the most part, looked away from the development of refractory compositions exhibiting a high coefficient of linear expansion, for the very reason that the more a refractory composition expands, the more likely it is to spall or crack or otherwise fail when subjected to rapid heating or cooling.

SUMMARY OF THE INVENTION

As an overall object, the present invention seeks to provide a model base for ceramic dies used for dental prostheses having a coefficient of expansion which accommodates fireable ceramic dies such that the dies and the model base can be fired together.

More specifically, an object of the invention is to provide a model base composition of the type described usable with ceramic tooth dies containing as essential constituents, magnesium oxide and ammonium dihydrogen phosphate, added as a mixture to a colloidal silica solution, the mixture containing as possible additives aluminum oxide and a soda-lime silicate glass.

In accordance with the invention, a dry blend is formed comprising a mixture of 47 to 50 percent by weight of at least one refractory oxide selected from the group consisting of magnesia, alumina and zirconia, 6 to 8 percent by weight of an alkali phosphate and 42 to 47 percent by weight of an alkali-earth fluoride. Four to five portions by weight of this dry blend is then mixed with one portion by weight of a colloidal silica sol of about 40 weight percent solids content. It is possible, although not necessary, to add up to about 1 percent by weight of a metal oxide to the dry blend prior to mixing with the colloidal silica sol for the purpose of coloring the model base material.

The resulting composition has good as-fired dimensional stability as evidenced by an as-fired dimension change of 0 to +0.2 percent, and good thermal expansion characteristics as evidenced by a coefficient of thermal expansion of about 13.0 x 10^-6/in./°C. and higher.
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The above and other objects and features of the invention will become apparent from the following detailed description taken in connection with the accompanying drawings which form a part of this specification, and in which:

FIG. 1 is a perspective view of a ceramic die with a group of teeth showing the manner in which the die is supported on a model base;

FIG. 2 is a cross-sectional view of a rubber or wax mold impression from which the model of FIG. 1 is formed;

FIG. 3 illustrates the first step in the formation of the model of FIG. 1 by pouring a fireable refractory material into the mold of FIG. 2 and inserting a dowel therein; and

FIG. 4 illustrates the final step in the formation of the model of FIG. 1, comprising pouring the refractory material of the invention over the previously formed refractory material and dowel to form a model base.

With reference now to the drawings and particularly to FIG. 1, a stone model of a group of teeth is shown. It will be assumed that the two items identified by the numerals 10 and 12 are models of teeth which have been previously ground to remove a portion of the surface thereof preparatory to the formation of a porcelain prosthetic restoration. Models 10 and 12 as well as the remainder of the teeth in the bridge model are a castable-refractory composition, hereinafter described in detail, to form an upper portion 14 of the overall model. This upper portion 14, it will be noted, conforms to the teeth of the bridge as well as the gum portion which supports these teeth. Beneath the upper portion 14 is a lower model base portion 16 which is formed from the material of the present invention.

Projected through the base portion 16, the upper portion 14, and into the two teeth models 10 and 12 are dowels 18 and 20. It is often necessary to remove from the model of the complete group, the individual tooth dies 10 and 12, and it is for this reason that the dowels 18 and 20 are included. To remove an individual die such as die 10, for example, saw cuts 22 and 24 are formed in the upper portion 14 and base 16 on either side of the die. Thereafter, as illustrated by the die 12, the dowel is pushed upwardly whereupon the area 26 beneath the die breaks away from the remainder of the overall bridge model, thereby producing an individual tooth die. Thereafter, this die may be utilized as a base upon which a porcelain jacket crown, inlay, restoration or the like is formed.

With reference now to FIG. 2, the initial step in forming a model of FIG. 1 comprises forcing a wax or mass of soft plastic material such as rubber or wax over the teeth which have been previously ground to form the mold 28 of FIG. 2. The thus formed mold has a plurality of teeth cavities therein, one of said cavities being indicated in FIG. 2 by the reference numeral 30.

After the mold 28 of FIG. 2 is formed, a castable-refractory composition is poured into the mold (FIG. 3) to the level indicated by the reference numeral 32. As will be understood, this forms the upper portion 14 of the complete model shown in FIG. 1. The castable-refractory material 34 comprises a dry blend of magnesium oxide and ammonium dihydrogen phosphate, the dry blend being mixed with a colloidal silica sol of about 40 weight percent solids. Added to the dry blend of magnesium oxide and ammonium dihydrogen phosphate, depending upon the required firing temperature and other factors, are possibly a soda-lime silica glass and aluminum oxide.

The dry blend, when mixed with the colloidal silica sol, forms a thixotropic slurry which is poured directly into the mold cavity 30 up to the level 32. After the refractory composition and colloidal silica sol are thus cast into the impression, it is allowed to remain therein for a time sufficient to enable the cast material to set to a hard mass. However, before the hard mass is formed, a dowel 36 is inserted therein above the impressions 10 and 12, for example, shown in FIG. 4. After the refractory material 34 has thus hardened with the dowel 36 inserted therein, the refractory material of the present invention is poured over the previously formed refractory material up to the level 40. This, of course, forms the lower model base portion 16 of FIG. 1.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The castable-refractory composition of the present invention is made by first forming a dry blend of refractory oxide, such as alkali phosphate, and alkaline-earth fluoride, and then mixing the dry blend, in the ratio of 4 to 5 parts of dry blend to 1 part of a colloidal silica sol of about 40 weight percent solids content. This yields a castable-refractory composition that sets in about 30 minutes at room temperature, is capable of withstanding firing in a furnace at temperatures up to about 2,000°F. without cracking (even upon repeated re-firing), and exhibiting at the same time a high coefficient of thermal expansion, greater than 13.0x10⁻⁶ in./in./°C, or greater, and preferably about 20x10⁻⁶ in./in./°C, such as to suit the composition for use as a model base in the manufacture of dental prostheses.

The refractory oxide used in the making of the above-indicated castable-refractory composition is one selected from the group consisting of magnesia, alumina and zirconia. Other refractory oxides might be used as well, but it is advisable to avoid the use of lime, since this tends to form with the silica of the silica sol the compound calcium orthosilicate, which tends to undergo a phase transformation upon repeated re-firings, becoming brittle and causing spalling or other forms of failure.

Indeed, it is rather not to be expected that the compositions disclosed herein as constituting embodiments of the present invention would (in spite of their containing ingredients permitting the formation of the calcium orthosilicate in substantial amounts, such as over 3 percent) perform satisfactorily in respect to the avoidance of the development of cracking upon repeated re-firing.

Although, as indicated above, satisfactory results may be obtained with the use of various refractory oxides as indicated above, we find that we prefer to use a composition wherein the magnesia amounts to 38.0 to 39.0 percent by weight of the dry blend, the magnesia being in the form of a finely divided precipitate, and the remainder of the refractory oxide is made up with 9.0 to 10.0 percent of alumina, preferably a finely divided alumina in tabular form. Using this particular combination of magnesia and alumina gives good values for strength and hardness, and at the same time, dimensional accuracy and a high coefficient of thermal expansion are obtained.

The alkali phosphate may be any of a great variety of materials, among which may be mentioned the various phosphates of sodium, potassium, and other members of the alkali-metal group, as well as the phosphates of the ammonium radical. We have obtained satisfactory results, working with ammonium dihydrogen phosphate, NH₄H₂PO₄. This is used in the dry blend to the extent of 6 to 8 percent by weight.

The dry blend also contains a substantial proportion of an alkaline-earth fluoride, such as calcium difluoride (fluorspar). This is also used in finely divided form to the extent of 42 to 47 percent by weight.

The dry blend preferably also contains a small addition, up to about 1 percent by weight, of an oxide that imparts to it a color distinguishing it from the die material. We have obtained satisfactory results by using 0.6 percent by weight of ferric oxide, which is preferably used in the form of a finely divided powder. This imparts a pink tone to the unfired composition, and although the intensity of the color is somewhat diminished upon firing, the addition of ferric oxide imparts a distinctive color difference between the die composition and the model base composition in the fired state. Those skilled in the art will readily perceive how other oxides, such as nickel oxide or cobalt oxide, might be substituted for the ferric oxide.

The ingredients indicated above as comprising the dry blend are thoroughly mixed with one another, and then the dry blend so made is mixed, in a ratio of 4 to 5 parts by weight of dry blend to 1 part of liquid, with a colloidal silica sol of 40 weight percent silicon dioxide solids content, such as that sold under the name "Ludox" by E. I. DuPont de Nemours & Company. Those skilled in the art will readily perceive how other commercial silica sols in about the same composition may be substituted.
This yields a castable-refractory composition that will remain workable for about 5 to 7 minutes and will set to hardness within 20 to 30 minutes. The castable-refractory composition is used, at least initially, in substantially the same manner as any of the model base compositions known in the prior art, e.g., plaster of Paris or the like. That is to say, in the making of dental prostheses, the various steps up to the pouring of the model base over the dies and dowels assembled in the impression are exactly the same as before. Also the same as before is the step of allowing the model base composition to harden.

At this point, however, the practice changes somewhat. The model base compositions heretofore known have not been capable of withstanding furnace temperatures of 1,800° F. or the like. It has hitherto been necessary, before firing the porcelain on the dies, to remove the dies and their dowels from the model base prior to placing them into the furnace. This has meant that it has been necessary to expend not only the time and labor for such removal of the dies from the model base and the replacement of the dies therein after they have been fired but also to suffer the disadvantage of the increased likelihood of warpage during the firing operation that is caused by having the dies present unsupported in the furnace. Moreover, the number of firings that may need to be done is not necessarily limited to one. If, for example, there are a few places found, after the first firing operation, in which the porcelain is somewhat too thin, it is customary to paint additional porcelain over them and refire. This implies that the above-indicated tedious steps and dangers of warpage are doubled, and all this is avoided when there is provided, as in accordance with the present invention, a model base composition that will withstand furnace heat up to 1,800° F. and at the same time exhibit the necessary other characteristics.

The invention described is illustrated by the following specific example:

**EXAMPLE I**

There is prepared and used a model base composition in accordance with the invention. To be somewhat more precise, there is first prepared a dry blend consisting essentially of 38.4 parts by weight of magnesia, 9.6 parts of alumina, 6.4 parts of ammonium dihydrogen phosphate, 44.5 parts of fluorspar and 0.6 part of ferric oxide. This dry blend is then mixed with silica sol of 40 weight percent solids content in the proportion of 20 grams of dry blend per 4 cubic centimeters of silica sol.

The resultant mixture is poured over dies and greased dowels established in a dental impression, and the mixture is then permitted to harden, forming a model base for the above-mentioned dies and dowels. The entire assembly—dies, dowels, and model base—was then suitably baked to produce the desired end product—a model base surmounted by doweled dies appropriately positioned with respect to the desired positions of the individual original teeth in the mouth of the patient being worked upon. Further characteristics of the model base compositions so produced are indicated below:

<table>
<thead>
<tr>
<th>Sample</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>Total refractory oxide</th>
<th>NH₄H₂PO₄</th>
<th>CA₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-B</td>
<td>43.01</td>
<td>6.45</td>
<td>49.46</td>
<td>7.88</td>
<td>42.86</td>
</tr>
<tr>
<td>P-A</td>
<td>41.45</td>
<td>8.29</td>
<td>49.74</td>
<td>7.40</td>
<td>41.84</td>
</tr>
<tr>
<td>J-D</td>
<td>38.62</td>
<td>9.65</td>
<td>48.27</td>
<td>6.90</td>
<td>44.83</td>
</tr>
<tr>
<td>J-E</td>
<td>39.30</td>
<td>9.82</td>
<td>49.12</td>
<td>7.02</td>
<td>43.86</td>
</tr>
<tr>
<td>J-B</td>
<td>41.40</td>
<td>10.37</td>
<td>51.83</td>
<td>7.41</td>
<td>40.74</td>
</tr>
<tr>
<td>J</td>
<td>43.08</td>
<td>10.77</td>
<td>53.88</td>
<td>7.69</td>
<td>38.46</td>
</tr>
<tr>
<td>V</td>
<td>38.62</td>
<td>11.03</td>
<td>49.65</td>
<td>5.92</td>
<td>44.83</td>
</tr>
<tr>
<td>V</td>
<td>38.57</td>
<td>11.43</td>
<td>50.06</td>
<td>7.14</td>
<td>42.86</td>
</tr>
<tr>
<td>W</td>
<td>37.14</td>
<td>12.86</td>
<td>50.06</td>
<td>7.14</td>
<td>42.86</td>
</tr>
</tbody>
</table>

The data presented above may be interpreted as follows. The composition of sample J-D is substantially the same as that of example I given above and the reported properties, though somewhat poorer, are nevertheless a substantial improvement over those of any castable-refractory composition known prior to the present invention as respects the particular properties useful for model base purposes. The sample V is another nonpreferred embodiment of the invention. The sample W exhibits an undesirably low coefficient of thermal expansion, and this may due in part to its relatively high alumina content. The alumina content should not, in most instances, exceed 12 percent, and there are data to indicate that even in a range of 8 to 12 percent, increasing the alumina content lowers the observed coefficient of thermal expansion. In this regard, the results of sample V are not typical. The results of sample J-E are disappointing; although within the chemical composition limits specified above, it gives an unsatisfactory as-fired shrinkage and a borderline or unsatisfactory coefficient of thermal expansion. Similarly, samples P-A and P-B are too low in coefficient of thermal expansion to find use as model base compositions. Sample J-B is too high in refractory oxide content and too low in fluorspar content, and it withstand only two firings (without die) before developing cracking. On the other hand, sample J, which is similar high in refractory oxide and low in fluorspar, withstood six firings before it developed in cracking but its performance was poor in modulus of rupture and was borderline in coefficient of thermal expansion. Sample Y, low in ammonium dihydrogen phosphate, gave an unsatisfactory coefficient of thermal expansion.

From the foregoing data, it can be seen that substantially different results can be obtained as a result of seemingly slight alterations in the chemical composition of the castable-refractory composition. The compositions that are useful for the making of model bases lie within the ranges indicated above, but observation of those ranges is not, of itself, enough to ensure that a satisfactory combination of properties will be obtained. Indeed, the data now available appear rather contradictory of one another concerning the effects of changing the amounts used on the various ingredients. We have established, however, in the example, that a combination of properties can be achieved that will be useful for model base purposes, and that (from the data available), those skilled in the art may well devise others that have combinations within the relatively narrow ranges indicated above that will serve as well, if not better. We, accordingly, lay claim to the invention as it is defined in the appended claims.

We claim as our invention:

1. A castable-refractory composition consisting essentially of a mixture of (a) 4 to 5 parts of dry blend consisting essen-
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tially of about 43 weight percent of magnesia, about 10 weight percent of alumina, about 7 weight percent of ammonium dihydrogen phosphate, about 38 weight percent of calcium fluoride, and (b) 1 part of colloidal silica sol of about 40 weight percent solids content, which composition has good as-fired dimensional stability as evidenced by an as-fired dimension change of no more than 0.2 percent, and a good coefficient of thermal expansion of about 13.0×10⁻⁶ in./in./°C and higher.

2. The composition of claim 1 wherein the dry blend also consists of up to about 1 weight percent of a metal oxide as colorant.

3. In the making of dental prostheses by a method including the casting of dies of castable-refractory material capable of maintaining its physical integrity when solidified and then heated to 2,000°F, the positioning in said castable-refractory material while in its fluid state of dowels, the subsequent solidification of said castable-refractory material, and the casting about said dies and dowels of a model base composition to form a structure, the steps of preparing a model base of castable-refractory composition consisting essentially of a mixture of (a) 4 to 5 parts of a dry blend consisting essentially of about 43 weight percent of magnesia, about 10 weight percent of alumina, about 7 weight percent of ammonium dihydrogen phosphate, about 38 weight percent of calcium fluoride, and (b) 1 part of a colloidal silica sol of about 40 weight percent solids content, casting said model base composition about said dowels and dies, permitting said model base composition to solidify, heating said structure to a temperature of ranging from about 1,800°F to 1,850°F, and cooling to room temperature.

4. The method of claim 3 wherein the dry blend also consists of up to about 1 weight percent of a metal oxide as colorant.

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