

porosity being varied so as to yield, with the incorporation of an inorganic or organic material infiltrant, the desired properties. Generally porosity in the resulting framework or skeleton is about 25–50% by volume, preferably 35–40% by volume.

In certain circumstances, such as in forming dental restorations, extremely fine particle size of ceramic particles on the order of 0.5 micrometer, are desirable especially to avoid excess wear on the opposing tooth. Such particles sizes are operative within the present invention.

The organic material selected from the pre-ceramic forming material is a material which forms the necks binding the individual ceramic particles under appropriate firing conditions. By appropriate firing conditions, we mean from 1 minute to 1 hour at temperatures of from about 500° C. to about 1000° C. Preferred firing conditions are about 10 minutes at about 655° C. Sintering atmospheres should not degrade either the ceramic powder or the function of the pre-ceramic forming organic material. Thus, inert atmospheres are acceptable, though not critical. Sintering in air is preferable. In certain circumstances, reactive atmospheres, such as nitrogen, can be employed. Both temperatures and pressure can be varied to control the nature of the resulting porous framework.

A suitable glass-forming pre-ceramic inorganic or organic material is a polymer of poly(dimethylsiloxane). Most preferably, we employ a poly(dimethylsiloxane) having a kinematic viscosity of about 1000 centistokes which polymer is trimethylsiloxy terminated. Such a polymer forms a high-silica content glass at moderate temperatures in air. The polymer can suitably be mixed with the ceramic powder by use of a solvent. Content of the pre-ceramic organic material can vary between about 2.5% by weight, to about 20% by weight, although greater or lesser amounts of polymer can be employed. We have employed five percent (by weight) of poly(dimethylsiloxane) in a solvent such as cyclohexane.

Preferred suitable inorganic and organic materials include polyorganozirconates, polyorganoaluminates, polysiloxanes, polysilanes, polysilazanes, polycarbosilanes, polyborosilanes, etc. Suitable pre-ceramic forming materials are currently commercially available from Gelest, Inc. of Tullytown, Pa., such as zirconium tetramethacrylate, zirconyl dimethacrylate, or zirconium 2-ethylhexanoate; aluminum III s-butoxide, aluminum III diisopropoxide-ethylacetoacetate; 1,3-bis(chloromethyl) 1,1,3,3-Tetrakis(trimethylsiloxy)disiloxane; 1,3-bis(3-carboxypropyl) tetramethyldisiloxane; 1,3,5,7-tetraethyl-2,4,6,8-tetramethylcyclotetrasilazane; tris(trimethylsilyl)phosphate; and tris(trimethylsiloxy)boron. Average molecular weight of the organic precursor materials varies between about 150 to about 200,000.

In addition to the various inorganic and organic materials discussed above, other precursor polymers suitable for use in the invention include polyphosphazenes, polyorganotinates and other organometallic polymers. Monomeric and oligomeric forms of the various polymeric materials mentioned as infiltrants also may be used to infiltrate the porous ceramic framework or skeleton. Additionally, various combinations of the above polymers, polymer/monomer, and monomer/monomer mixtures can be used as the infiltrant.

In addition to the infiltrants mentioned above, which can also be used as the ceramic-forming precursor, it is within the scope of the present invention to use infiltrants other than the pre-ceramic precursor materials to form a second phase within the porous framework.

The infiltrants may perform multiple functions, such as toughening the skeleton or framework, such as in providing

“active” sites to aid in bonding the infiltrated composite (IPC), via an adhesive or cement, to a substrate through chemical bonding. In the past, prostheses, such as dental restorations, formed from a ceramic, were typically bonded, via an intervening adhesive or cement, to a substrate exclusively through mechanical interlocks. Such mechanical interlocks were formed by abrading or etching the prosthesis to form mechanical sites into which the adhesive or cement could penetrate and interlock. While such mechanical sites may still be provided on the composites of the present invention, the infiltrant can also be a source for chemical (in addition to the mechanical) bonding. Reactive functionality in the infiltrant can be preserved even after the polymerization of the infiltrant within the skeleton or framework, which functionality assists in the formation of chemical bonds to the adhesive or cement.

Thus, the present invention has utility for forming dental restorations, including crowns or partial dentures, onlays and inlays. The restorations may be molded in conventional gypsum dental molds. Alternatively, restorations may be formed from a mixture of ceramic particles, pre-ceramic precursor and a light, e.g., ultraviolet (UV) or visible light, curable resin to sustain formed shapes and impart workability for the technician. Still further, the composites of the present invention may be made into blocks of restorative material and machined to the final shape.

Such machining processes include computer assisted design/computer assisted machining (CAD/CAM) which utilize very simple block shapes of restorative material, removing many of the traditional processing restrictions which limited material choices for restorative dentistry.

Other uses of the composite materials of the claimed invention are as a coating for implants, e.g., coatings on titanium pins or screws. In corrective surgery, there is usually a requirement to remove a pin or screw necessitating a second surgery. The space around the screw does not reliably fill with new bone growth. By forming a ceramic coating, such as calcium hydroxyapatites and pre-ceramic precursor according to the invention, the coating will bind the porous skeleton firmly to the surgical implants, such as onto metal pins or screws. The porous nature of the composite facilitates bone growth into the hydroxyapatites framework.

The nature of the composite material also permits its use as a directly implantable body, i.e., a cranial or bone plate or bone implant, where the porosity of the framework facilitates bone growth within the framework.

Even where the framework is infiltrated to modify the properties (e.g., toughen) of the framework, the infiltrant can be partially etched or leached from the framework to expose the porous structure to facilitate bone growth. Alternatively, the framework can be selectively impregnated to different degrees by the infiltrant or impregnated with a bioresorbable material.

The present invention provides low cost, low temperature benefits which may be utilized outside of prosthetics, such as commercially as chip resistant coatings for enamelware, whiteware fabrication and tile fabrication.

The fabrication of IPC blocks according to the invention will now be described in detail in the following Examples.

#### Example 1

Starting blocks of ceramic framework were formed as follows:

A feldspathic ceramic (sold under the tradename Ceramico II, from Johnson & Johnson, Inc.) was mixed with