Porous Calcium Phosphate Biomaterials Made Compatible with Bone

The Pitch

Current technologies to manufacture calcium phosphate biomaterials for surgical bone repair have not yet been optimized. They traditionally involve processes such as the synthesis of bioceramics containing tricalcium phosphate [$Ca_3(PO_4)_2$] or apatite [$Ca_{10}(PO_4)_6$] from aqueous solutions, sintering, sol-gel processing, and casting polymeric foams mixed with slurries of calcium phosphate. All of these methods are energy- and labor-intensive, and each requires several time-consuming steps. For example, a process such as sintering is disadvantageous because at the high temperatures required, more of the biologically compatible phases such as β-$Ca_3(PO_4)_2$ become converted to the relatively inert α-$Ca_3(PO_4)_2$ phase. At the Colorado School of Mines, combustion synthesis is used to make porous multiphasic calcium phosphate biomaterials for bone repair and replacement based on specifications provided by the biomedical field. Combustion synthesis involves self-propagating, high-temperature synthesis to produce materials both for devices and for component powders.

Porous β-$Ca_3(PO_4)_2$ is the form desired for bone replacement. It can act as a scaffold for bone-forming tissue that becomes directly attached to and grows into the bone. Within about two years, the porous β-$Ca_3(PO_4)_2$ usually is dissolved and assimilated by the body and replaced with natural bone. This porous multiphasic material mimics the bone environment better chemically and morphologically than currently used technology and is more biocompatible.

The most recent estimates in terms of need for this technology show that more than 500,000 joint replacement procedures are performed each year; an additional 40 million Americans suffer from some type of arthritic condition. The U.S. Department of Health and Human Services' most recent report (2000) estimates that the annual cost of craniofacial reconstruction procedures is more than \$60 billion. Some recent projections indicate that this cost alone could increase by more than 50% as baby boomers age.

TECHNOLOGY ADVANCES seeks materials developments on the threshold of commercialization. Send suggestions to Renée G. Ford, Renford Communications, renford@comcast.net.

The Technology

The inorganic component of bone is a multiphasic calcium phosphate composed of tricalcium phosphate, tetracalcium phosphate, and several forms of apatite (a natural calcium phosphate usually containing fluorine). The biomaterials group at the Colorado School of Mines synthesizes these ceramics as biomimetic replacements for bone tissue in order to effect a more beneficial response.

The reactant powders, CaO (325 mesh, 99.99% pure) and P_2O_5 (100 mesh, 99.99% pure), are mixed in the desired Ca:P mole ratio in a ball mill for 24 h. A 3:1 Ca:P reactant ratio produces an apatite in a tricalcium phosphate matrix, and a 4:1 Ca:P ratio produces a tricalcium phosphate in a tetracalcium phosphate matrix. All preparation is done in a desiccated argon atmosphere due to the strong hygroscopic and reactive nature of P_2O_5. To form pellets for the reac-

tion, four grams of powder are pressed into a cylinder. The reaction is initiated by heating a tungsten filament to the point of igniting the bottom of the pellet. Combustion propagates through the reactants in ~3–5 s. Following the reaction, the pellet is allowed to cool to room temperature in an atmosphere selected to guide the formation of the desired product. Humid air favors the formation of hydrated carbonate apatites, while a rapid quench in liquid nitrogen suppresses the formation of secondary phases, resulting in a pure product based on the reactant stoichiometry.

The final product is a porous mixture of crystalline and amorphous components (shown in Figure 1). The porosity is in the range of 100–500 µm, which has been shown to be advantageous for bone tissue ingrowth. The product can be synthesized in a net shape to create a specific device or can be ground to make precursor powder.

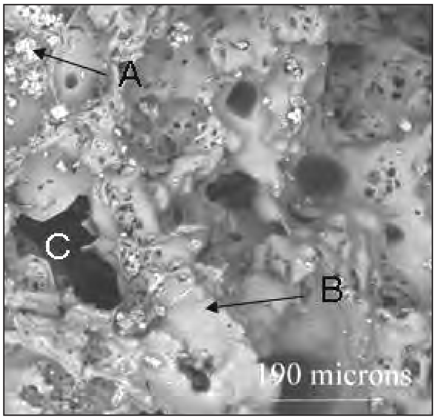

Figure 1. Scanning electron microscope image of tricalcium phosphate produced by combustion synthesis, showing (a) amorphous and (b) crystalline phases as well as (c) porosity.

The effectiveness of these materials has been demonstrated by a study in which multiphasic calcium phosphates produced by self-propagating, high-temperature-synthesis stimulated biomineralization in bone by producing cells *in vitro* when these cells were conditioned to be dormant. The implication of this research is that multiphasic calcium phosphates can stimulate increased biomineralization and reduce healing time.

Some of the uses for the synthesized material that are being investigated are a shim used in tibial osteotomy (surgical bone sectioning), a scaffold for bone tissue engineering, powders for bone cements, precursor powders for orthopedic device coatings, and fillers for dental and craniofacial reconstruction.

Opportunities

The Colorado School of Mines has several patent applications pending and is seeking partners to develop this technology exclusively or nonexclusively. Partners are also being sought to develop additional applications for this technology such as filter systems.

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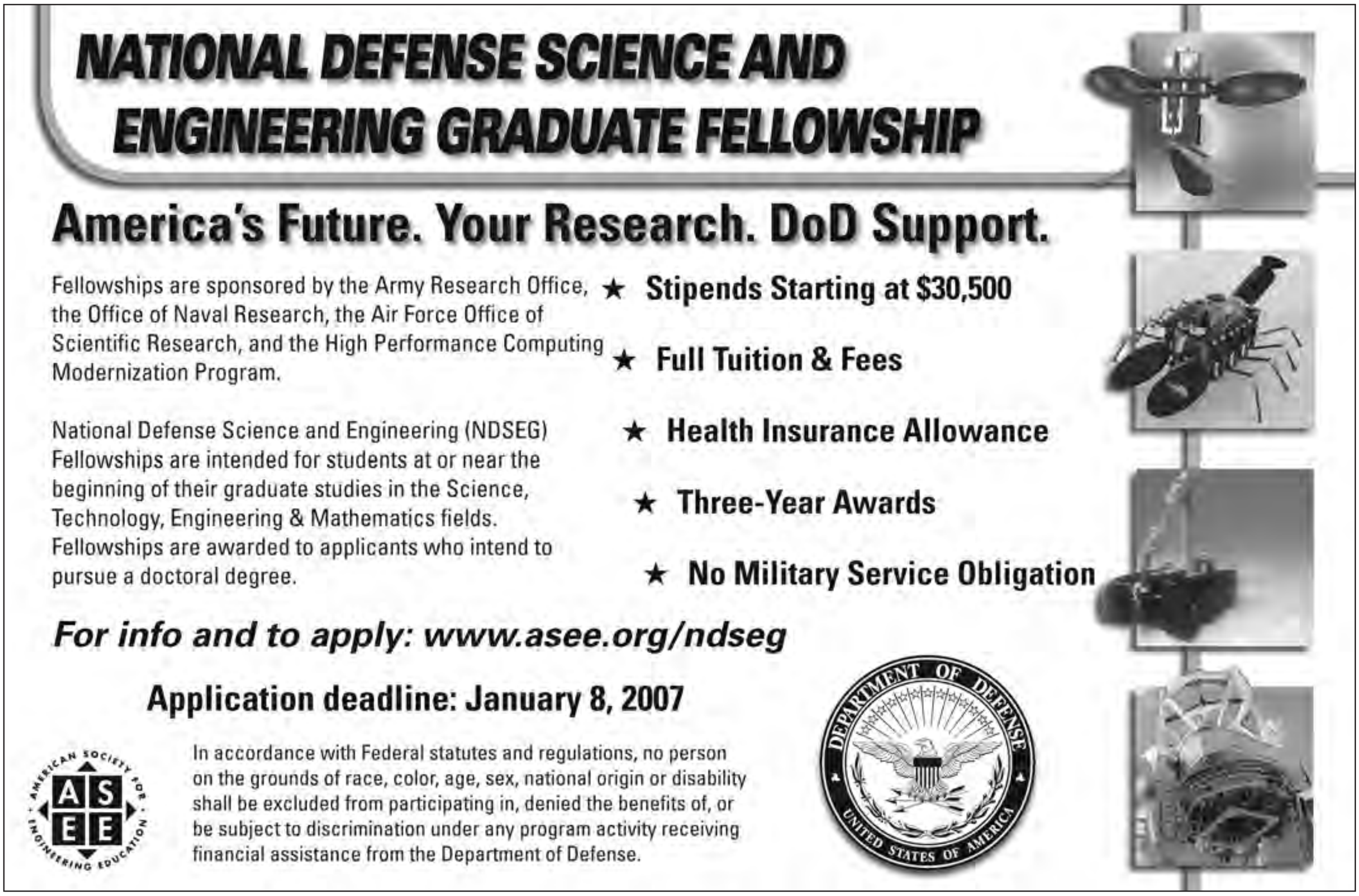

Bendable Concrete Minimizes Cracking and Fracture Problems

The Pitch

Bendable concrete (technically called "engineered cementitious composites," or ECCs), which is reported to overcome the brittleness of conventional concrete, is under development at the University of Michigan. In direct tension, ECCs, which have a tensile strain capacity of 3%, are 300 times more deformable than typical concrete. Their tensile stress–strain curves resemble that of a ductile metal with a yield point and subsequent strain-hardening behavior. However, only 2% by volume of short-fiber reinforcement is required to achieve ease in casting or field construction. This cost-effective technology enhances concrete structural and product performance while reducing both initial and long-term costs. While concrete brittleness can be compensated to a large extent with steel reinforcement on a structural scale, the intrinsic tensile ductility of bendable concrete eliminates cracking and fracture problems. This results in increased structural durability and safety as well as improved performance in infrastructure sustainability.

The initial cost savings of introducing bendable concrete depends on the particular product in which the material is used. Cost savings are associated with more efficient design as well as reductions in material volume, labor cost, and steel reinforcement. Markets that can benefit from the introduction of ECCs include transportation, building, water, and energy supply infrastructure as well as the housing, architectural, and concrete manufactured product industries. The U.S. market size for the precast and prestressed concrete product industry alone, for example, has been estimated at over $9 billion. The civil infrastructure repair business in the highway, street, bridge, and tunnel construction industries had annual revenues of about $60 billion in 1997. The market size for decorative concrete for housing applications is on the order of several billion dollars per year. By eliminating one of the most significant shortcomings of conventional concrete, ECCs could further extend the use of concrete as a major construction material. Potential customers include owners and contractors of constructed facilities, precast product manufacturers, fiber cement producers, and repair professionals.

Figure 1. Bendable engineered cementitious composites (ECCs) subjected to flexural loading. The beam specimen measures 304.8 mm long by 76.2 mm wide by 12.2 mm deep; deflection is 22 mm at a peak load of 0.6 kN. The maximum tensile strain capacity shown here reaches 3–5%.

Figure 2. The Glorio Tower Roppongi high-rise residential building, located in central Tokyo, which uses ECC coupling beams in its core for seismic resistance. The building is 27 stories (95 m) high. Built by Kajima Corp., construction on the building was completed in 2005.

The Technology

The non-brittle nature of ECCs can be visualized in a flexural test of an ECC beam, shown in Figure 1. The beam is withstanding a high load and a large deformation (hence ECCs' common name, "bendable concrete") without succumbing to the brittle fracture typical of normal concrete, even without the use of steel reinforcement. The ductile behavior of ECCs is the result of the deliberate selection of combinations of type, size, and amount of ingredients guided by micromechanical models also developed by its University of Michigan developers. These ingredients are specifically tailored to produce a composite that gives under excessive loading through controlled microcracking while suppressing brittle fracture localization.

A sample composition for an ECC in mass percent is 27.9% cement, 22.3% sand, 33.5% class F fly ash, 14.2% water, 0.9% superplasticizer, and 1.2% polyvinyl alcohol (PVA) fiber. The volume fraction of the fibers, which are pretreated with a proprietary oil coating, is 2%. ASTM Type I Portland cement and low-calcium ASTM class F fly ash are used. Large aggregates are excluded in the ECC mix design, and only fine sand is incorporated. The silica sand has a maximum grain size of 250 μm, with an average grain size of 110 μm. The PVA fibers, which constitute 1.2% by weight, are 39 μm in diameter, 12 mm long, and have an overall Young's modulus of 25.8 GPa. The apparent fiber strength when embedded in the cementitious matrix is 900 MPa.

Lightweight ECCs with a density between 900 kg/m^3 and 1600 kg/m^3 and a high early-strength ECC that delivers a compressive strength of 23 MPa within four hours after placement have been developed within the past few years. ECC varieties adapted for casting, extrusion, and shotcrete applications have been developed through the rheological control of properties. For on-site casting execution, ECCs use conventional construction equipment and are self-consolidating without the use of vibration. On-site casting of bridge decks and off-site manufacturing of coupling beams for tall building applications (shown in Figure 2) have been demonstrated. Thin-walled, bendable ECC pipes and an ECC shotcrete for repair applications have been commercialized.

Opportunities

The University of Michigan researchers welcome inquiries about joint application R&D. The licensing of ECC technologies, which are owned by the University of Michigan, is also available.

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