United States Patent [19]

Long

[11] **3,905,047**

[45] **Sept. 16, 1975**

[54] **IMPLANTABLE CERAMIC BONE PROSTHESIS**

[75] Inventor: **Roger A. Long,** Escondido, Calif.

[73] Assignee: **John J. Posta, Jr.,** Northridge, Calif.

[22] Filed: **June 27, 1973**

[21] Appl. No.: **373,959**

[52] **U.S. Cl.** ..... **3/1.9;** 128/92 C; 106/39.5; 106/55; 264/43

[51] **Int. Cl.²** **A61F 1/24**

[58] **Field of Search** ..... 3/1, 1.9–1.913; 128/92 C, 92 CA, 92 R, 92 G; 32/10 A; 106/39.5, 55

[56] **References Cited**

UNITED STATES PATENTS

3,314,420	4/1967	Smith et al.	128/92 C
3,662,405	5/1972	Bortz et al.	3/1
3,787,900	1/1974	McGee	3/1

FOREIGN PATENTS OR APPLICATIONS

2,008,010	8/1971	Germany	3/1

Primary Examiner—Ronald L. Frinks

Attorney, Agent, or Firm—John J. Posta, Jr., Esq.

[57] **ABSTRACT**

The improved bone prosthesis of the invention comprises a unitary body containing an eutectic of metal pyrophosphate and refractory oxide. Preferably, the body also contains discrete particles of refractory oxide bonded together by the eutectic which serves as a matrix bonder. Moreover, the particles are preferably of the same refractory oxide, such as alumina, as is present in the eutectic and are of extended surface area for improved strength. The pyrophosphate preferably is calcium pyrophosphate so that the prosthesis is biodegradable. The prosthesis can be prepared, in accordance with the present method, by forming the eutectic, preferably a pourable mixture of the particles and the molten eutectic, and pouring the mixture into and filling a mold of a bone to be duplicated, solidifying the mold and recovering it from the mold. The surface of the prosthesis can be texturized, as by acid etching it, to increase bond ingrowth and/or tissue attachment when implanted.

10 Claims, 1 Drawing Figure

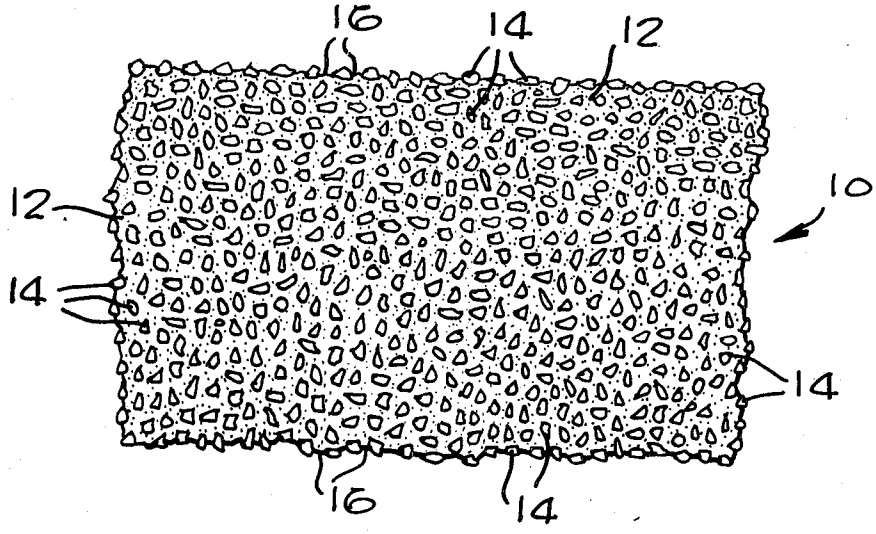
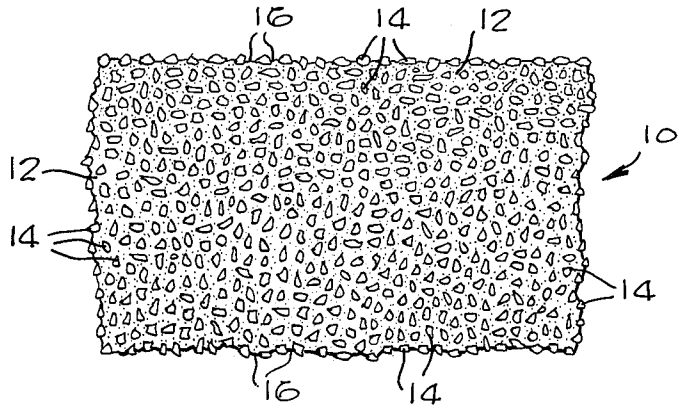


Fig. 1



IMPLANTABLE CERAMIC BONE PROSTHESIS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention generally relates to prostheses and more particularly to implantable bone prostheses and methods of making the same.

2. Description of Prior Art

A bone prosthesis is an artificial device to replace a missing bone in the body. For example, a bone may have to be removed surgically because of extensive injury thereto, e.g., erosion by disease, crushing by mechanical injury, or the bone may be missing due to a congenital defect or as a result of an explosion or the like. An artificial bone or bone portion (prosthesis) can be implanted in the body to restore the function of the affected body portion and to provide the necessary cosmetic effect.

Various types of bone prostheses have been employed. In most instances, an attempt is made to simulate the appearance, i.e., size and shape of the missing bone or bone portion for cosmetic purposes and also to provide a durable structural support. Metal prostheses have been widely used in the past because of their high strength. However, the metal used must be carefully selected with due regard to the possibility of corrosion of the metal by body fluids and/or a possible "foreign body" reaction, i.e., rejection of or reaction to the metal by the body because of toxicity or incompatibility thereto.

More recently, ceramic bone prostheses more compatible with the body than metals have been used with some success. However, such prostheses are usually not very durable, being brittle and so are easily chipped and broken. Moreover, they cannot be rapidly or easily fabricated as by melting and casting into exact duplicates of the bone to be replaced, because of very high temperatures required to melt such ceramics. Instead, other procedures must be employed which takes considerable time and raise their cost. For example, the prostheses can be formed by press and sintering techniques, often with grinding and fitting to size required after initial fabrication.

It has been found that a close mechanical fit between a prosthesis replacing all or a portion of a bone and the adjacent living bone portions when the prosthesis is in place is important in order to stimulate ingrowth of living bone to bridge the gap with the prosthesis and bond the prosthesis tightly to the living bone. Such tight mechanical bonding enables the assembly to function at an early date in the manner of the original unimpaired bone. In order to obtain the required fit, the missing bone or bone portion must be exactly duplicated in situ and then made permanent. Continued exposure of the impaired area first for bone duplication and then for prosthesis fitting, normally involves trauma, so that minimizing the exposure time becomes important in many instances. As pointed out above, conventional, standard size ceramic prostheses normally take considerable time to fabricate and do not meet this requirement.

Accordingly, there is a need for a prosthesis which can be made economically, easily and rapidly into the exact duplicate of the bone or bone portion to be replaced and thus reduce exposure time, while providing good body compatibility and high structural strength.

It has also been found that growth of living bone into the prosthesis can be achieved and good mechanical bonding of the prosthesis to adjacent bony parts and to adjacent connecting tissue can be accomplished when the surface porosity of the prosthesis is carefully controlled within certain limits. Metal prostheses normally are smooth and, therefore, are unsuitable from this standpoint without substantial texturizing. Ceramic prosthesis usually also are smooth surfaced and difficult to render porous while retaining their structural integrity.

Certain investigations have been made concerning the possibility of forming ceramic prostheses of material which is resorbable by the body, the prosthesis gradually being replaced by ingrowing bone until the prosthesis is completely or substantially completely substituted by living bone. While such materials can, with some problems, be made porous to stimulate bone ingrowth, they are structually weak and are further weakened during resorption, so that total immobilization of the bony area may be required, even if only minor bone replacement is made, until resorption is complete, a considerable inconvenience. Mechanical working of a structurally weak prosthesis may result in its failure. Moreover, it has been found that movement between the weak prosthesis and adjacent bony parts inhibits the healing process, impairing bone ingrowth.

Accordingly, there is a need for a biodegradable resorbable type of prosthesis which provides improved structural integrity during resorption, which can be made with a surface porosity easily and without weakening the same and which can easily be fabricated to exact dimensions for best initial fit of the part to be replaced.

SUMMARY OF THE INVENTION

The improved bone prosthesis of the present invention and the novel method of making the same satisfy the foregoing needs. The prosthesis and method are substantially as set forth in the Abstract above. Such prosthesis can be made either permanent or resorbable (biodegradable). Both versions exhibit high structural strength, good impact resistance, controlled surface porosity and compatibility with body fluids, and are capable of economically, rapidly and easily being fabricated by the present method into exact duplicates of the bones and bone portions to be replaced. They stimulate rapid bone ingrowth and can provide a source of material used in formation of living bone. Other advantages are set forth in the following detailed description and accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

The single FIGURE of the drawings schematically depicts in enlarged cross section one embodiment of a portion of a prosthesis in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

As depicted schematically in cross section in the single FIGURE, a portion of a preferred embodiment of the bone prosthesis of the invention is shown. Thus, prosthesis **10** is a unitary ceramic body comprising a matrix **12** of an eutectic within which a plurality of discrete particles **14** of refractory oxide are embedded

and bonded together. The eutectic is of metal pyrophosphate and refractory oxide.

The metal pyrophosphate, due to its atomic bonding structure, imparts great strength to the ceramic material. It is preferred that calcium pyrophosphate be utilized as the metal pyrophosphate because it has controlled biodegradability and is completely compatible with the body. Calcium pyrophosphate has the general chemical formula $Ca_2P_2O_7$, with a melting point of **1356°** C.± **2°** C. and a stoichiometric composition of **44.1%** CaO and **55.9%** P_2O_5. It has a density of **3.09** g./cc. in the beta or low temperature (=**1140°** C.) form. An inversion occurs on heating or cooling of this material and it has been noted that molten calcium pyrophosphate has a tendency to supercool and then freeze rapidly to the beta form, which is more dense than the alpha form.

Calcium pyrophosphate can be made by established chemical procedures. However, in order to obtain the most pure form for use in body implants and the like, it is preferred to calcine dicalcium phosphate at about **900°** C. to calcium pyrophosphate as per the following:

$$2(CaHPO_4 \cdot 2H_2O) \rightarrow Ca_2P_2O_7 + 5H_2O$$

Calcium pyrophosphate can be hydrolyzed slowly to the ortho monomolecular form, the rate being dependent on pH and temperature, increasing with acidity and temperature. Calcium pyrophosphate is biodegradable to the ortho monomolecular form in body fluids, assisted by P—O—P splitting body enzymes, so that calcium and phosphate are supplied to the body sera. In turn, the body sera supply calcium and phosphate back to the implant in the formation of normal body bone tissue as a replacement for the absorbed calcium pyrophosphate. It is believed that the living bone building mineral crystalline apatite is supplied in the body through hydrolysis of a less basic calcium phosphate salt. Moreover, residual phosphate salts are known to nucleate apatite. Current theory indicates that in bone, the apatite crystals are small and comprise only a part of the total mineral present, a second mineral being present in the form of a non-crystalline (amorphous) calcium phosphate. Whatever the exact mechanism for the building of living bone involved, it is believed that the availability of a ready supply of calcium and phosphate adjacent to the replacement site stimulates bone ingrowth and rapid replacement of a biodegradable bone implant. Calcium pyrophosphate serves as such a source of supply.

Magnesium pyrophosphate, sodium pyrophosphate and potassium pyrophosphate can also be used a biodegradable metal pyrophosphates, but are less preferred separately since they do not supply calcium for bone building. These pyrophosphates are slowly soluble in water or acidic media and therefore should only be used with a biodegradable or non-biodegradable metal pyrophosphate which is essentially water insoluble, so as to control the rate of degrading of the prosthesis. Their use in combination with the calcium pyrophosphate assists in controlling the hydrolysis reaction.

In the event that it is desired to make the implant non-biodegradable, then an inert metal pyrophosphate such as manganese pyrophosphate, titanium pyrophosphate, iron pyrophosphate, ziconium pyrophosphate or similar inert pyrophosphate, such as is set forth in U.S. Pat. No. **3,131,073** issued Apr. **28, 1964**, can be employed in the present eutectic.

The refractory oxide component of the eutectic preferably comprises any suitable refractory metal oxide such as alumina, zirconia, titania, magnesia, chromia or the like which is insoluble in water and non-toxic to the body. Of the above, it is preferred to use alumina, since it is very inexpensive, readily available, totally inert and non-biodegradable, and it is known, from long term testing, to be completely non-toxic and compatible with the body and its fluids.

A eutectic of the metal pyrophosphate and refractory oxide is formed by any suitable procedure, such as by blending the pyrophosphate with the refractory oxide, both in fine particulate form, e.g., **200** to **300** mesh, and in the proper proportions. The mixture is then melted.

The proper proportion of ingredients for the eutectic is that which just begins to melt and flow at the processing temperature. This can be determined experimentally by utilizing various pyrophosphate-refractory oxide mixtures, varying the concentration of the refractory oxide from mixture to mixture, compacting each mixture, as by pressing up to **10,000** psi, and then heating the mixtures, observing which of the samples just begins to flow, as by rounding of the corners of the sample at the lowest temperature. The test temperature is then lowered while minor changes are made in the concentration of refractory oxide in new pressed samples containing the pyrophosphate. The lowest temperature at which corner rounding occurs gives a reliable indication of the proper eutectic composition. Such a procedure is set forth in detail in U.S. Pat. No. **3,131,073,** described above.

In the case of a mixture of, by weight **92.5%** manganese pyrophosphate ($Mn_2P_2O_7$) and **7.5%** alumina (Al_2O_3), the eutectic temperature is **1,987°** F., well below the melting point of the oxide, **3,720°** F. It is a characteristic of the eutectic that it melts well below the melting point of its refractory oxide component, so that it can be used to form at lower temperature high strength ceramics. In the case of an eutectic employing calcium pyrophosphate (**87.5%** by weight) and alumina (**12.5%** by weight), the eutectic temperature is about **2275°** F. Such temperature is sufficiently low to permit melting of the eutectic and casting of the same in high temperature resistant molds such as graphite, ceramic, or the like, while the free particles of refractory oxide, e.g., alumina, are maintained.

The eutectic used in the improved bone prosthesis of the invention is highly desirable since it imparts great strength to the prosthesis, acts as a binder for solid particles of refractory oxide when they are dispersed therein and permits melting and casting of exact bone duplicates at temperatures sufficiently low such that conventional molding materials can be used.

Moreover, of considerable importance is the fact that when free particles of refractory oxide are present in the prosthesis and are of the same refractory oxide as that in the eutectic, no substantial degradation of those particles by the eutectic occurs. In other words, the eutectic represents a saturated solution in which the free refractory oxide particles are not dissolved during processing. Accordingly, the concentration and physical structure of such free particles is preserved in processing, leading to a precise prediction of the prosthesis strength, and the size and arrangement of particles, as well as the biodegradability of the prosthesis.

It will be understood that the free refractory oxide particles can be eliminated from the prosthesis, but it usually is much preferred that they be present, since

they increase the strength, reduce the brittleness and decrease the shrinkage of the prosthesis. Accordingly, in the preferred embodiment of the invention, the particles are present.

In order to provide proper melting and total bonding of the free refractory oxide particles together by the eutectic, it is preferred to use an initial concentration of the refractory oxide in the eutectic mixture which is very slightly less than that necessary for complete saturation of the eutectic. Accordingly, when the liquid eutectic is formed and the free particles of the refractory oxide are added, a slight melting or dissolving of the outer surface of the particles occurs, assuring their proper bonding together in and with the binder-matric of the eutectic.

The particles of refractory oxide filler particles bonded together by the eutectic usually are of extended surface area, such as high modulus fibers, flakes, or the like, to improve bending strength or stiffness of the prosthesis. Preferably, the particles are of chemically inert refractory metal oxide, such as alumina, zirconia, titania, magnesia or the like. Most preferably, those particles are of the same refractory oxide as is present in the eutectic. Thus, the novel casting method of the invention is impractical to employ when it is desired to use fibers of lengths in excess of about ⅛ inch. In such instances, either the press and sinter, hot press technique, or similar fabrication can be used or the fibers can be formed into bundles, placed in a mold and then eutectic can be vacuum cast around them.

The novel prosthesis can be fabricated by any suitable method such as conventional slip casting and cold pressing followed by sintering or hot pressing. However, it is preferred to employ the novel method of the present invention, since precisely shaped and sized prostheses can be made rapidly and economically by the novel method. Such method is, however, limited to specific compositions and particle shapes.

In forming the novel prosthesis in accordance with the present novel method, the eutectic preferably is rendered molten and, preferably, refractory oxide particles are mixed therewith to form a pourable mixture, which is then cast into a mold and solidified therein, as by cooling, after which the mold is separated therefrom and the finished prosthesis recovered.

The pourable mixture usually contains less than **20%** by weight of oxide filler particles, with the minimum filler oxide concentration being only that necessary to make a good casting ceramic.

However, when the cold press, slip cast and sintering or hot press technique is employed, the refractory oxide filler particles may be present in a substantially greater concentration by weight, for example, in excess of that of the eutectic binder-matric. Thus, the filler particles in such instances may be present, for example, in a concentration of between about **20** and about **75** percent, by weight of the prosthesis, the eutectic comprising the remainder.

It will be understood that other substances can be added to the prosthesis for certain purposes, i.e., structural supports, such as metal sponge or the like, texturizing or pore-forming agents, eutectic temperature-lowering agents, such as sodium phosphate, etc. Such substances usually are present in minor concentrations. In addition, the prosthesis can be made in several parts, e.g., can be provided with a shell or core of the same or different material.

It will also be understood that since the novel prosthesis of the present invention preferably incorporates at least two distinctive components, that is, the eutectic binder-matric of metal pyrophosphate and refractory oxide, plus the filler of refractory oxide particles, it is readily subject to control of the nature, size and extent of its surface pores. Such pores can facilitate live bone ingrowth and locking to or replacement of the prosthesis, and further facilitate the mechanical attachment of adjacent tissue to the prosthesis.

Surface texturizing of the prosthesis can be accomplished by selectively surface etching or leaching out, as by acid or the like, one of the components of the prosthesis, an advantage over single component ceramics. As shown in the single figure, surface pores **16** are present in prosthesis **10,** the size and extent depending on the size and shape of filler particles **14** and the nature of any texturizing treatment applied to exterior of prosthesis **10.** The nature of the filler and binder-matrix is such that the biodegradability, if any, of the prosthesis **10,** as well as its structural strength, impact resistance, and other factors, can easily be controlled by careful selection of the pyrophosphate(s) and the refractory oxide(s) and their relative concentrations, as well as the size and shape of the filler particles. Accordingly, the prosthesis has far greater flexibility in physical and chemical characteristics than conventional ceramic prostheses. Certain further features of the prosthesis of the present invention and the present method are illustrated in the following specific examples:

EXAMPLE I

A missing central portion of a human femur is replaced by a bone prosthesis implanted between the two existing end portions of the femur, with a gap therebetween of not in excess of five thousandths of an inch. The prosthesis almost exactly duplicates the missing portion of the femur and is prepared by the following procedure:

A wax impression is made of the missing central portion of the femur by filling in the gap between the two existing femur portions and checking the impression against the cavity defined by the surrounding leg tissue. The wax impression is then removed, a high temperature resistant ceramic mold is formed there around from a dip slurry from which the slurry liquid medium is then removed. The ceramic cast is baked and the wax is then melted, removed from the mold and the mold is then further hardened by firing.

A pourable mixture of a molten eutectic of calcium pyrophosphate and alumina with added solid particles of alumina is then formed. The eutectic has the composition of about **87.5** percent by weight of calcium pyrophosphate and about **12.5** percent by weight of alumina. The eutectic comprises **80** percent by weight of the eutectic mixture with the alumina particles constituting the remainder.

The pourable mixture while at about **2300°** F. is poured into the mold to fill the mold and is then allowed to solidify, after which the mold is released and the prosthesis recovered. The total time for forming the impression, manufacture of the mold, and fabrication of the prosthesis is about **60** minutes. The ceramic prosthesis is then inserted into the femur gap and fits substantially perfectly. The surgical opening is then closed and the femur is immobilized, since the two ends of the femur adjacent the prosthesis will need time to

solidly fuse with the prosthesis. The prosthesis is biodegradable, its resorption and replacement by living bone occurring over a time period. The prosthesis is economical, hard, durable, of controlled biodegradability, functions very well, cosmetically and structurally knits tightly with the remainder of the femur and stimulates bone ingrowth and bone replacement.

In a parallel test, the eutectic alone is used (without filler oxide) as the pourable mixture and the results are essentially the same. However, it is noted that the ceramic cast body is slightly more brittle and shrinkage is slightly greater.

In a parallel test, titania is substituted for the alumina in the eutectic and as the filler. The eutectic contains about **14** percent by weight of titania and has a melting point of about **2275°** F. Comparable results are obtained, since the major eutectic component is biodegradable, while the titania is not, the relative proportions of each determining the rate of biodegradation. The product is strong, of controlled surface porosity, and easy and rapid to make and use.

In an additional parallel test, calcium pyrophosphate eutectic of the first run is used. It is blended with alumina in a ratio of **40** weight percent eutectic to **60** weight percent alumina, to form a dry mixture. This mixture is then pressed into a body at **10,000** psi, and then fired at about **2300°** F. for **30** minutes, resulting in a dense ceramic body which is then ground to the desired size and shape to provide a hard, biodegradable prosthesis.

EXAMPLE II

The procedure of Example I is followed, except that a non-biodegradable inert prosthesis is fabricated from a molten eutectic of **92.5** percent by weight of manganese pyrophosphate and **7.5** percent by weight of alumina in which alumina particles in a concentration of about **20** percent by weight of the prosthesis are dispersed. The eutectic has a melting point of about **1987°** F. and comprises the remainder of the prosthesis. A hard, high structural strength, high impact resistance, chemically inert prosthesis compatible with the body is provided by the economical and rapid casting and molding procedure of Example I. Total time of obtaining the wax impression, making the mold, casting, cooling and recovering the prosthesis is only about **60** minutes, so that the procedure permits customized fabrication of bony parts for substantially immediate emplacement.

In a second parallel run, an eutectic of **87.5** percent by weight of manganese pyrophosphate and **12.5** percent by weight of titania is melted at **1910°** F. and mixed with titania flakes in a weight ratio of about **4:1.** The molding and casting procedure of Example I is followed, utilizing a casting temperature of about **1950°** to **2000°** F., followed by solidification and recovery of the desired prosthesis. The prosthesis exhibits the improved properties described above for the alumina-manganese pyrophosphate product, including great strength, impact resistance, durability and total inertness to body fluids.

In a third parallel run, a prosthesis is fabricated using the components of the second run except the filler, titania flakes, are added in a weight percentage of about **80** percent to the eutectic mixture and blended together in a rubber-lined ball mill. The mixture is then shape pressed into a body at **10,000** psi, and sintered for **30** minutes at above **1910°** F. The body when cooled is then ground to the desired size and shape to provide a hard, durable inert prosthesis. The overall processing time is considerably longer than in the first two runs of this Example, nor are the dimensions of the prosthesis as accurate as those of the first two runs, and the cost is higher.

EXAMPLE III

Prostheses identical to those of Example I (first and parallel second and third runs) are surface texturized by contacting the prosthesis in each instance with dilute hydrochloric acid at elevated temperature (about **120°** F.) for about **3** minutes, until the calcium pyrophosphate eutectic at the surface of the prosthesis has been eroded to an average depth of about **44** microns, thereby increasing the porosity of that surface and facilitating live bone growth and/or other tissue thereinto. Accordingly, secure attachment of the prosthesis to adjacent femur bone portions is accomplished rapidly and full functioning of the femur is restored at an early date.

The preceding Examples clearly establish that the bone prosthesis of the present invention can be controllably biodegradable or made totally inert to body fluids. It is non-toxic, very strong and durable with good to high impact strength and can be made very easily and rapidly by the present method. The prosthesis can be surface texturized to control its porosity and can be formed in an exact size and shape for substitution for a missing bone or bone portion. The type of bones for which the described prosthesis can be substituted is not limited to the bones described herein, but are applicable to any desired bone in the body. Likewise, the prosthesis can be substituted for either part or all of any particular bone in the body. Likewise, the prosthesis can be substituted for either part or all of any particular bone in the body. Constituents of the prosthesis can stimulate bone ingrowth, due to the calcium and phosphate supplied by the prosthesis to the body sera. Other advantages are as set forth in the foregoing.

Various modifications and changes can be made in the present prosthesis and the components and in the present method, its steps, constituents and parameters. All such changes and modifications as are within the scope of the appended claims form part of the present invention.

What is claimed and desired to be secured by Letters Patent is:

1. An improved implantable bone prosthesis, said prosthesis comprising a unitary ceramic body containing a eutectic of metal pyrophosphate and refractory oxide, wherein said body includes discrete particles of refractory oxide bonded together by said eutectic, whereby said eutectic bonds together the discrete particles of refractory oxide in such a manner that no substantial degradation of said discrete particles by the eutectic occurs.

2. The improved bone prothesis of claim **1** wherein said particles are in the form of fibers.

3. The improved bone prosthesis of claim **1** wherein said particles are in the form of flakes.

4. The improved bone prosthesis of claim **1** wherein said refractory oxide comprises refractory metal oxide.

5. The improved bone prosthesis of claim **1** wherein said particles are of the same refractory oxide as that of said eutectic.

6. The improved bone prosthesis of claim 1 wherein said metal pyrophosphate comprises calcium pyrophosphate, whereby said prosthesis is biodegradable.

7. The improved bone prosthesis of claim 4 wherein the refractory oxide in said eutectic comprises alumina.

8. The improved bone prosthesis of claim 4 wherein said particles comprise alumina.

9. The improved bone prosthesis of claim 6 wherein said eutectic consists essentially of calcium pyrophosphate and alumina and wherein said particles consist essentially of alumina.

10. The improved bone prosthesis of claim 9 wherein said particles are of extended surface area for improved structural strength, and wherein said eutectic is present in a concentration in excess of about 80 percent, by weight, of said prosthesis.

* * * * *