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REFRACTORY

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This invention relates to refractories and refractory molds for the casting of metallic articles. More particularly it relates to such refractories and refractory molds suitable for the formation of metallic articles of exact size and shape, such as dentures.

In the casting of alloys and simple metals it is often necessary to produce castings of predetermined exactness as to shape and dimensions. Normally such a goal constitutes a problem of considerable intricacy for the following reason: on cooling, most cast metals shrink considerably, the shrinkage for each particular metal composition being normally quite constant under reasonably constant and controlled casting conditions. For simple straight line objects the problem is a simple one, in that allowance for the metal shrinkage can be easily made in the mold design. However, when the pattern is of an involved design, and particularly when it contains a multiplicity of vari-curved surfaces, it is extremely difficult, expensive and often impossible to make proper allowance for metal shrinkage in every size and shape detail in the mold itself. One field where this proper allowance is normally impossible is the casting of denture alloys for bridges, inlays, crowns and the like, in which the casting mold is formed of a refractory material.

In the dental field, an exact model of the dental and oral picture is duplicated in a suitable refractory material. The refractory model is prepared by well known procedures and methods, and the alloy then cast in place. It is obvious that even a minor variation from required dimensions in the metal piece for denture work would cause discomfort, abrasion and laceration when used in the mouth. The dental laboratory technician, where possible, compensates for the shrinkage of the alloy in this wise: he compounds his refractory so that on heating to a certain laboratory-determined temperature, the refractory material will expand exactly to the amount of shrinkage the alloy undergoes on cooling and solidifying. The molten alloy is then cast into the refractory heated to the desired temperature, and on cooling the alloy piece is normally found to produce an exact and comfortable fit.

In the last few years the question of thermal expansion in dental refractories has been enormously complicated by the fact that a large number of new alloy compositions have been devised for dental work, each of which undergoes shrinkage to a different degree on cooling, each of which requires a refractory possessing a corresponding degree of expansion in a temperature range suitable for handling the particular metal. A large number of these newer alloy compositions have been practically eliminated simply because a compatible refractory could not be devised with the proper expansion characteristics in the desired temperature range, even though such alloy compositions have properties more desirable from a dental standpoint than metals already in use. This is particularly true because the normal thermal expansion of most refractory materials is rather limited.

It is therefore an object of this invention to provide refractory compositions and molds which expand when fired at high temperatures. It is another object to provide such refractory compositions and molds in which the amount of such expansion can be accurately controlled. It is a further object to provide refractory compositions and molds which expand uniformly in all directions when fired at high temperatures. It is a still further object to provide refractory compositions and molds of any desired degree of expansion, the degree of expansion obtained being susceptible to controlled variation to such an extent that any metal or alloy shrinkage, such as dental alloys, can be properly compensated for. Other objects will appear hereinafter.

These objects are accomplished by incorporating in a refractory base a material which, as the result of a chemical change, will undergo a pronounced and uniform expansion at high temperatures, this expansion being uniformly transmitted to the refractory base. Such a material should of course not be of such a nature as to react with other ingredients of the refractory to such an extent that the properties of the refractory are impaired or destroyed.

It has been found in accordance with this invention that the amount of expansion in a refractory can be accurately controlled by varying the amount of expanding material of the above class which is added to the refractory base. Normally sufficient expansion variance is obtained by additions of 0.5% to 5% of expanding material by weight (based on the weight of the fired refractory), depending upon the amount of expansion desired. This of course is with relation to the formation of dental castings. If materials of a higher degree of expansion than the customary dental castings are required to be made, the amount of expanding material and consequently the amount of expansion of the refractory can be suitably varied.

Expanding materials which have been found most satisfactory for this purpose are the thermal

reaction products of zirconium or zirconium compounds and carbon, or zirconium or zirconium compounds and nitrogen, with or without the inclusion of other elements, such as oxygen; the corresponding compounds of titanium, thorium, cerium and hafnium; and to a lesser extent the corresponding compounds of silicon. Examples of such materials are zirconium carbide, zirconium nitride, zirconium oxycarbide (described in U. S. Patent No. 2,110,733), zirconium cyanonitride (described in U. S. Patent No. 1,342,084), titanium carbide, titanium nitride, titanium cyanonitride, silicon carbide, thorium carbide, cerium carbide, hafnium carbide, thorium nitride and hafnium nitride. The expression "compound of zirconium and carbon" or "thermal reaction product of zirconium and carbon" and similar expressions, as used throughout this specification and claims, is understood to include compounds formed by the reaction of zirconium or zirconium compounds (such as zirconium oxide) with carbon, with or without the inclusion of other elements. For example, zirconium carbide can be formed by the reaction of either zirconium or zirconium oxide with carbon. Likewise, zirconium oxycarbide and zirconium cyanonitride (containing zirconium, oxygen, carbon and nitrogen) is included in the expression "thermal reaction product of zirconium and carbon." Mixtures of these materials may be used. By "thermal reaction products" is understood to means compounds customarily formed at extremely high temperatures, such as electric furnace temperatures.

By heating such thermal reaction products to a sufficiently high temperature in an oxidizing atmosphere they are transformed into the corresponding oxide, and at the same time undergo a uniform increase in volume in all directions, amounting usually to at least twice and sometimes to as much as four to five times the original volume of the material. Normally the zirconium compounds are more efficient in this respect than the titanium compounds, the silicon compounds being still less effective. For example, the zirconium compounds oxidize and expand easily at approximately 1400° F. The titanium compounds oxidize with somewhat more difficulty and require temperatures up to 2000° F., while temperatures up to 2500° F. are required for oxidation of the silicon compounds, and even then the oxidation takes place slowly. In fact the temperature of oxidation of the silicon compounds is so high when used alone as to be entirely outside the range of practicability for dental work. However, the oxidation of the silicon compounds can be made to take place in a lower and more practical range by the addition of an oxidizing agent or booster, as explained below.

Normally dried and fired cast refractories are sufficiently porous to allow easy access of oxidizing air to efficiently oxidize the expanding material. Occasionally, however, a cast refractory may be made sufficiently dense so that easy access of oxidizing air is partially or wholly prevented. To prevent the possibility of the expanding materal remaining unoxidized, it is desirable to incorporate with a refractory a small amount of a material which is an efficient oxidizing agent at elevated temperatures, in addition to the expanding material. Suitable oxidizing agents are the nitrates of the alkali or alkaline earth metals, the oxide of lead known as red lead, lead peroxide, etc. Of these, red lead (Pb_3O_4) is the most suitable, particularly in the case of the compounds of silicon, where oxidation is enabled to take place fairly rapidly at about 2000° F. Normally, no more than 1 to 2 parts of red lead to every 4 parts of expanding material is required for complete oxidation.

In order to obtain the best results, the size of particles and the nature of the impurities present is also of importance. Although these materials expand irrespective of these factors, it has been found that both these factors will affect the uniformity of the results obtained. Where the particle size is too large the possibility arises of uneven expansion in various parts of the refractory. It is therefore desirable that the particle size of the expanding material be finer than the coarsest particles of the refractory base, and preferably should be close to the fineness or equal to the fineness of the smallest particles in the refractory base. The dispersion of the expanding material should be completely uniform throughout the refractory in order to obtain uniform expansion in all directions. The particles of expanding material should preferably be sufficiently fine to pass a 325 mesh screen, although up to 200 mesh material can be used. If an oxidizing agent is used it should be of comparable fineness.

In regard to impurities, it has been found that the presence of excessive quantities of free carbon or graphite, or of the carbides of the alkali and alkaline earth metals, or of iron compounds, causes a slight pimpling of the refractory surface. Removal of these ingredients results in a product which produces uniform and even expansion in all directions without any evidence of surface pimpling or cracking. The impurities mentioned may be removed by leaching with hot dilute acid, such as hydrochloric or sulfuric. In these leaching agents the desired zirconium, titanium or silicon compounds are relatively insoluble, while the carbides of the alkali and alkaline earth metals and the compounds of iron are soluble in these media. The reaction of the warm acids on the soluble constituents causes a froth to form which carries practically all the free carbon or graphite, which is then removed by surface skimming. The washed and dried residue is a completely satisfactory expansion agent.

Complete dispersion of the oxidizing and expanding materials is effected by mixing these ingredients with the finely divided portions of the refractory base, adding water and mixing thoroughly by grinding for a short period in a ball mill. The water is then removed by drying in air. Any portion of the refractory composition which is not affected by mixing in the presence of water may be compounded with the expanding material in this manner. The refractory is next cast and then heated to the temperature at which the expanding material is sufficiently oxidized.

The expansion which takes place in the expanding material in accordance with this invention also varies somewhat with the particle size of the refractory base, since the larger particles may contain relatively more pore space, and may therefore be less dense initially than the smaller particles. For example, addition of 2% of expanding material to a refractory base consisting chiefly of 35 mesh material will show less expansion than the addition of 2% of the same expanding material to a refractory base consisting chiefly of 200 mesh material. The size of the particles in the refractory base also affects

the uniformity of the expansion. For these reasons, it is desired that none of the particles of the refractory base exceed ⅛ inch in size.

Suitable refractory materials which can be used in the refractory base in the practice of this invention are: zircon, aluminum oxide, silicon dioxides, quartz, rutile, fused zirconium dioxide, mullite, sillimanite, olivine, forsterite, chromite, refractory clay, kaolin, beryl, spinel, kyanite, thorium oxide, thorite, ceria, feldspar, andalusite, talc, baddeleyite, porcelain, calcined or uncalcined, alone as stated or in suitable mixture.

In accordance with the usual practice, it is also desirable or necessary to incorporate in the refractory base a bonding agent, in order to insure the proper cohesion in the entire mass. Examples of such agents are: magnesium zirconate, phosphoric acid, water, and many others. Other materials may also be added for other purposes well known in the art. The term "refractory base," as used throughout the specification and claims, is intended to include a refractory material in combination with these well known desired, customary or necessary additions.

Having described the invention, the following specific examples are now given.

Example 1

44 parts of 200 mesh quartz, 20 parts of magnesium zirconate, 3 parts of 325 mesh cleaned and washed zirconium carbide (the expanding material), 1 part of red lead (oxidizing agent) and 20 to 60 parts of water are added together and ground in a ball mill for about an hour, The mixture is then dried, disintegrated, and thoroughly mixed with 44 parts of 35 mesh quartz, after which 24 parts of water and 12 parts of phosphoric acid are well mixed in. The material is then cast into shape and fired at a temperature of at least 1400° F. At the temperature of 1600° F. the material showed a uniform linear expansion in all directions of 1.55%, in excess of the initial dimensions at room temperature before firing. The same procedure, without the addition of any zirconium carbide or red lead, showed an expansion of 0.52%.

Example 2

The same procedure is followed as in Example 1, except that only 2 parts of zirconium carbide is used. After firing, the expansion obtained (measured at 1600° F.) is 1.23%.

Example 3

The same procedure is followed as in Example 1, except that only 1 part of zirconium carbide and 0.5 part of red lead is used. After firing, the expansion obtained (measured at 1600° F.) is 0.87%.

In accordance with this invention, there is superimposed on the normal thermal expansion of the refractory base and of the expanding material a second expansion, which is the result of chemical change of the expanding material and which is greatly in excess of the thermal expansion of such expanding material. By varying the amounts of such expanding material, any desired expansion can be obtained in the refractory. With only moderate amounts of expanding material, expansions as much as 3% to 5% are possible, which enables the shrinkage of practically any casting alloy to be properly compensated for.

When parts are specified, it is understood that parts by weight are meant.

As many variations are possible within the scope of this invention, it is not intended to be limited except as defined by the appended claims.

We claim:

1. A refractory composition comprising a refractory base and a minor quantity of a material capable of a substantial and uniform expansion at a high temperature as the result of chemical change, said material being taken from the class consisting of thermal reaction products of zirconium and carbon, titanium and carbon, thorium and carbon, cerium and carbon, hafnium and carbon, silicon and carbon, zirconium and nitrogen, titanium and nitrogen, thorium and nitrogen, cerium and nitrogen, hafnium and nitrogen, silicon and nitrogen, said material being in finely divided form and uniformly distributed throughout said base, the amount of said material being predetermined to control the expansion and contraction characteristics of the refractory composition.

2. A refractory composition comprising a refractory base and a minor quantity of a thermal reaction product of zirconium and carbon, said reaction product being in finely divided form and uniformly distributed throughout said base, the amount of said reaction product being predetermined to control the expansion and contraction characteristics of the refractory composition.

3. A refractory composition comprising a refractory base and a minor quantity of zirconium carbide, said zirconium carbide being in finely divided form and uniformly distributed throughout said base, the amount of said zirconium carbide being predetermined to control the expansion and contraction characteristics of the refractory composition.

4. The refractory composition of claim 1 characterized in that it contains an oxidizing agent.

5. The refractory composition of claim 2 characterized in that it contains an oxidizing agent.

6. The refractory composition of claim 3 characterized in that it contains an oxidizing agent.

7. A refractory composition comprising a refractory base, 0.25% to 2.5% of red lead and 0.5% to 5% of zirconium carbide, said zirconium carbide being of sufficient fineness to pass a 200 mesh screen and being uniformly distributed throughout said base, the amount of said zirconium carbide being predetermined to control the expansion and contraction characteristics of the refractory composition.

8. A refractory composition comprising a refractory base, an oxidizing agent, and a minor quantity of titanium carbide, said titanium carbide being in finely divided form and uniformly distributed throughout said base, the amount of said titanium carbide being predetermined to control the expansion and contraction characteristics of the refractory composition.

9. The refractory composition of claim 1 characterized in that the quantity of expansible material is 0.5% to 5%.

10. The refractory composition of claim 2 characterized in that the quantity of expansible material is 0.5% to 5%.

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