REPORT NUMBER 3

MANAGEMENT OF HARD TISSUE AVULSIVE WOUNDS AND MANAGEMENT OF OROFACIAL FRACTURES

ANNUAL REPORT

Thomas D. Driskell, Martin J. O'Hara,
Dale E. Niesz, and Gerald A. Grode

OCTOBER, 1972

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Porous tricalcium phosphate ceramics with good distribution and uniformity of large pores were developed. These materials consisted of about 36 percent large pore porosity and 14 percent matrix porosity with a compressive strength of about 3000 psi. These materials were prepared by conventional sintering isostatically compacted masses consisting of laboratory-prepared calcium phosphate powders and sized naphthalene as the pore-forming additive. Studies were conducted at the U. S. Army Institute of Dental Research, using small 2-mm-diameter by 2-mm-long porous tricalcium phosphate specimens implanted in the tibia of rats. These were found to be well tolerated, rapidly invaded by new bone, gradually resorbed, and replaced by remodelling bone over a period of about 8 weeks. In addition, larger pieces of the material were used to successfully augment alveolar ridge defects in dogs.

The implant studies have made apparent the potential desirability of these materials for the correction of many bone defects. Future research will be directed toward further development and evaluation of calcium phosphate materials for implant applications

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FOREWORD

This study has been conducted by the Ceramic Research Division of the Materials Processing and Fabrication Department and the Biochemistry and Biomedical Engineering Division of the Biology, Environment and Chemistry Department at Battelle's Columbus Laboratories, Columbus, Ohio. This is the third annual report of progress under Contract No. DADA17-69-C-9118 "Management of Hard Tissue Avulsive Wounds and Management of Orofacial Fractures". The principal investigator was Thomas D. Driskell, assisted by Martin J. O'Hara, principal ceramist. The valuable assistance of M. V. Weaver of the Ceramic Research Division is gratefully acknowledged. The extensive efforts of personnel at the U. S. Army Institute of Dental Research under the direction of Gen. S. N. Bhaskar in conducting the implant studies, in communicating experimental findings, and in relating and consulting on new materials concepts and applications have been invaluable toward the development and evaluation of the new concepts in ceramics for use in the repair of avulsive wounds and orofacial fractures emanating from this program.

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MANAGEMENT OF HARD TISSUE AVULSIVE WOUNDS
AND MANAGEMENT OF OROFACIAL FRACTURES

by

Thomas D. Driskell, Martin J. O'Hara,
Dale E. Niesz, and Gerald A. Grode

SUMMARY

Research studies were continued in the further development of resorbable ceramics for use in management of hard tissue avulsive wounds and orofacial fractures. Some research effort was also devoted toward protein impregnation of nonresorbable ceramics as an approach toward minimizing the possibility of implant rejection and enhancing the rate of bone growth into porous ceramics.

In previous work(1)*, emphasis was directed toward producing porous calcium phosphate ceramics consisting of a single phase of $Ca_3(PO_4)_2$, $Ca_2P_2O_7$, or $Ca(PO_3)_2$. Porous samples of $Ca(PO_3)_2$ and $Ca_3(PO_4)_2$ were developed at Battelle and then evaluated by in vivo studies conducted at the U. S. Army Institute of Dental Research (USAIDR). Porous calcium metaphosphate [$Ca(PO_3)_2$] samples implanted in the tibia of rats were found to be well tolerated, invaded by new bone, gradually resorbed, and ultimately replaced entirely by new bone. Subsequently, similar results were obtained using porous tricalcium phosphate [$Ca_3(PO_4)_2$] samples. Suitable samples of $Ca_2P_2O_7$ for implant evaluation were not successfully fabricated.

During this year's effort, significant additional progress has been made in the selection, development, and evaluation of experimental calcium phosphate resorbable ceramics. Of the various porous calcium phosphate materials already investigated, tricalcium phosphate was selected for continued development and evaluation on the basis that it was the easier to fabricate and was found to be biocompatible and resorbable. Also, studies were initiated to investigate the feasibility of producing resorbable ceramics consisting of the decomposition phases, $Ca_3(PO_4)_2$ and $Ca_4P_2O_9$, of calcium hydroxyapatite. We were successful in preparing samples of porous tricalcium phosphate with good distribution of large pores and uniformity of pore size. The porous samples had a compressive strength of about 3000 psi and contained about 50 volume percent porosity of which 36 volume percent was large pores. The matrix material had an average grain size of about 2.6 microns, and the matrix was about 72 percent of theoretical density.

Large samples of porous tricalcium phosphate were formed by isostatic pressing at 20,000 psi a mixture consisting of 68 and 72 parts by weight, respectively, of a laboratory-prepared calcium phosphate powder and

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* References are listed on page 40.

sized (minus 40 plus 100 mesh) naphthalene as the pore-forming additive. The laboratory-prepared powder, designated as B26 material, was made by reacting tribasic calcium phosphate (approximate hydroxyapatite composition) with phosphoric acid in solution, subsequently drying the material, and then calcining the material to 1400 F. After calcining, the reacted mass was pulverized to minus 100 mesh. Large isostatically pressed specimens containing naphthalene were first heated at low temperatures to remove the naphthalene and then heated to 2025 F to sinter the porous mass. Samples formed in this manner consisted of the β form of tricalcium phosphate.

Preliminary sintering studies indicated that pressed specimens of the B26 material developed optimum strength when sintered at about 2000 F. Specimens sintered at 2100 and 2200 F were weaker. The lower strength of specimens sintered at the higher temperatures was attributed to the effects of grain growth and a phase inversion on properties. Numerous porous tricalcium phosphate samples varying in size and shape from small 2 mm in diameter by 2 mm long to larger 20 mm wide by 15 mm thick by 35 mm long were prepared for implant studies. Samples of a previously developed nonresorbable porous phosphate-bonded alumina(2) with and without protein impregnation were also prepared for in vivo evaluation. Extensive implant studies were conducted at USAIDR to evaluate the potential of calcium phosphates to facilitate the repair of hard tissue defects(3,4,5). Results of the implant studies at USAIDR have indicated that porous calcium phosphate consisting of the mineral phase β-$Ca_3(PO_4)_2$ was well tolerated by the tissue. It appeared to be nontoxic, resorbable, and permitted the rapid invasion of new bone. In initial studies, small calcium phosphate pellets were evaluated as intraosseous implants and were found to permit healing of the defect area comparable to that of blood clot. These implant studies were conducted using rats with the ceramic implants inserted in the tibia. These findings indicate that the materials definitely have potential for use in the filling in of bony defects, intrabony pockets, and fracture sites.

Continued research in this program will be directed toward further development of porous calcium phosphate ceramic bodies with particular emphasis on improving strength and fully characterizing specimens to be used for in vivo evaluation. The objectives will be to identify processing methods suitable for tailoring implant materials to meet specific experimental needs in terms of rate of bioresorption, physical properties, and structural characteristics. Samples of these experimental materials will be supplied to USAIDR as requested for implant studies.

The relative merit of protein-impregnated porous phosphate-bonded alumina and porous calcium phosphate implants remains unknown. Little emphasis was placed on in vivo studies with this material because of the overriding interest stirred by the highly encouraging experimental results obtained using the calcium phosphate biodegradable ceramics.

PROBLEM AND APPROACH

Since earliest recorded history, man has employed various techniques in the repair and/or treatment of osseous diseases, deformities, and wounds. A brief historical review by Hulbert, et al.(6) on man's attempts to repair bone defects reveals early studies were conducted using both treated and untreated heterogenous, homogenous, and autogenous bone for bone grafting applications. Of these, autogenous bone grafting remains the most satisfactory approach but is not without disadvantages. Autogenous bone grafting involves transplantation of healthy bone from one area to a defect area, thus requiring a double operation. Also, the procedures are not always conducive to repair of massive osseous defects.

Porous ceramics have been developed in many laboratories and experimentally evaluated as permanent prostheses for partial replacement of hard tissue(1,2,6,7,8,9,10). Also, some material characteristics related to biocompatibility and structural design have been defined.(7) Some ceramics have potentially desirable properties for prosthesis application. These properties include a chemical inertness or lack of reactivity with body fluids and a propensity toward permitting hard and soft tissue ingrowth(8,9,10). However, most ceramics are inherently brittle and subject to easy fracture. Nonresorbable porous ceramics, once proliferated by bone, tissue, and blood vessels, in theory become an integral and permanent part of the repaired member section.

Of particular interest to the current study using resorbable ceramics are the historical results of using plaster of paris as a filler material in bone defects.(6) As early as 1892, plaster of paris was used to facilitate repair of bone diseases and defects. In the treatment of seven tuberculosis cavities, four were successfully repaired through resorption of the plaster and regeneration of new bone. In the treatment of an osteomyelitis defect and a defect caused by removal of an anchondroma, the use of plaster of paris facilitiated complete repair of the defects.(6) Since those early studies, other investigators have experimented with plaster of paris in orthopedic surgery. In general, results reported were encouraging and, in general, showed some indications of success. Little information is available on the mechanism or sequence of events of plaster of paris resorption and the possible adverse biological effects. However, the studies make apparent the feasibility of using a temporary, bioresorbable material to facilitate the repair of bone defects.

Calcium phosphates differ from plaster of paris in that they contain the two essential elements, calcium and phosphorous, in the inorganic hydroxyapatite phase in natural bone. Porous calcium phosphate implants have been shown to resorb in vivo(3,4,5) and conceivably could serve as a source for formation of hydroxyapatite.

Battelle's Columbus Laboratories has been conducting research on the project "Management of Hard Tissue Avulsive Wounds and Management of Orofacial Fractures" since April, 1969. The initial objectives of this program were directed toward the development and evaluation of porous ceramic materials and ceramic-coated fixation devices for potential application in the management of hard tissue avulsive wounds and orofacial fractures.

In April, 1970, the in vivo portion of this program was transferred to the U. S. Army Institute of Dental Research (USAIDR) at Walter Reed Army Research Center. In May, 1970, the objectives of this program were redefined as follows:

(1) To experimentally develop a porous ceramic material that is bioresorbable and which over a short period of time in a defect area becomes ingrown with new bone and, in turn, is gradually resorbed. After a period of time the ceramic material is completely dissolved and eliminated from the body, leaving only the subject's own bone in the defect area.

(2) To experimentally develop a protein-impregnated porous ceramic material in order to stimulate increased bone ingrowth and also to eliminate the normally void areas of a porous ceramic material which may lend themselves as sites for infection or other phenomena which might result in the rejection of the implant.

Both of these objectives complemented the original overall goals of the program.

Battelle's Columbus Laboratories since May, 1970, has concentrated efforts on the development of bioresorbable ceramics for potential application in the repair of hard tissue avulsive wounds. The basic materials selected have been calcium phosphates. Initially, porous calcium phosphates consisting of the mineral phases $Ca(PO_3)_2$ or $Ca_3(PO_4)_2$ were developed. Porous materials were selected for development because it has been shown that bone can proliferate into porous ceramics$^{(1,2)}$.

Implant studies in animals conducted at USAIDR indicated that the porous calcium phosphate materials developed were well tolerated and rapidly invaded by new bone. The ceramic was gradually resorbed and considered potentially effective as a bony void filler to be used in surgical correction of hard tissue defects. Therefore, in view of the apparent potential of bioresorbable ceramics for repair of bony defects, research efforts have been continued to further develop and characterize calcium phosphate biodegradable materials and to provide samples for continued in vivo evaluation.

MATERIALS AND METHODS

In this study, the primary research efforts were directed toward continued development of bioresorbable calcium phosphate ceramics and preparation of samples for in vivo evaluation. In addition, samples of a previously developed nonbiodegradable, porous phosphate-bonded alumina were prepared. Both protein-impregnated and as-processed samples of porous tricalcium phosphate and porous phosphate-bonded alumina were prepared for implant evaluation.

Bioresorbable Ceramics

In the further development of calcium phosphate ceramics, studies were conducted (1) to prepare calcium phosphate powders and characterize the powders for physical properties and chemical composition, (2) to investigate various sintering treatments to produce specimens with improved strength over that of previously developed specimens, and (3) to fabricate porous calcium phosphate samples for in vivo evaluation. These studies are discussed in the following sections.

Materials Preparation and Characterization

In initial studies on the development of tricalcium phosphate specimens$^{(2)}$, a shelf sample of reagent-grade material was used. However, in attempts to replenish the material, we were unable to locate a commercial supplier of tricalcium phosphate. Therefore, laboratory batches of materials were prepared by reacting reagent-grade tribasic calcium phosphate (approximate hydroxyapatite composition) with reagent-grade phosphoric acid. In preparing the materials, calculations were made to determine the stoichiometric amount of phosphoric acid required to convert tribasic calcium phosphate to tricalcium phosphate. Calculations were based on the following reactions:

$$(1)\quad Ca_{10}(OH)_2\,(PO_4)_6 \rightarrow 2\,Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O\uparrow$$

$$(2)\quad 3\,Ca_4P_2O_9 + 2H_3PO_4 \rightarrow 4\,Ca_3(PO_4)_2 + 3\,H_2O\uparrow.$$

It was calculated that 15.3 grams of 85 percent H_3PO_4 was the required amount of acid to convert 200 grams of $Ca_{10}(OH)_2(PO_4)_6$ to tricalcium phosphate, $Ca_3(PO_4)_2$.

Physicochemical changes produced by heat treatment of experimental acid-powder mixtures and the as-received tribasic powder were studied. Batch compositions and phase analyses data are given in Table 1. On the basis of experimental data and reported studies, a diagram (Figure 1) was prepared showing physicochemical changes produced by heat treatment of the laboratory-prepared Batch B26 material and the as-received calcium phosphate material.

In processing material mixtures, 200 grams of tribasic calcium phosphate was reacted at 180 F for at least 16 hours in a solution of 8 or 16 grams of 85 percent H_3PO_4 in 600 ml of distilled water. Each mixture was dried at 200 F, and then calcined at 1400 F for 4 hours. In Batch B26, a slight excess of the required amount of acid was used to account for possible loss of some P_2O_5 by vaporization when heating to elevated temperatures. As shown in Figure 1, the conversion of the B26 starting mixture of acid and calcium phosphate to $Ca_3(PO_4)_2$ involves several physicochemical changes. X-ray diffraction analyses of the reacted and 200 F dried Batch B26 materials indicated the presence of only two phases. The dried material consisted

TABLE 1. EFFECT OF HEAT TREATMENT ON THE PHASE CONSTITUTION OF AS-RECEIVED AND EXPERIMENTAL MIXTURES OF ACID AND TRIBASIC CALCIUM PHOSPHATE

	Batch Designation		
	B26	B97A	B97B
Starting Materials:			
Tribasic calcium phosphate, g(a)	200	200	200
Phosphoric Acid, 85% H_3PO_4, g(b)	16	8	---
Distilled Water, ml	600	600	---
Phase Constitution After Heat Treatment(c):			
Calcined at 1400 F			
β-$Ca_3(PO_4)_2$	S	S	S
$Ca_4P_2O_9$	VW	VW	M
β-$Ca_2P_2O_7$	M	M	---
Calcined at 2200 F			
α-$Ca_3(PO_4)_2$	---	---	S
$Ca_4P_2O_9$	---	---	S

(a) Reagent grade, J. T. Baker Chemical Co., Phillipsburg, N. J.
(b) Reagent grade, J. T. Baker Chemical Co.
(c) Presence of phases indicated by X-ray diffraction pattern intensities.

Code: S - strong; VW - very weak; M - medium.

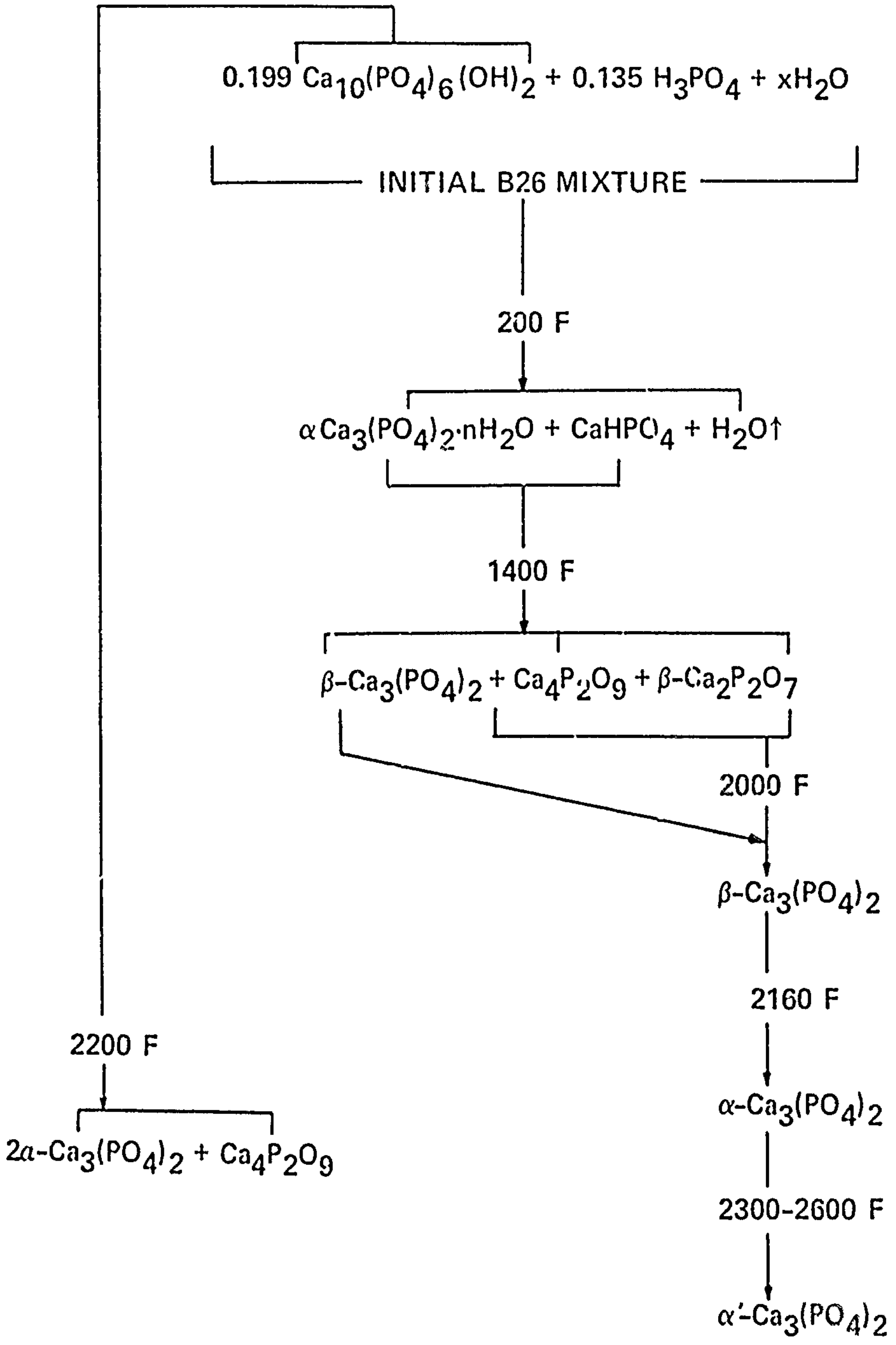

FIGURE 1. PHASE CONSTITUTION OF AS-RECEIVED AND ACID-CALCIUM PHOSPHATE MIXTURE AFTER HEATING AT INDICATED TEMPERATURES

essentially of hydrated tricalcium phosphate and a minor amount of $CaHPO_4$. No analyses were made on the Batch B97A materials.

After calcining the B26 mixture to 1400 F, at least three phases are present. It is questionable whether the hydrated phase of tricalcium phosphate or $Ca_4P_2O_9$ is the phase present after heat treatment to 1400 F. The diffraction patterns of those two phases are very similar, making positive identification difficult. Studies(11) on the dehydration of hydrated tricalcium phosphate have indicated that the phase conversions produced by heat treatment of hydrated tricalcium phosphate are complex, and the alpha form having the apatite structure is stable to about 930 F. At about 1300 F, the hydrated tricalcium phosphate is completely converted to β-$Ca_3(PO_4)_2$. This indicates that laboratory-prepared materials of Batch B26 when dried at 200 F apparently consist of a mixture of hydrated tricalcium phosphate, $CaHPO_4$, and another undetected phase or phases. On heating to 2025 F, the sintering temperature required to attain optimum strength of the calcium phosphate material, only β-$Ca_3(PO_4)_2$ was detected. This indicates that phases present after calcining at 1400 F react to form β-$Ca_3(PO_4)_2$.

Tricalcium phosphate undergoes phase inversions at elevated temperatures (12,13). The following inversions occur:

$$(3)\quad \beta\text{-}Ca_3(PO_4)_2 \xrightarrow{2156\ F} \alpha\text{-}Ca_3(PO_4)_2$$

$$(4)\quad \alpha\text{-}Ca_3(PO_4)_2 \xrightarrow{2304\text{-}2606\ F} \alpha'\text{-}Ca_3(PO_4)_2.$$

The β form converts to a lower density α form which is the more soluble phase in citric acid(13).

Through X-ray diffraction analyses, the as-received tribasic calcium phosphate when heated to 2200 F was found to decompose to form two phases. The phases present indicate that the material decomposes according to the following reaction:

$$(5)\quad Ca_{10}(OH)_2(PO_4)_6 \rightarrow 2\beta\text{-}Ca_3(PO_4)_2 + Ca_4P_2O_9 + H_2O\uparrow.$$

Intermediate physicochemical changes produced over the temperature range from 200 to 2200 F were not studied.

The laboratory-prepared and calcined Batch B26 calcium phosphate powder was examined with a scanning electron microscope to determine such characteristics as particle size and shape. The as-prepared powder is shown in the scanning electron photomicrograph of Figure 2. As apparent from the photomicrograph, the individual grains are predominately acicular and submicron size, measuring about 0.2 to 0.3 micron wide and about 0.7 to 1.0 micron long. Also, the prepared materials ground to minus 100 mesh consist predominately of clusters of the submicron particles.

10,000X

FIGURE 2. SCANNING ELECTRON MICROGRAPH SHOWING PREPARED CALCIUM PHOSPHATE POWDER

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A brief study was made to investigate the feasibility of pulverizing the prereacted and calcined calcium phosphate by standard ball-milling procedures. Materials pulverized by ball milling tended to cake excessively. Therefore, direct ball milling of the powders was found to be impractical. However, dry milling of powders containing additives, such as organic acids or wet milling using water or organic liquids may be feasible. Currently, the prepared laboratory powders are pulverized to at least minus 100 mesh by hand using mortar and pestle.

Processing Studies

Sintering studies were made with the ultimate objective of defining procedures for producing calcium phosphate samples with improved strength. In previous studies(2) it was found that pressed specimens of the B26 materials sintered to 2270 F for 4 hours were mechnically weak. In the initial studies of this report, the effects of firing temperature and forming pressure on the final density and strength of tricalcium phosphate samples were determined. In this work, disk specimens about 0.75 inch in diameter by 0.50 inch thick were formed by pressing in a steel die. Formed specimens were sintered at a heating rate of 100 F per hour and soaked at the selected maximum temperature for 2 hours. All specimens were evaluated for density and strength. Strength data were obtained using the diametral compression test(14). In this test a disk specimen is loaded in compression perpendicular to its axis between two parallel platens. The maximum tensile stress develops perpendicular to the loaded diameter and can be calculated from the following equation:

$$\alpha = \frac{2P}{\pi Dt}$$

where

α = maximum tensile stress
P = applied load
D = specimen diameter
t = specimen thickness.

In evaluating specimens for diametral tensile strength, 1/16 x 0.4 x 0.5-inch neoprene rubber pads were placed above and below the specimen to overcome problems with variations in strength data associated with sample surface irregularities. Table 2 shows the variation in density and diametral tensile strength with respect to firing temperature of pressed (20,000 psi) and sintered samples. On the basis of a plot of the strength data versus firing temperature, it was determined that the optimum strength was developed when specimens were fired to about 2025 F. Sintering of ceramics accompanied by densification usually produces a simultaneous decrease in porosity and an increase in grain size. Studies have been reported on the effects of porosity and grain size on the strength of sintered ceramics, particularly aluminum oxide(15). The coincident influence of porosity or density and grain size on strength are apparent when correlating the microstructural characteristics shown in the photomicrographs of Figure 3 with the strength data in Table 2.

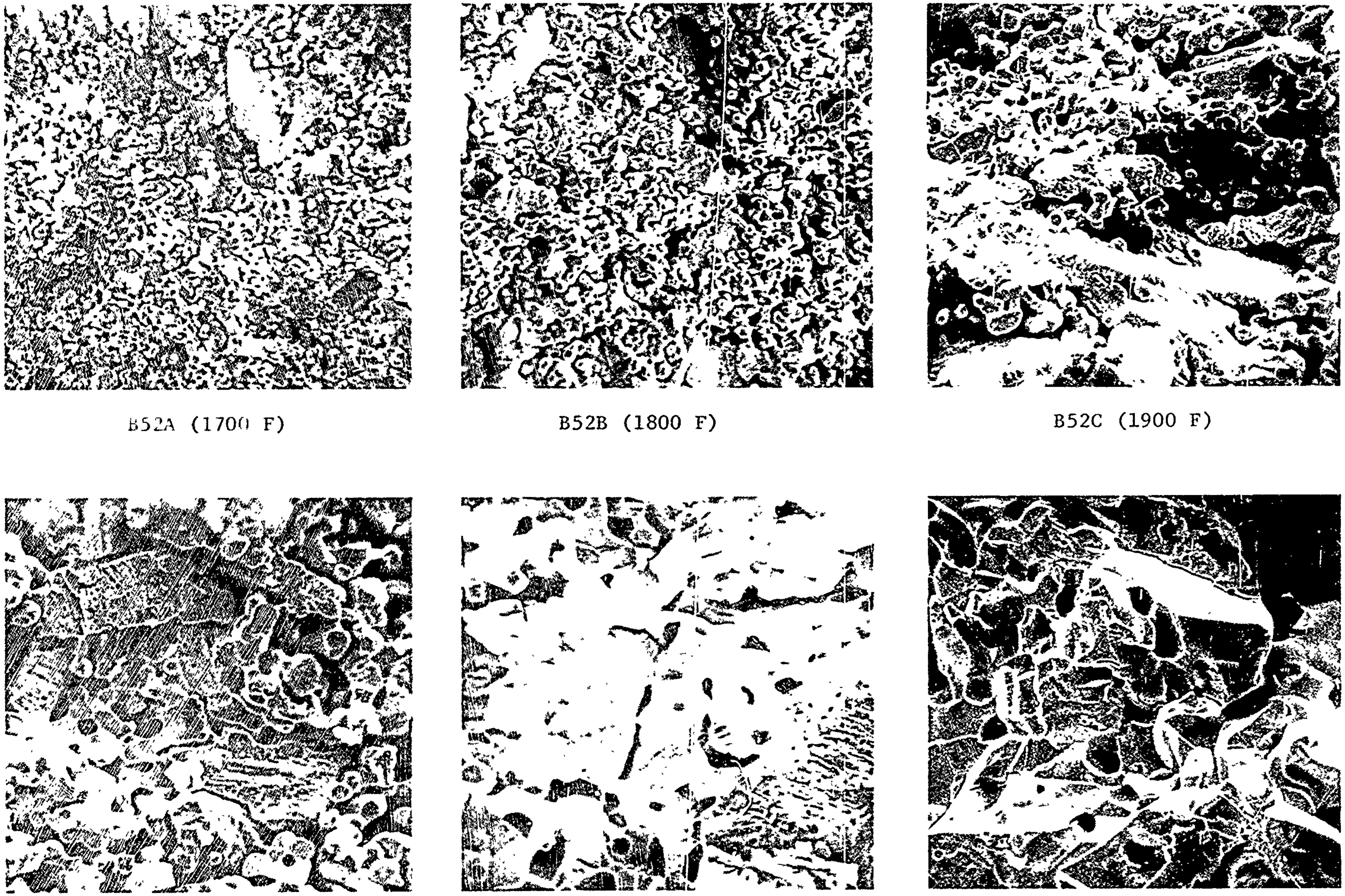
TABLE 2. STRENGTH AND DENSITY DATA ON SPECIMENS PRESSED(a) FROM LABORATORY PREPARED B26 MATERIAL AND SINTERED TO NOTED TEMPERATURES

Group	Maximum Sintering(b) Temperature, F	Bulk Density(c), g/cc	Diametral Tensile Strength, psi
B52A	1700	1.85	870
B52B	1800	2.22	1130
B52C	1900	2.16	1500
B52D	2000	2.24	1970
B52E	2100	2.29	1770
B52F	2200	2.24	600

(a) All specimens were pressed at 20,000 psi.

(b) Each group of specimens were heated at 100 F/hr to the corresponding noted maximum temperature and soaked for 2 hours at temperature.

(c) Calculated on basis of weight and volume measurements; the average pressed density of specimens was 1.64 g/cc.



B52A (1700 F)

B52B (1800 F)

B52C (1900 F)

B52D (2000 F)

B52E (2100 F)

B52F (2200 F)

FIGURE 3. TYPICAL MICROSTRUCTURES OF GROUPS B52A THROUGH B52F SINTERED AT NOTED TEMPERATURES, MAGNIFICATION 2000X

As the density of the specimens is increased through sintering, the specimens become stronger. However, the coincident increase in grain size during sintering decreases strength and has an overwhelming effect on strength at the higher density levels.

The effect of forming pressure on pressed and fired densities of samples and on the strength of sintered specimens is shown in Figures 4 and 5, respectively. Although forming pressure had a significant effect on the pressed densities of specimens, the densities of sintered specimens were not appreciably different, particularly among specimens pressed at 20,000 to 40,000 psi, as evident from Figure 4. All sintered specimens were fired to 2025 F. In reference to Figure 5, specimens pressed at 20,000 psi had the highest average strength value as compared with the values for specimens pressed at lower and higher pressures. This was anticipated since the optimum maximum firing temperature was selected on the basis of the data in Table 2 corresponding to specimens pressed at 20,000 psi.

One of the most important variables which dictates the required firing schedule to develop optimum properties of sintered ceramics is the pressed density of the powder compact.(16) A forming pressure of 20,000 psi was selected as the most suitable on the basis that (1) it was difficult to form specimens at higher pressures without producing laminations and (2) the specimens could be sintered at a lower temperature than would be required to develop optimum strength of specimens formed at pressures lower than 20,000 psi. The deviation of the strength data from the projected curve noted in Figure 5 for specimens pressed at 30,000 and 40,000 psi probably reflects the variations in strength values associated with flaws produced in the specimens when formed at the higher pressures.

Further studies were conducted to correlate material composition and processing procedures with properties of sintered specimens of experimental laboratory processed calcium phosphate materials. Material compositions, calcining temperatures, and property data of sintered specimens are given in Table 3. Scanning electron micrographs in Figures 6 and 7 show microstructural characteristics of fractured surfaces of specimens sintered at 2000 F.

To a limited extent, physical properties of sintered specimens of the compositions, as given in Table 3, can be correlated with physicochemical changes produced during heat treatment. Specimens of Compositions B26, B97A, and B97B all had lower density values after sintering to 2100 and 2200 F than those sintered to 2000 F. Also, specimens of the three compositions sintered to 2100 and 2200 F were appreciably weaker than those sintered to 2000 F. These changes in physical properties most likely are associated with a phase transformation of $Ca_3(PO_4)_2$ as discussed earlier.

A significant finding was the difference in the relative decrease in strength of specimens sintered to 2200 F as contrasted to that for specimens sintered to 2100 F for the three compositions. The decrease in strength of specimens of Compositions B97A and B97B when sintered to 2200 F was negligible as compared with the significant drop in strength of the B26 specimens. These findings suggest that some addition of acid in excess of

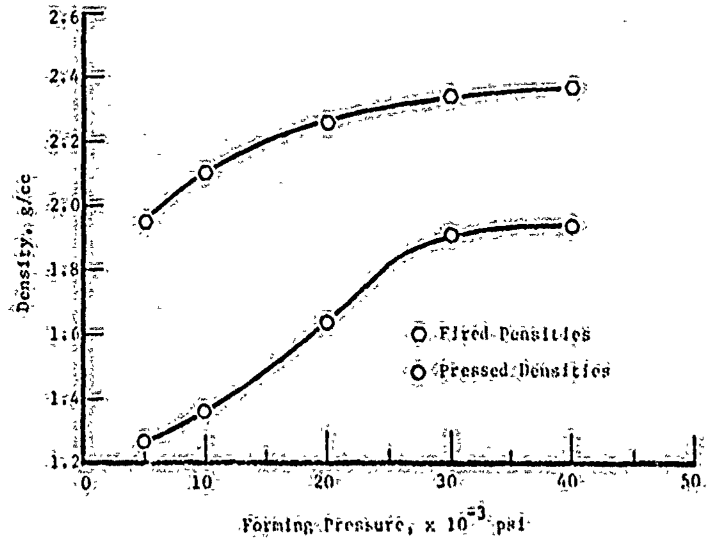


FIGURE 4. VARIATION IN PRESSED AND FIRED DENSITIES OF TRICALCIUM PHOSPHATE SAMPLES AS A FUNCTION OF FORMING PRESSURE

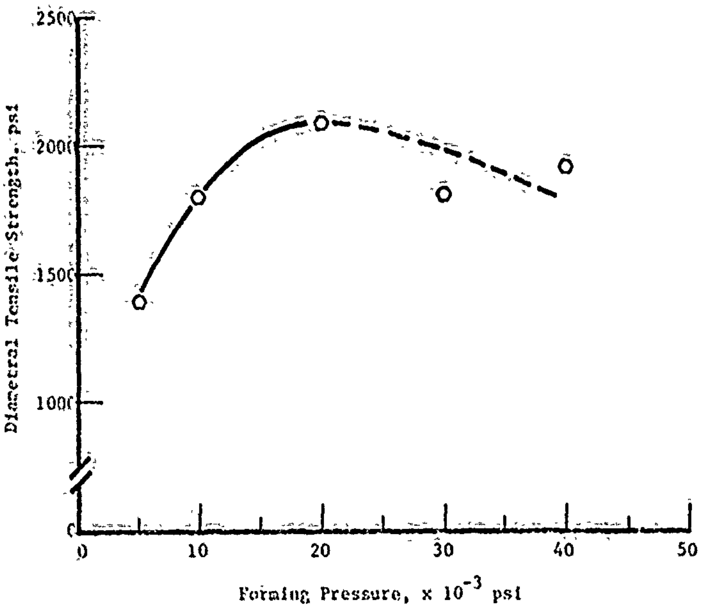


FIGURE 5. VARIATION IN DIAMETRAL TENSILE STRENGTH OF TRICALCIUM PHOSPHATE SAMPLES FIRED AT 2025 F AS A FUNCTION FORMING PRESSURE

TABLE 3. COMPOSITIONS AND PROPERTIES OF EXPERIMENTAL CALCIUM PHOSPHATE SAMPLES

	Batch Designation			
	B26	B97A	B97B	C8
Starting Materials:				
Tribasic Calcium Phosphate, g(a)	200	200	200	200
Phosphoric Acid, 85% H_3PO_4, g(b)	16	8	-	-
Distilled Water, ml	600	600	-	-
Calcining Temperature, F	1400	1400	1400	2200
Pressed Density, g/cc(c)	1.67	1.66	1.55	1.70
Apparent Density, g/cc:				
After Sintering at 1900 F	2.03	2.15	2.16	-
After Sintering at 2000 F	2.29	2.47	2.66	-
After Sintering at 2100 F	2.12	2.31	2.52	-
After Sintering at 2200 F	2.17	2.38	2.50	1.80
Diametral Tensile Strength(d), psi:				
After Sintering at 1900 F	2260	2470	2400	-
After Sintering at 2000 F	3310	3500	3200	760
After Sintering at 2100 F	2600	2750	2050	-
After Sintering at 2200 F	1690	2720	2030	-

(a) Reagent grade, J. T. Baker Chemical Co., Phillipsburg, N. J.

(b) Reagent grade, J. T. Baker Chemical Co.

(c) Based on weight-volume measurements. All specimens were pressed at 20,000 psi.

(d) Specimens were approximately 0.5 inch in diameter by about 0.3 inch thick.

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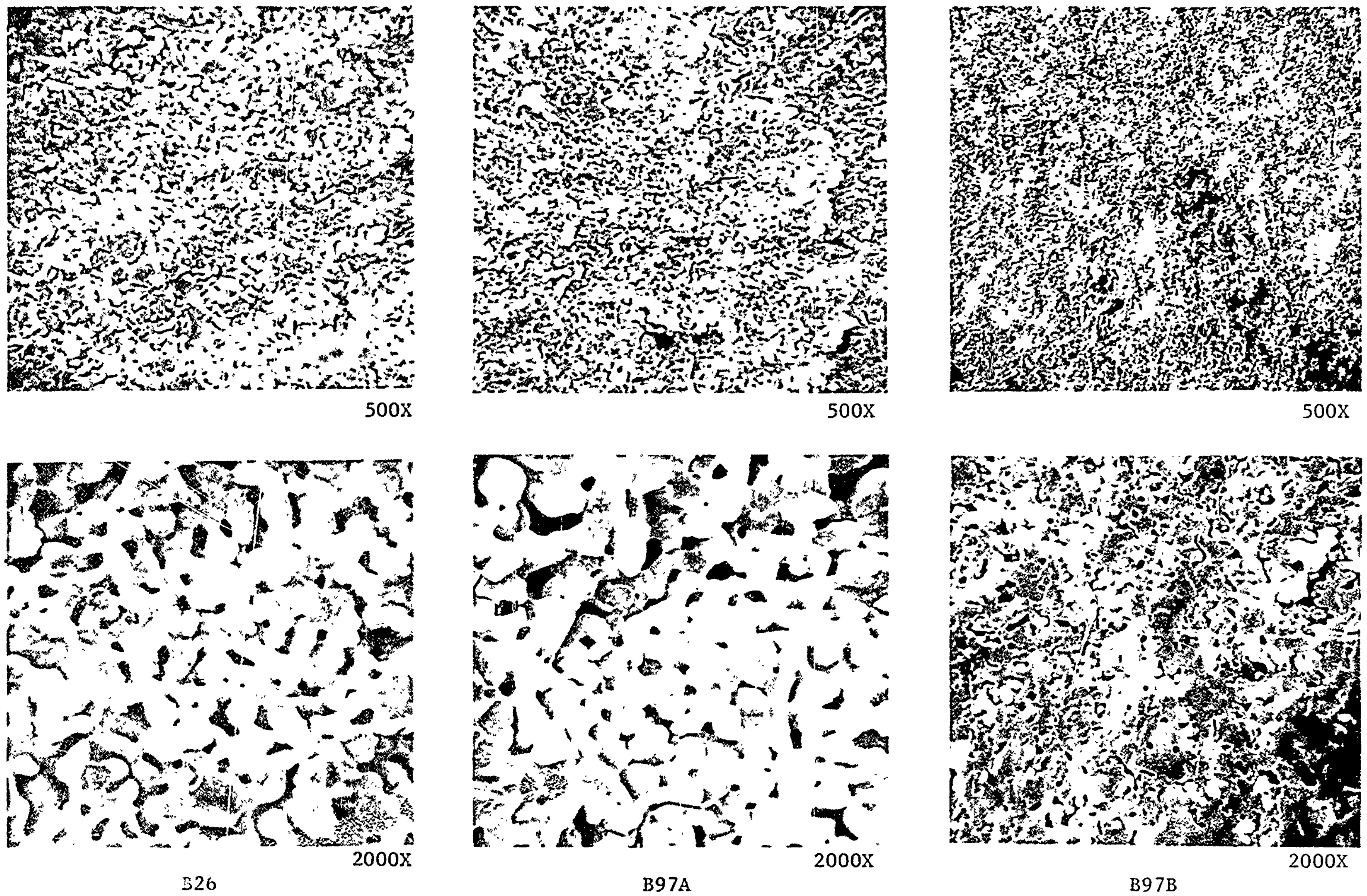

FIGURE 6. SCANNING ELECTRON PHOTOMICROGRAPHS SHOWING MICROSTRUCTURES OF FRACTURED SURFACES OF CALCIUM PHOSPHATE SPECIMENS SINTERED AT 2000 F FOR 2 HOURS

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2000X

FIGURE 7. SCANNING ELECTRON MICROGRAPHS SHOWING MICROSTRUCTURE OF FRACTURED SECTION OF CALCIUM PHOSPHATE SPECIMEN OF COMPOSITION C8 SINTERED AT 2000F

8 but less than 16 grams per 200 grams of starting material may provide specimens with higher strength values.

The significant drop in strength of the B26 specimens sintered to 2200 F may be related to excessive grain growth effected by localized sintering in the presence of a liquid (eutectic) phase. As previously discussed, microstructural analyses revealed that samples of Composition B26 sintered to 2025 F contained large grains dispersed throughout a fine grain matrix. Use of a slight excess of acid may produce phases which, when in contact with other phases, form liquid phase eutectics. The presence of a liquid phase in sintering ceramics commonly leads to a substantial increase in grain size during the sintering process.(17) Reactions between $Ca_2P_2O_7$ and $Ca_2P_2O_6$, if present, can result in some liquid phase formation at temperatures as low as about 1800 F based on published phase diagrams(18).

Scanning electron micrographs of fractured surfaces of sintered specimens prepared from Compositions B26 and B97A materials and the as-received material are shown in Figure 6. The microstructures of the B26 and B97A specimens sintered to 2000 F were not notably different but had a much more uniform grain structure than that of the Group B52D specimens (see Figure 3) of the same composition and fired to 2000 F. There were no isolated large grains produced by grain growth during sintering as detected in the Group B52D specimen. The more uniform microstructures of the second group of specimens of Composition B26 as contrasted to that of the initial Group B52D specimen may account for the significant differences in strength properties of the two groups of specimens. However, the factors accounting for the differences in microstructure of the two groups of specimens are not known.

Sintered specimens of the as-received material had, in general, a finer grain matrix structure than the sintered specimens of the laboratory-prepared B26 and B97A materials. However, appreciable grain growth occurred during sintering to produce large isolated grains.

Samples prepared from ball-milled (-325 mesh) C8 (Table 3) batch materials calcined to 2200 F were very weak after sintering at 2000 F. These results were attributed to producing a less sinterable (large median particle size) material by calcining to 2200 F as contrasted to materials calcined at 1400 F. Only a cursory effort was made to mill the materials to produce a more sinterable powder. The micrographs of Figure 7 reveal that the samples consisted of large grains and clusters of grains. The specimens did not densify appreciably during sintering.

Studies were conducted to investigate whether specimens of the Composition B26 material could be made stronger by sintering for long soak periods at a temperature below the inversion temperature of tricalcium phosphate. Specimens pressed at 20,000 psi were sintered at 2030 F for periods of 2, 4, 6, and 10 hours, and these are identified as Groups C19A through D in Table 4. Density and strength data are compiled in Table 4.

Although the specimens were made more dense with increased soak time at temperature, the data showed a trend of decreasing strength with

TABLE 4. EFFECT OF SOAK TIME AT TEMPERATURE ON THE DENSITY AND STRENGTH OF SINTERED SPECIMENS OF B26 CALCIUM PHOSPHATE MATERIALS

Group	Sintering Temperature, F(a)	Soak Time, hours	Apparent Density, g/cc	Diametral Tensile Strength, psi(b)
C19A	2030	2	2.17	1640
C19B	2030	4	2.28	1630
C19C	2030	6	2.32	1630
C19D	2030	10	2.35	1520
C21	1985	2	2.06	1760

(a) All specimens were heated at a rate of 100 F per hour.

(b) Average of five values. Specimens were approximately 0.5 inch in diameter by about 0.3 inch thick.

soak time. One additional Group C21 (Table 4) specimens were sintered at 1985 F. These specimens were less dense than the Group C19A specimens sintered at 2030 F but slightly stronger than the latter. In general, all groups of specimens were appreciably weaker than that of sintered (2000 F) specimens of the B26 calcium phosphate powder noted in Table 3.

Scanning electron micrographs showing typical fractured surfaces of samples of Groups C19A through C19D are shown in Figures 8 and 9. The specimens contained more isolated large grains produced by grain growth during sintering than did the 2000 F sintered specimens noted in Table 3. This is apparent by comparing the photomicrographs in Figure 8 corresponding to the sample soaked for 2 hours at temperature with that in Figure 6 corresponding to the sample of Composition B26.

In general, the studies make apparent the need to further study the densification behavior of tricalcium phosphate materials. The studies must be such as to identify factors accounting for variability in properties and microstructural characteristics. Ultimately, it is believed possible to be able to establish materials preparation and processing conditions to permit attaining greater densities and strength values than have been attained to date.

Fabrication of Porous Bodies

Large samples consisting of a mixture of, respectively, 68 and 32 parts by weight, of the prepared B26 calcium phosphate powder and sized (minus 40 plus 100 mesh) naphthalene were formed by isostatic pressing. To insure uniform mixture of the naphthalene (pore-forming additive) and powders, the materials, premixed by shaking in an air-filled plastic bag, were twice passed through a 40 mesh U. S. Standard sieve. After mixing, the materials were placed in a 1000 ml filter flask, and a rubber bag* was placed over the large opening of the flask. Air was introduced through the flask side tube so as to partially inflate the rubber bag. The flask then was inverted and the materials shaken into the inflated rubber bag. Following this, the filled rubber bag was removed and the excess air allowed to escape. Cotton was placed in the open end of the rubber bag, followed by insertion of a rubber stopper wired in place to close off the opening. A vacuum of about 30 inches of mercury was drawn on each sample for 1 hour. The vacuum was drawn through a hypodermic needle inserted through the rubber stopper and extended into the cotton, which facilitated drawing the vacuum without clogging the needle. Each sample then was isostatically pressed to 20,000 psi. Typical isostatically pressed samples are shown in Figure 10. Pressed samples were removed from the rubber bags and heated at 140 F for at least 6 hours and then heated at 180 F for at least 16 hours to vaporize the naphthalene. All specimens were then sintered by heating to 2025 F according to standard procedures.

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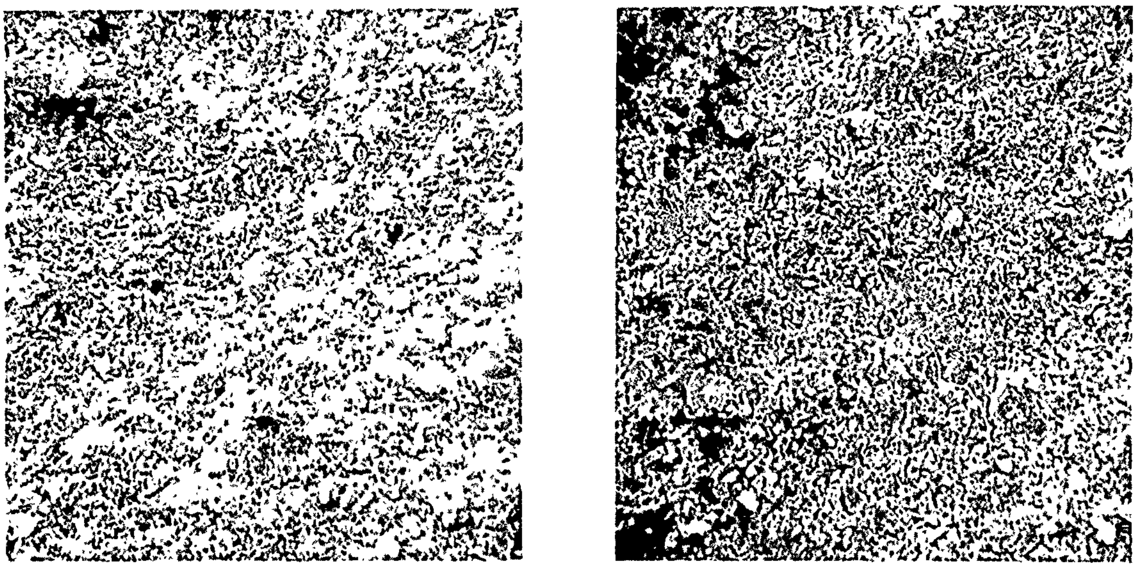
* No. 830 rubber bags. Trexler Rubber Company, Ravenna, Ohio.



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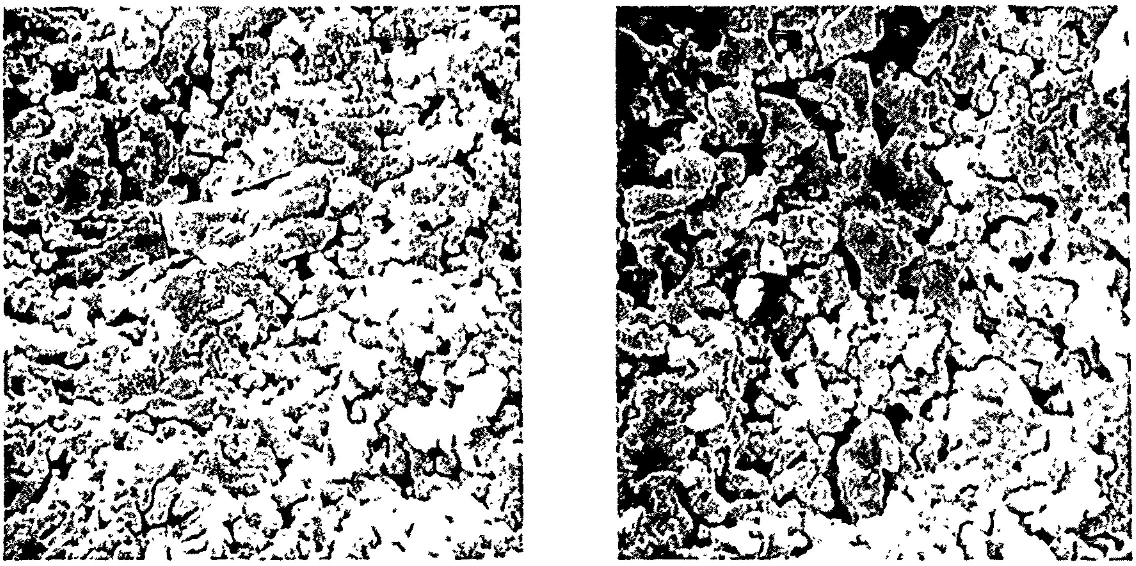
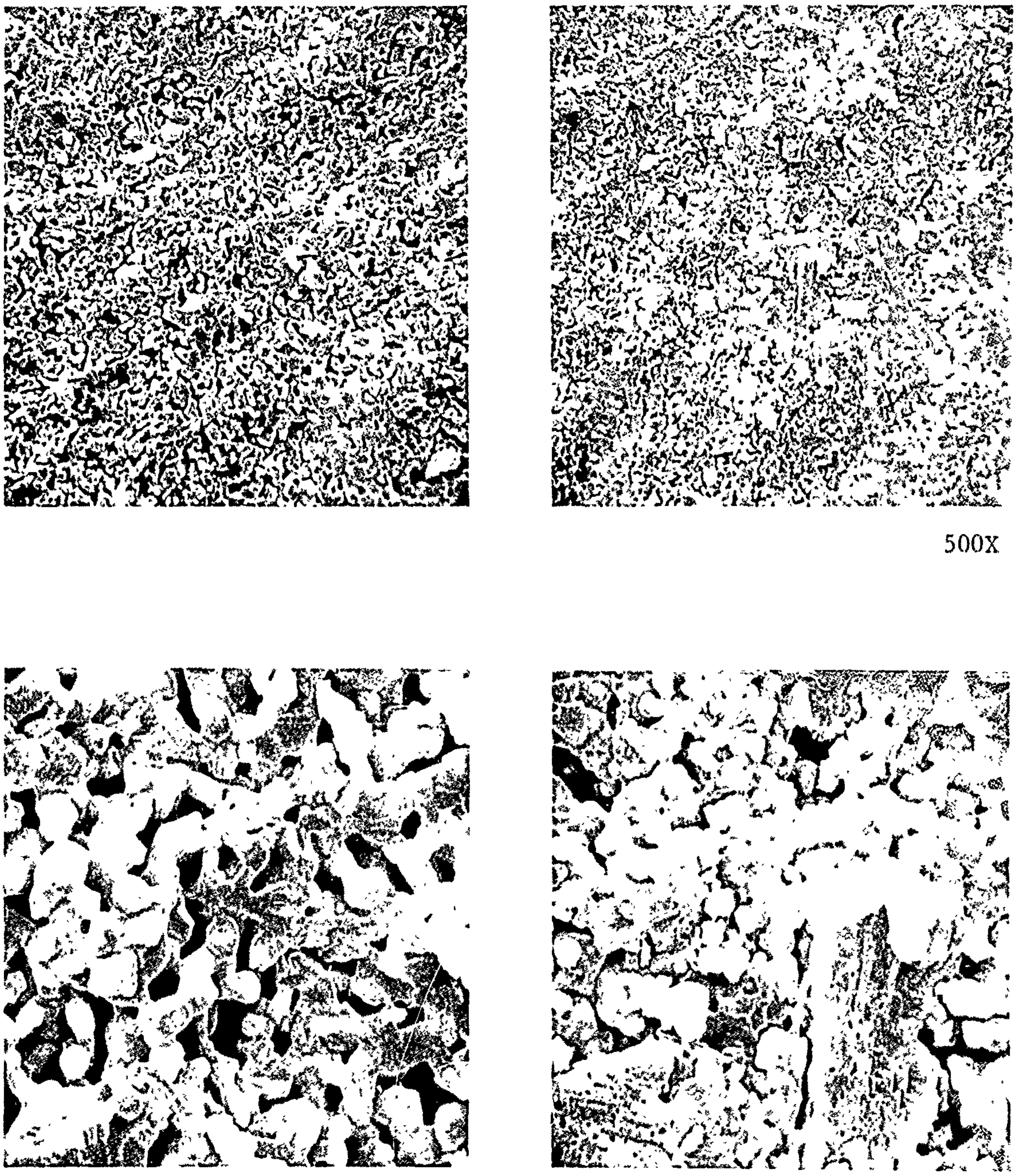


2 Hours
C19A

4 Hours
C19B

2000X

FIGURE 8. SCANNING ELECTRON PHOTOMICROGRAPHS SHOWING MICROSTRUCTURES OF FRACTURED SURFACES OF CALCIUM PHOSPHATE SPECIMENS PREPARED FROM B26 MATERIAL SINTERED AT 2030 F FOR 2 AND 4 HOURS



500X

2000X

6 Hours
C19C

10 Hours
C19D

FIGURE 9. SCANNING ELECTRON PHOTOMICROGRAPHS SHOWING MICROSTRUCTURES OF FRACTURED SURFACES OF CALCIUM PHOSPHATE SPECIMENS SINTERED AT 2030 FOR 6 AND 10 HOURS

Large samples like those shown in Figure 10 were cracked after sintering. Conceivably, several factors could contribute toward producing cracks in these specimens

(1) A differential compaction and spring-back ratio between the naphthalene and tricalcium phosphate.

(2) A differential expansion between the two materials when heated at low temperatures to vaporize the naphthalene.

(3) Incomplete removal of naphthalene before final sintering.

(4) A differential shrinkage between the outer portion of the specimen as compared with the inner portion associated with thermal gradients in the large samples during sintering.

Of the four noted possibilities, the last was the most likely cause of cracking. Cracks were not detected by microscopic examination of specimens after pressing and low-temperature heating. Also, large samples in which the naphthalene was completely vaporized prior to high-temperature exposure developed cracks during sintering. Therefore, to sinter larger samples without developing cracks, a slow heating schedule would be required to minimize the temperature gradient and thus minimize the differential shrinkage rate between the outside and the interior of the samples. However, further sintering studies will be required to establish a heating schedule for sintering large specimens to prevent cracking and produce specimens with optimum strength. To circumvent the problem, smaller 1 to 1-1/2-inch-diameter cylindrical specimens were prepared. The smaller specimens did not crack when sintered.

The procedure of passing mixed materials through a 40-mesh sieve before compaction and drawing a vacuum for a period of 1 hour aided in producing samples with improved uniformity of pore distribution and pore size.

Studies were conducted to characterize the sintered porous tricalcium phosphate samples for physical properties. Data are given in Table 5. The materials had an average compressive strength of 3060 psi. Other data show that the specimens had about 36 volume percent large pores ranging in size from about 0.1 to 0.3 mm, an average grain size of about 2.6 microns, and a matrix of about 72 percent apparent theoretical density. A typical 1/2-inch-square by 3/4-inch-long porous tricalcium phosphate sample, along with photomicrographs of the pore structure and microstructure, are shown in Figure 11. To examine the microstructure, a sample was first impregnated with resin, polished, and etched in 0.25 percent nitric acid solution for 1 second. The prepared sample surface was gold coated by vapor deposition and examined with a scanning electron microscope. The pore and grain structures shown in Figure 11 are not easily distinguishable; however, the pore structure is the continuous phase. Several large dense areas reflecting the extent of localized grain growth can be noted in the photomicrograph. Specimens prepared from the large porous samples for implant studies were designated as Groups B73 and B81 of Composition B42.

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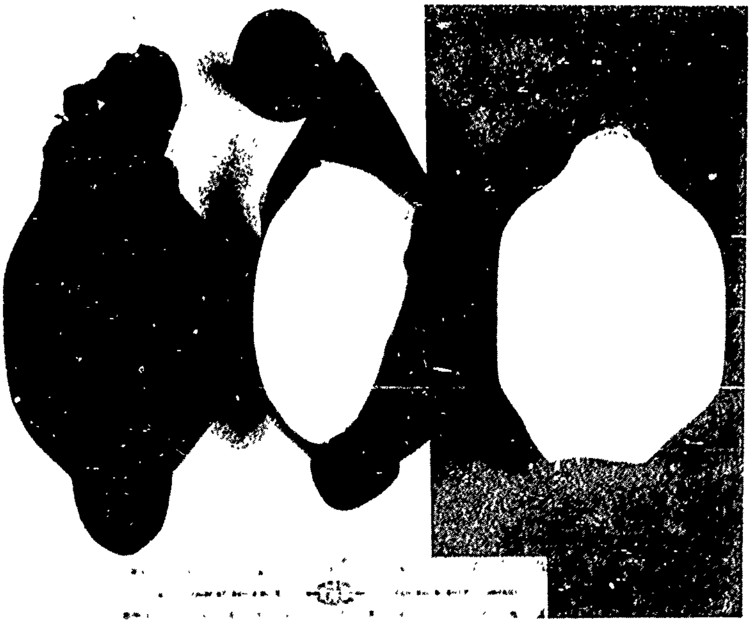


FIGURE 10. PHOTOGRAPH SHOWING ISOSTATICALLY PRESSED SAMPLE IN RUBBER BAG, IN PARTIALLY OPENED BAG, AND REMOVED FROM BAG

TABLE 5. PROPERTIES OF POROUS TRICALCIUM PHOSPHATE SAMPLES

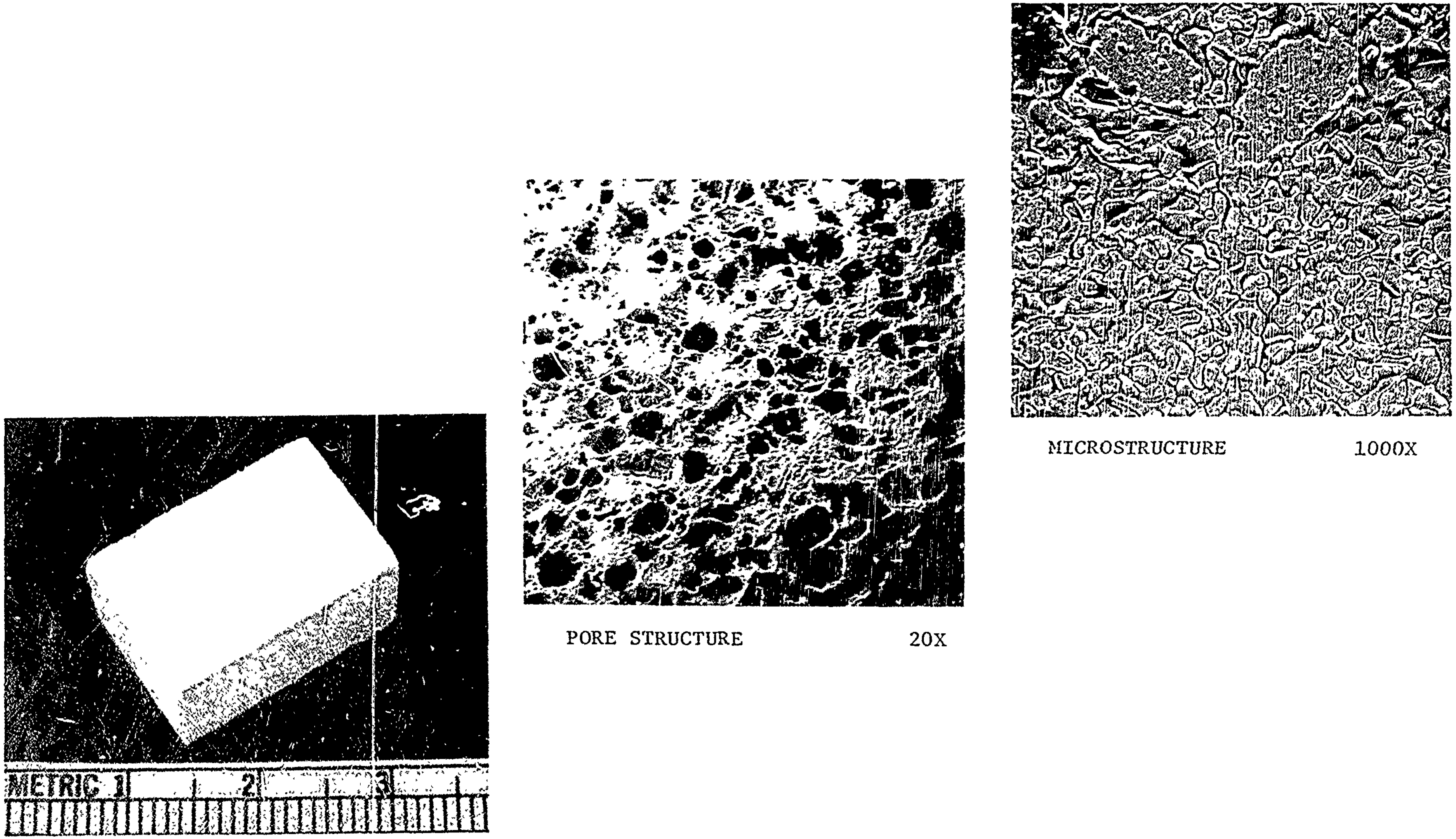
	Low Density Specimens	High Density Specimens
Percent Theoretical Density	49.2	71.7
Strength, psi:		
Compressive	3060	(6200)(d)
Diametral Tensile	(1000)(d)	2080
Pore Size Range, mm	0.1-0.3	N.A.(c)
Average Grain Size, micron	2.58	(2.58)(b)
Matrix Density, percent theoretical	(71.7)(a)	N.A.
Percent Apparent Porosity	50.8	28.3
Volume Percent Large Pores	36.0	N.A.

(a) Measured on the less porous specimens.

(b) Measured on the porous specimens.

(c) NA - not applicable.

(d) Estimated values.



GROSS SAMPLE

PORE STRUCTURE 20X

MICROSTRUCTURE 1000X

FIGURE 11. PHOTOGRAPH OF GROSS POROUS TRICALCIUM PHOSPHATE SAMPLE AND MICROGRAPHS SHOWING PORE STRUCTURE AND MATRIX MICROSTRUCTURE

The initial porous calcium phosphate specimens formed from the standard mixture of B26 material and sized naphthalene were not passed through a sieve and were evacuated for only 10 minutes. These specimens had some large pores associated with aggregates of naphthalene particles and entrapped air. Large areas of dense matrix materials associated with agglomeration of the tricalcium phosphate powder also were present in these specimens. Samples prepared from these materials were designated as Group B60 of Composition B42. Scanning electron micrographs (Figure 12) reveal the physical nature and size of pores and microstructural characteristics of a bulk, porous tricalcium phosphate sample. It can be seen that the distribution of large pores was rather uniform. However, there were present in the samples some large nonporous areas associated with powder agglomerates in the mixed powder materials. Photomicrographs showing the microstructure at 1000 and 5000 magnification reveal the large grain size developed during sintering. The grain boundaries are very distinct and appear to show a separation of grains in mutual contact. This porous tricalcium phosphate material had a compressive strength of 2040 psi and a bulk density of 1.27 g/cc.

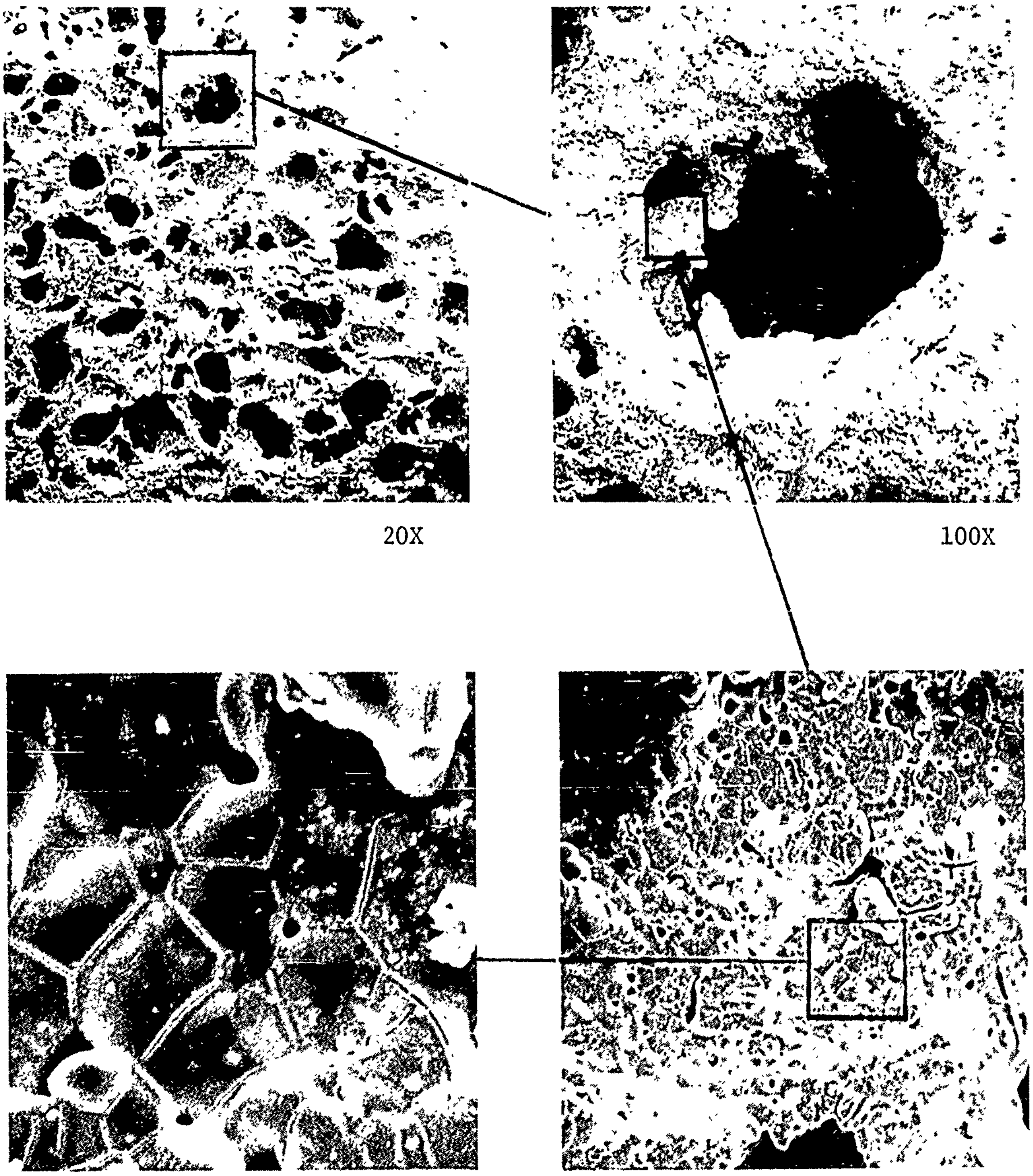
In preparing small specimens, slices about 2 mm thick were cut from the large samples using a diamond saw. Small cylindrical specimens were cut from the slices using a diamond core drill. The Group B47 tricalcium phosphate samples were formed by pressing small samples to size and then sintering the specimens. These techniques were not the most satisfactory because of the problem of these materials segregating when filling the small die. Scanning electron micrographs (Figure 13) showing typical Groups B47 and B60 specimens reveal the differences in the large pore distribution in the two samples. The core-drilled Group B60 specimen shows a uniform distribution of large open pores over the surface. In contrast, the Group B47 specimen had a nonuniform open pore distribution with large smooth surface areas. The poor large pore distribution in the Group B47 specimen reflects the degree of segregation of the pore-forming additive, naphthalene, and the fine powder when filling the small die.

A method of blending the naphthalene and tricalcium phosphate powder by tumble mixing was investigated. The method was found to be unsatisfactory. When tumbled, the powder material tended to form dense aggregates. Formed and sintered specimens prepared from the tumble-mixed materials contained numerous large dense areas of matrix material.

Nonbiodegradable Ceramics

Phosphate-bonded alumina ceramic foam materials were previously developed for experimental use as nonstructural "building block" materials for hard tissue voids in the maxillofacial area. Compositions and property data are compiled in Table 6.

Ceramic foams were prepared by a whipping technique using a common household-type mixer. Large portions of the materials were placed in Teflon-lined pans, heated at 140 F for at least 16 hours, removed from the pans, and then heated at 100 F per hour to 650 F and soaked at temperature for 4 hours, to develop a strong, chemically bonded structure.



20X

100X

5000X

1000X

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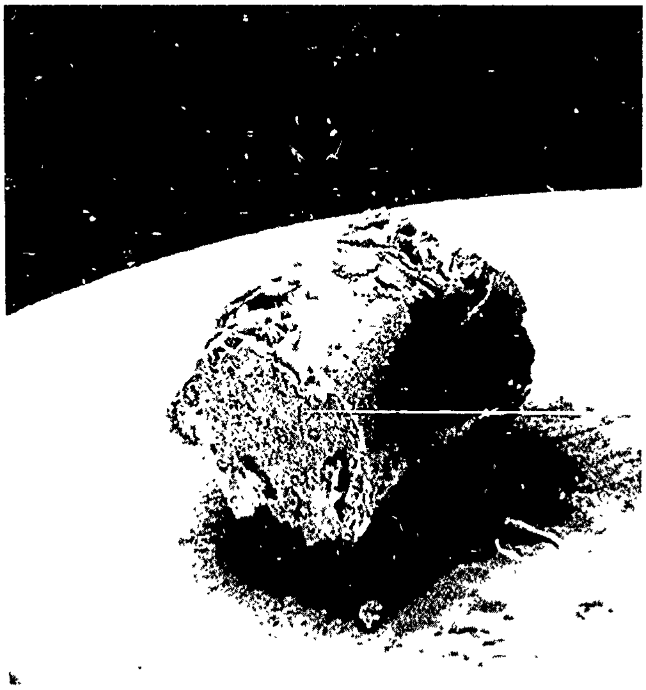
FIGURE 12. SCANNING ELECTRON MICROGRAPHS SHOWING GROSS PORE STRUCTURE AND MICROSTRUCTURE OF POROUS TRICALCIUM PHOSPHATE (Group B60)



Group B47 Specimen

Group B60 Specimen

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FIGURE 13. SCANNING ELECTRON MICROGRAPHS SHOWING TYPICAL GROUPS B47 AND B60 POROUS TRICALCIUM PHOSPHATE SPECIMENS, 20X

TABLE 6. FORMULATION AND PROPERTY DATA ON PHOSPHATE-BONDED ALUMINA FOAMED CERAMIC OF COMPOSITION A-10

Materials, parts by weight	
Alumina, Minus 325 mesh, T-61(a)	400.0
Alumina, Fine Powder, XA-15(a)	100.0
Distilled Water	50.0
Acid, 85 percent H_3PO_4	83.0
Product BCO(b)	0.2
Properties	
Porosity, percent	52
Bend Strength, psi	2310
Modulus of Elasticity, x 10^6 psi	5.3
Compressive Strength, psi	8140
Pore Size Range, mm	0.05-0.4

(a) Alcoa, East St. Louis, Illinois.

(b) Surface Active Agent, du Pont, Wilmington, Delaware.

Small, 2-mm-diameter by 2-mm-long specimens were formed from the phosphate-bonded alumina foam in the same manner as that described for forming small calcium phosphate samples by slicing the material into 2-mm-thick slabs and then core drilling out specimens.

Protein Impregnation of Samples

Protein impregnation was accomplished in the manner described in last year's annual report.(1)

Samples for In Vivo Evaluation

Over 900 samples were sent to the U. S. Army Institute of Dental Research. Identification of samples and the size, number, and description of samples sent are compiled in Table 7. All specimens were sterilized and packaged in "Steril Peel" strip packages. Porous phosphate-bonded alumina specimens were sterilized by autoclaving. Porous tricalcium phosphate specimens were sterilized in a vacuum desiccator using ethylene oxide. Each package was marked according to the standard method of sample identification.* Typical porous tricalcium phosphate specimens are shown in Figure 14.

Small 2-mm-diameter by 2-mm-long specimens were implanted in the tibia of rats. Large 1/2-inch-square by 3/4-inch-long and the 35 by 20 by 15mm specimens were used for large section bone repair studies.

CONCLUSIONS AND FUTURE WORK

More than 900 samples of biodegradable and nonbiodegradable porous ceramics of various shapes and sizes were prepared and supplied to USAIDR for implant evaluation. Protein-treated samples were also prepared for evaluation.

Concurrent with supplying specimens for implant evaluation, research was directed toward further development of porous bioresorbable calcium phosphate materials. In the current work, porous tricalcium phosphate materials having a compressive strength of about 3000 psi, a matrix density of about 72 percent of theoretical and an improved uniformity in distribution of large pores ranging in size from approximately 0.1 to 0.3 mm were developed. The porous material prepared consisted of the single calcium phosphate phase of β-$Ca_3(PO_4)_2$. The properties of tricalcium phosphate materials developed during the period of this report represent a significant improvement over previously developed materials.(2)

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* See Appendix for method of sample identification.

TABLE 7. IDENTIFICATION, NUMBER, SIZE, AND DESCRIPTION OF BIOCERAMIC SAMPLES SENT TO USAIDR FOR IMPLANT STUDIES

Identification	Sample Size	Number of Specimens	Description
III·PS·B42·B47·BD	2 mm diameter by 2 mm long	100	Porous tricalcium phosphate
I·PS·A10·B58·ND	"	60	Porous phosphate-bonded alumina
I·PS·A10·B58·ND-AT	"	60	Albumin treated porous phosphate-bonded alumina
I·PS·A10 B58·ND-CT	"	60	Collagen treated porous phosphate-bonded alumina
III·PS·B42·B60·BD	"	60	Porous tricalcium phosphate
III·PS·B42·B60·BD-AT	"	120	Albumin treated porous tricalcium phosphate
III·PS·B42·B60·BD-CT	"	120	Collagen treated porous tricalcium phosphate
II·PS·B31·B68·BD	"	60	Porous calcium phosphate, $Ca(PO_3)_2$
I·PS·A10·B73·ND	1/2 inch square by 3/4 inch long	50	Porous phosphate-bonded alumina
III·PS·B42·B65·BD	"	79	Porous tricalcium phosphate
III·PS·B42·B81·BD	35 mm long by 20 mm wide by 15 mm thick	75	Porous tricalcium phosphate
III·PS·B42·C22·BD	4 mm diameter by 8 mm long	100	Porous tricalcium phosphate

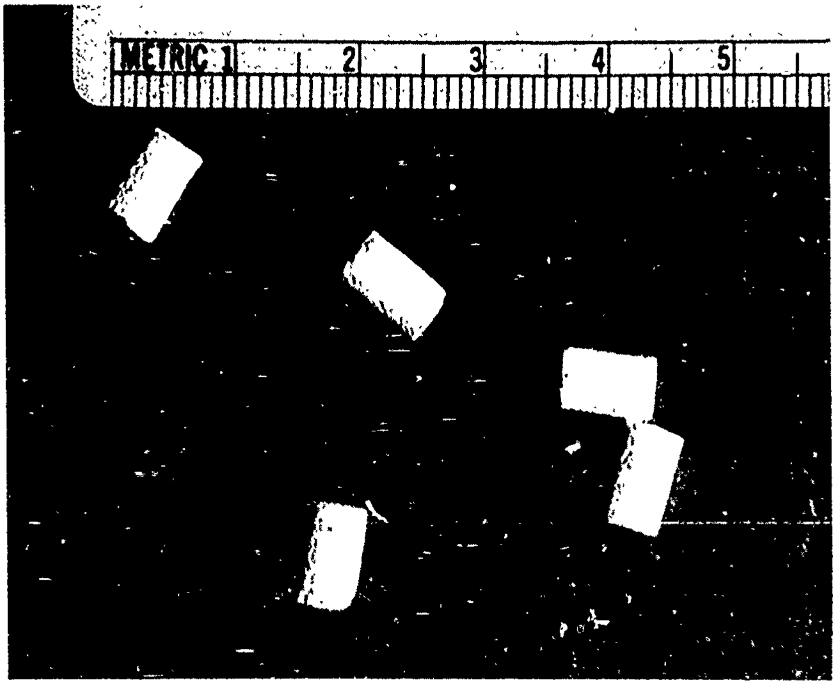

FIGURE 14. PHOTOGRAPH SHOWING TYPICAL 4 MM DIAMETER BY 8 MM LONG POROUS TRICALCIUM PHOSPHATE SPECIMENS

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A calcium phosphate powder was prepared by reacting commercially available reagent-grade phosphoric acid and tribasic calcium phosphate powder in such proportions as to produce tricalcium phosphate, $Ca_3(PO_4)_2$, when sintered. It was not possible to sinter pressed pellets of the laboratory-prepared material to greater than 75 percent of theoretical density under the various sintering schedules studied. Specimens sintered at 2030 F for 2 to 10 hours showed little change in densification with sintering time. In general, the number of large grains produced by grain growth increased with sintering time or temperature in specimens sintered to greater than about 72 percent of theoretical density.

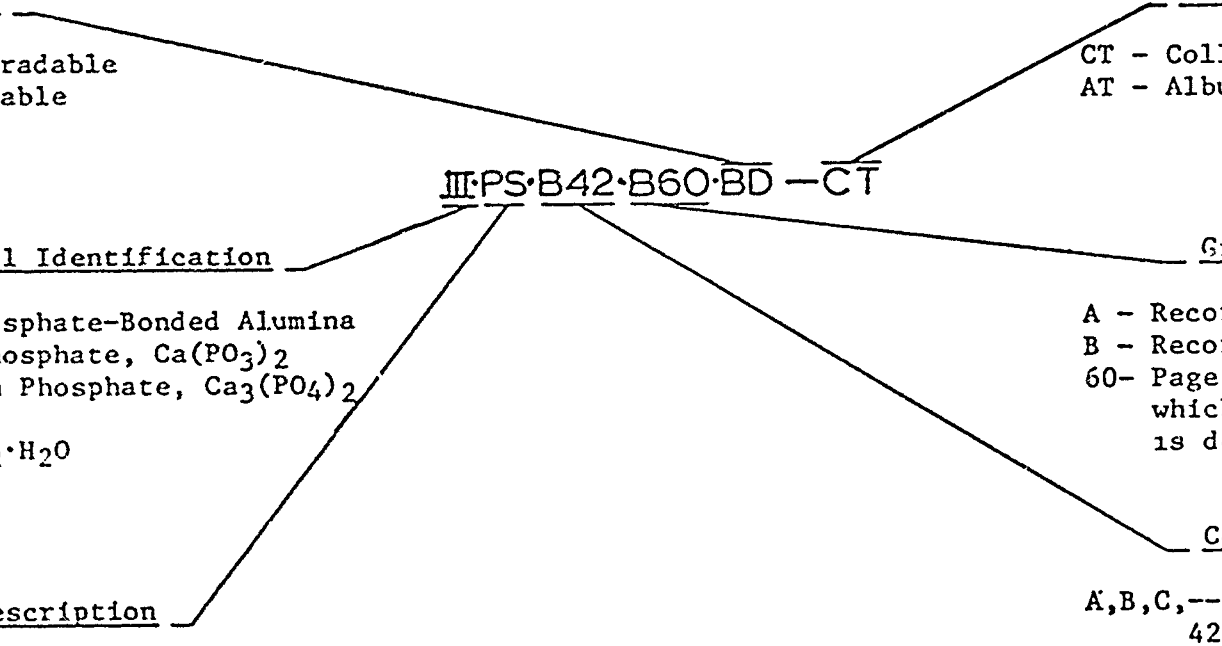
In the continuation of this program, studies will be conducted to correlate material characteristics with compaction behavior, density, strength, and microstructural features of as-formed and sintered specimens. The ultimate objective will be to identify those material compositions and processing procedures which provide optimum specimens in terms of mineral phase uniformity, density, and strength.

Continuing efforts will also be devoted to improving the physical characteristics of bulk, porous tricalcium phosphate samples used for implant studies. Emphasis will be placed on further improving the uniformity and distribution of large pores. New materials for use as pore-forming additives will be investigated. Also, additional studies on methods to produce uniformly dispersed mixtures of pore-forming additives and powder will be undertaken.

APPENDIX

STANDARD SYSTEM OF SAMPLE IDENTIFICATION

A system was adopted so as to provide a code method of identifying samples as to chemical composition, physical characteristics, treatment, and type (biodegradable or nonbiodegradable). The following shows the general scheme of sample identification.



Type

ND – Nonbiodegradable
BD – Biodegradable

Treatment*

CT – Collagen treated
AT – Albumin treated

Material Identification

I-Porous Phosphate-Bonded Alumina
II-Calcium Phosphate, $Ca(PO_3)_2$
III-Tricalcium Phosphate, $Ca_3(PO_4)_2$
IV-$Ca_2P_2O_7$
V-$CaH_4(PO_4)_2 \cdot H_2O$
VI-$CaHPO_4$

Group Identification

A – Record Book No. 26929
B – Record Book No. 28381
60– Page number in record book on which preparation of the samples is described

Material Description

PS – Porous Structure
PP – Prepared Powder
CP – Commercial Powder
HD – High Density Structure

Composition Identification

A,B,C,--,-Identification of record books
42 -Page number in record book on which material preparation and composition is described.

* Deleted if no treatment.

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