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SYNTHESSES OF NEAR-NET SHAPED MONOLITHIC HYDROXYAPATITE AND HYDROXYAPATITE-ASTM F75 COMPOSITES BY THE OXIDATION OF SOLID METAL-BEARING PRECURSORS

DISSER TATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University by

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ABSTRACT

1. SYNTHESIS OF MONOLITHIC HYDROXYAPATITE (HA) FROM SOLID METAL-BEARING PRECURSORS (SMP)

A novel powder-metallurgical route has been used to fabricate near net-shaped calcium hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA), bodies. An intimate mixture of metallic calcium and calcium pyrophosphate, $\beta\text{-Ca}_2\text{P}_2\text{O}_7$, possessing an overall stoichiometry consistent with HA, was prepared by high-energy mechanical alloying. The malleable Ca-$\beta\text{-Ca}_2\text{P}_2\text{O}_7$ powder mixture was compacted, formed into desired shapes (13 mm diameter x 1-2 mm thick disks and 30 mm x 7 mm x 3-4 mm bars) by uniaxial pressing and machining, and then converted into HA through a series of isothermal heat treatments. Exposure to flowing oxygen at $\leq 600^\circ\text{C}$ resulted in complete oxidation of the calcium within 3 h (at $600^\circ\text{C}$). Post-oxidation annealing at $\leq 1150^\circ\text{C}$ in a water-vapor-bearing atmosphere yielded (XRD) phase-pure HA. The reduction in solid volume associated with the oxidation of calcium ($V_m[\text{CaO}] < V_m[\text{Ca}]$) was offset by the increase in solid volume associated with the conversion of CaO and $\beta\text{-Ca}_2\text{P}_2\text{O}_7$ into HA. As a result, the overall dimensional changes upon transformation of $\text{Ca}+\beta\text{-Ca}_2\text{P}_2\text{O}_7$ precursors into HA can be relatively small. In this thesis, the fabrication of near net-shaped monolithic HA-bearing bodies from $\text{Ca}+\beta\text{-Ca}_2\text{P}_2\text{O}_7$ precursors is demonstrated. The phase and microstructural evolution at various stages of transformation are also discussed.

Superheating ($600^\circ\text{C}$) within a disk-shaped specimen (14 mm diameter x 4 mm thick, 82% dense) was detected via DT analyses with thermocouple embedded within the precursor disks. The superheating (also termed thermal runaway) was caused by exothermic nature of calcium oxidation. This event might have assisted in HA transformation within the disk-shaped specimen; while, on the other hand, have caused catastrophic cracking of bar-shaped specimens (30 mm x 7 mm x 3 mm, 74% dense). The difference in the results is attributed to the amount of heat generated, the rate of heat dissipation, as well as the densities of the samples.

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II. SYNTHESIS OF HA/CO-CR-MO ALLOY COMPOSITES FROM SOLID METAL-BEARING PRECURSORS

The SMP approach mentioned in the previous section is applied to the fabrication of HA+ Co-Cr-Mo alloy composites. A mixture of Co-Cr-Mo powder with the precursor prepared from metallic calcium and $\beta$-Ca$_2$P$_2$O$_7$, targeted to yield a 75 to 25 volume ratio of Co-Cr-Mo to stoichiometric HA upon conversion, was prepared by high-energy mechanical alloying. The malleable Co-Cr-Mo/Ca-$\beta$-Ca$_2$P$_2$O$_7$ powder mixture was compacted, formed into desired shapes by uniaxial pressing and machining, and then converted into a Co-Cr-Mo/HA composite through a series of isothermal heat treatments. After sintering at 1150°C in a de-oxygenized, flowing argon atmosphere, a continuous network of the Co-Cr-Mo alloy, with HA/TCP present in the interstices between Co-Cr-Mo grains, was produced. Subsequent annealing at 850°C in a water-vapor-bearing atmosphere yielded a composite of Co-Cr-Mo alloy with phase-pure (by XRD) HA. The overall dimensional changes upon transformation of Ca+$\beta$-Ca$_2$P$_2$O$_7$+Co-Cr-Mo precursors into HA/Co-Cr-Mo composite were relatively small. In this thesis, the phase and microstructural evolution at various stages of transformation to HA/Co-Cr-Mo alloy composites are discussed, the mechanical strength (microhardness and flexural strength) of the annealed specimens were evaluated, the potential reaction between HA and CrO$_3$ were also investigated.

III. KINETIC STUDIES FOR CONVERSION OF HYDROXYAPATITE FROM CALCIUM OXIDE AND TCP

In order to understand the kinetics for hydroxyapatite formation from the reaction of calcium oxide and tricalcium phosphate, both planar reaction couples and powder compacts of CaO-TCP were prepared. Two Pt strips were placed between CaO and TCP in the planar reaction couples to serve as inert markers. These reaction couples were heated at 1150°C for various times in moist $O_2$. The results of powder compact analyses fits Carter's model very well, which indicated that the rate of HA conversion from CaO and TCP is limited by solid state diffusion. The results of the planar reaction couples indicated that the formation of new HA layer was primarily between the TCP/HA...
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Dedicated to my mother, Jo-Thung Su, my husband, 
Tien-Hsien Chang, and my friend, Julan Jau.
Their unconditional love and support bring this thesis into reality.
ACKNOWLEDGMENT

I wish to thank my advisors, professor Ken H. Sandhage, professor Alan S. Litsky and professor Patrick Gallagher for their intellectual support, encouragement, and enthusiasm which made this thesis possible. I would also like to thank professor Suliman Dregia for assisted in interpretation of various experimental results as well as professor Prabhat Gupta for serving as one of my dissertation committees. I am grateful to my colleagues, Pragati Kumar, John Gannon, Terry Detrie, and Dr. Kirk Rogers for their valuable discussions, assistance in problem solving and emotional support. Appreciation is expressed to Cameron Begg, Steve Bright, Henk Colijn, Gary Dodge, Kenneth Kushner, and Lloyd Barnhart for their assistance on the electron microscopes, microhardness tester, particle analyzer, BET, metallographic equipment, X-ray diffractometer, dilatometer, machining of fixtures, and Instron.

Special thanks are expressed to the following person and institutions outside of Materials Science department of the Ohio-State University. Professor L. S. Fan in Chemical Engineering supported first year of my graduate study in OSU. Tim Henthome in the glass shop of Chemistry department assisted in design and fabrication of the quartz tubes and other glassware. Kristin Frost in the Laser laboratory of Chemistry department assisted in the specimen analyses with Raman spectroscopy. Dr. John Olesik and his student, Savelas Rabb, in the Microscopic and Chemical Analysis Research Center of the Geological Science department assisted in ICP analyses. Jerry Czarnecki from the Thermo-interaction Co. assisted in problem solving of the Cahn 171 TGA and designed the heating unit for generate moist O₂. Suvankar Sengupta in the Superconducting Components, Inc. assisted in hot pressing the TCP pellet.

This research was supported by an OSU seed grant as well as by the National Institutes of Health.
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Figure 2.20: BSE Image and EDX analysis for 75/25 Co-Cr-Mo/HA specimen after 4 h annealing at 1150°C in Ar (a) an image showing Co-Cr-Mo particles within the HA matrix; (b) and (c) the EDX analyses on the coarse, irregular-shaped and fine, dispersed white precipitates, respectively; (d) an image of the HA matrix showing different contrast.

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Figure 4.6: X-ray Diffraction Patterns of 75/25 composites after various heat treatment at 500, 850, 1050°C.

Figure 4.7: SEM image and X-ray maps after 500°C oxidation.

Figure 4.8: SEM image of 75/25 composite disks. (a), (b) and (c) after 500°C 16 h in O₂; 850°C 4h in moist O₂ (d) and (e) after additional 1050°C 12 h in Ar.

Figure 4.9: SEM images of 75/25 composite disks. (a), (b) and (c) after 500°C for 16 h in O₂ - 950°C for 12 h in Ar; (d), (e) and (f) after 500°C for 16 h in O₂ + 1050°C for 12h in Ar.

Figure 4.10: SEM images of 75/25 composite disks. (a), (b) and (c) after 950°C 4 h in Ar (d), (e) and (f) after 950°C for 12 h in Ar + 850°C for 2 h in moist O₂.

Figure 4.11: SEM images of 75/25 composite disks. (a), (b), (c) and (d) after 1050°C for 12 h in Ar (e), (f) and (g) after 1050°C for 12 h in Ar + 850°C for 2 h in moist O₂.
CHAPTER 1

SYNTHESIS OF MONOLITHIC HYDROXYAPATITE VIA SOLID METALLIC PRECURSORS

A. INTRODUCTION

i. Biocompatible HA and TCP

Human bone implants have to be tough, corrosion resistant, mechanically strong, and biocompatible in the physiological environment. The specific requirements of biological and material performances vary according to the desired application. For low-load applications, biocompatibility is the major concern.

In recent years, the calcium phosphate system has caught significant attention in the application of implant materials and coatings. Most long-term investigations of calcium phosphate materials in solid or particulate forms (including HA) in animals have shown positive results [1-3], in that there were no observed local or systemic toxicities, nor inflammatory or allergy responses, nor pyrogenic responses. In addition, intervening fibrous tissue between implant and bone normally observed after implantation was absent [1-3].

Hydroxyapatite (HA, $\text{Ca}_{10}\text{(PO}_4\text{)}_6\text{(OH)}_2$) is the most important calcium phosphate compound used in implant applications. HA is the predominant mineral component in vertebral bone and tooth enamel. Synthetic HA has consistently exhibited highly-attractive biologic performance in vivo. Tissue growth and infiltration through the intentionally porous surface of HA and strong biofixation, have been reported on HA-bearing implants after they were placed in service [4-6].

Tricalcium phosphate (TCP) is another calcium phosphate of interest in implant applications. TCP is known for its biodegradability since it can be resorbed and replaced by tissues more readily than HA [7]. At room temperature, in the physiological
environment. α-type TCP is more reactive than β-TCP, which, in turn, is more reactive than HA [8]. Forming β-TCP+HA-bearing (biphasic) calcium phosphate (BCP) bodies has been reported by Daculsi [9, 10]. The resorbability of BCP can be controlled by varying the β-TCP/HA ratio.

The mechanical properties of bone and calcium phosphates are provided Table 1.1: a review of the crystal chemistry of HA and TCP is provided in Appendix A: and the thermodynamic properties of HA and TCP are provided in Table 1.14 for references.

<table>
<thead>
<tr>
<th>Material</th>
<th>Porosity (%)</th>
<th>Density (mg/m³)</th>
<th>Young's Modulus (GPa)</th>
<th>Micro-hardness (GPa)</th>
<th>Compressive strength (MPa)</th>
<th>Flexural strength (MPa)</th>
</tr>
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<tbody>
<tr>
<td>Cortical bone</td>
<td>-----</td>
<td>-----</td>
<td>13.8</td>
<td>-----</td>
<td>138</td>
<td>-----</td>
</tr>
<tr>
<td>Cancellous bone</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>41-62</td>
<td>-----</td>
</tr>
<tr>
<td>HA</td>
<td>0.1-3</td>
<td>3.05-3.15</td>
<td>7-13</td>
<td>4.2-4.5</td>
<td>350-450</td>
<td>-----</td>
</tr>
<tr>
<td>&quot;</td>
<td>10</td>
<td>2.7</td>
<td>4.2</td>
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<td>60-120</td>
<td>15-35</td>
</tr>
<tr>
<td>&quot;</td>
<td>30</td>
<td>---</td>
<td>---</td>
<td>60-120</td>
<td>15-35</td>
<td>---</td>
</tr>
<tr>
<td>&quot;</td>
<td>40</td>
<td>2.8-19.4</td>
<td>2.55-3.07</td>
<td>310-510</td>
<td>50-115</td>
<td>350-490</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.5-26.5</td>
<td>55-110</td>
<td>&lt;800</td>
<td>120-200</td>
<td>60-115</td>
<td>350-490</td>
</tr>
<tr>
<td>Ca₄P₂O₉ &quot;Dense&quot;</td>
<td>3.1</td>
<td>---</td>
<td>120</td>
<td>120</td>
<td>7-12</td>
<td>---</td>
</tr>
<tr>
<td>TCP &quot;Dense&quot;</td>
<td>3.14</td>
<td>---</td>
<td>120</td>
<td>7-12</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

*: These data are based mostly on measurements with functional biomaterials. (i.e., from materials that really have actually been used or developed for biomedical applications).

Table 1.1: Mechanical properties of bone and calcium phosphates [1, 2]

**ii. APPLICATIONS OF HA**

Monolithic calcium phosphate ceramics are usually used in low-load applications: dental implants; skin treatments; gum treatment; jawbone reconstruction; orthopedics; facial surgery; ear, nose, throat repair; and spinal surgery [7, 11-15]. Shaped HA-bearing components (e.g., for artificial middle ear bones, artificial intervertebral disks, repair of bone defects, maxillofacial implants, etc. [7, 11-15]) can be prepared from HA powder.
by conventional ceramic processing. Synthetic, porous HA blocks of 32 x 24 x 8 mm with 55 vol % porosity (50 to 2000 µm dia. pores) are used in applications involving tibia or femur implants [16]. These pores allow for ingrowth of new bone after implantation.

iii. PHASE EQUILIBRIA FOR THE \( \text{CaO-P}_2\text{O}_5 \) AND \( \text{CaO-P}_2\text{O}_5-\text{H}_2\text{O} \) SYSTEMS

Depending on the \( \text{CaO-P}_2\text{O}_5 \) ratio, the water vapor pressure and temperature, HA can be in equilibrium with \( \text{CaO} \), \( \text{Ca}_4\text{P}_2\text{O}_{9} \), or \( \text{Ca}_3\text{P}_2\text{O}_8 \) [17]. The stability of the apatite is limited in relation to its \( \text{CaO-P}_2\text{O}_5 \) ratio, water content, and temperature. Up to 1230°C, three quarters of the water content can be withdrawn from HA without a change of the basic crystal structure. The equilibrium reaction constant governing the dehydration is given by:

\[
K = 1.2 \times 10^8 \exp\left(-\frac{\Delta H}{RT}\right) \text{ (in torr)}
\]

where the standard enthalpy change (\( \Delta H^\circ \)) for the reaction at 1230°C is 60 kcal/mol (or 251 kJ/mol) [8].

The phase diagrams for the \( \text{CaO-P}_2\text{O}_5 \) and \( \text{CaO-P}_2\text{O}_5-\text{H}_2\text{O} \) systems are shown in Figure 1.1a and Figure 1.1b and c, respectively. Figure 1.1b shows the schematic representation of equilibria at a fixed \( P_{\text{H}_2\text{O}} \). \( T_1 \) is the temperature for \( \text{HA} \leftrightarrow 2[\text{Ca}_3(\text{PO}_4)_2] \)

\(- \text{Ca}_4\text{P}_2\text{O}_{9} + X_1 (\text{H}_2\text{O}) \) and \( T_2 \) is for \( \text{HA} + 2\text{CaO} \leftrightarrow 3[\text{Ca}_4\text{P}_2\text{O}_8] + X_2(\text{H}_2\text{O}) \). Figure 1.1c shows HA stability as a function of \( P_{\text{H}_2\text{O}} \) and temperature [18].

iv. CONVENTIONAL SYNTHESSES OF HA

a. Syntheses of HA Powder

HA powder can be prepared by a variety of methods, including preparation from solutions (e.g., by coprecipitation [8, 19, 20], sol-gel processing [21, 22] and hydrothermal syntheses [23, 24]) and preparation via solid-state reaction [25]. Two of these methods, coprecipitation and solid-state reaction, are briefly discussed below.

(1) Preparation by coprecipitation
Preparation of hydroxyapatite by coprecipitation usually involves several steps [8]. A precursor solution is prepared by dissolution as the first step. HA is then precipitated via adding one precursor solution to another at boiling temperature with vigorous stirring. The precipitated powder is fired at 900 to 1100°C in steam to remove the volatile impurities and to allow for carbonate decomposition. Calcium and phosphate-bearing precursors that have been used include Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O, CaHPO\textsubscript{4}, (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} and CaCO\textsubscript{3}, etc [8].

As summarized in Appendix Ai, the apatite structure is very flexible. The Ca/P ratio and the (OH) content can vary within a wide range for pure apatite: 1.3 to 2.0 [5] and 0.5 to 2.0 mole in one mole of HA [8], respectively. In addition, various impurities can be incorporated into the apatite lattice: Pb\textsuperscript{2+}, Cd\textsuperscript{2+}, or Zr\textsuperscript{2+} can replace Ca\textsuperscript{2+}; MnO\textsubscript{4}\textsuperscript{2–} can replace PO\textsubscript{4}\textsuperscript{3–}; and F\textsuperscript{–}, Cl\textsuperscript{–}, or CO\textsubscript{3}\textsuperscript{2–} can replace OH\textsuperscript{–}. Thus, the acid (or base) used to prepare the precursor solution has to be carefully selected to avoid undesired incorporation into the apatite lattice.

The precursors have to be fired at an elevated temperature (e.g., ≥ 500°C for CaCO\textsubscript{3}) prior to dissolution to remove potential volatile impurities. CO\textsubscript{2}-free water also needs to be used, since CO\textsubscript{2} can be easily incorporated in the apatite lattice [8]. To obtain a desired Ca/P ratio and (OH) content in the precipitated HA powder, the Ca/P ratio and pH in the solution need to be tightly regulated. Thus, stoichiometric HA (s-HA hereafter) is often produced in small quantities and only after using tedious laboratory methods [27].

(2) Conventional Solid State Synthesis

Solid-state preparation generally involves the use of CaO, CaCO\textsubscript{3}, or Ca(OH)\textsubscript{2} as a Ca precursor or CaHPO\textsubscript{4} or Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7} as a Ca-and-P-bearing precursor[8]. The precursors are milled followed by heat treatments to allow for solid-state reaction. Using CaCO\textsubscript{3} and Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7} as an example, the precursor mixture needs to be dried at 200°C and then heated under vacuum at 1100°C for 20 h to remove CO\textsubscript{2} [8]. A 15% wt loss is usually encountered at this stage. The precursor is then heated at 900°C for 24 h in 1.5 atm of steam in order to convert the precursor into HA. One problem with the conventional
solid-state reaction method is the relatively long annealing time that is typically required for complete reaction to pure HA (e.g., 24 h at 900°C) [8].

b. Fabrication of HA-Bearing Bodies

HA-bearing components can be fabricated with the aid of fugitive organic binders, such as polyvinyl alcohol. The HA powders are mixed with the binders [12, 13] and formed into the desired shape. The binder is burned off and the body is then sintered to produce a dense composite [28, 29]. The particle size of the starting material can be controlled by crushing, milling, and classifying. Classifying is achieved by sieving, or by air or water separation. Forming can be achieved by uniaxial or isostatic pressing, powder injection molding, or slip casting.

The amount of organic binder in conventional ceramic processing varies from 5 vol% for powder compaction by pressing to 30 vol% in tape casting to 50 vol% in injection molding [30, 31]. The organic binder is usually removed by pyrolysis or vaporization at modest temperatures (100-500°C) [30, 31]. Complete removal of the organic binder is required, if the binder is not biocompatible. The time required to remove the binder increases with the amount of binder in the green body and with the physical dimensions of the green body. This process needs to be conducted very slowly so as to avoid defects such as swelling, cracking, blistering, and warping. These defects, once created, can not easily be healed during subsequent sintering [30, 31]. In addition, the pores remaining in the matrix after the pyrolysis process necessitate the use of a high-temperature sintering process, if dense bodies are needed for an application [30, 31].

c. Hot pressing of HA

It is well-known that, for a similar phase content and average grain size, a dense ceramic body tends to exhibit a higher fracture strength than a porous one. It has been reported that HA bodies of density 54 to 98.8% can be fabricated by hot pressing at 900 to 1250°C [32]. The highest flexural strength obtained in the study of Halouani, et al [32] (98.8% dense bodies of average grain size = 0.4 μm) was 137 MPa and the corresponding fracture toughness was 1.2 MPa.m^{1/2}. 

5
v. SYNTHESIS VIA THE SOLID, METAL-BEARING PRECURSOR METHOD

a. General Process Description

The solid, metal bearing precursor method (SMP) is a novel method developed over the past few years at The Ohio State University for fabricating near net-shaped, bulk ceramic components [33-45]. In general, the SMP process involves three steps (see Figure 1.2):

- Precursor preparation: Synthesis of an intimate mixture of precursor powders.
- Deformation: Compaction/machining of the precursor mix into desired shapes (e.g., a rectangular bar or a circular disk).
- Thermal processing: Oxidation of the AE metals and conversion of the precursors into the desired ceramic body.

The SMP method has several advantages over conventional ceramic processing routes, owing to the inherent characteristics of the AE metals. Firstly, the AE metals (e.g., Ca, Mg, Sr, Ba) are ductile but not volatile. They can serve as non-fugitive binders to allow the precursor mixture of AE metal and oxides to be formed/machined to a desired shape. The forming methods include uniaxial pressing, drawing, rolling, extrusion, and machining. It should be noted that drawing, rolling, and extrusion of the precursors are conducted within a fugitive metallic can. Unlike the fugitive organic binders used in conventional ceramic processing, AE metals are retained (e.g., as CaO for calcium) in the shaped body upon oxidation. Therefore, the porosity generated upon the oxidation of AE metals is significantly less than the porosity obtained after the pyrolysis of a comparable amount of organic binder.

Secondly, AE metals oxidize rapidly at modest temperatures. In addition, the AE oxides can react with other precursor components to form desired ceramic compounds at relatively modest temperatures [35, 41, 42] (e.g., BaAl$_2$O$_4$, BaCeO$_3$ and BaTiO$_3$ can be synthesized at $\leq 900^\circ$C). Thus, the desired compound can be synthesized from a mixture of AE metal and oxides with a relative low energy cost.
Thirdly, most AE metals have larger molar volumes than the corresponding oxides (e.g., $V_m[\text{Ca}] > V_m[\text{CaO}]$). Thus, the solid volume is reduced upon oxidation of the AE metal. This reduction in solid volume can be offset by an expansion due to other reactions within the precursor (e.g., the oxidation of a non-AE metal or the reaction of the AE oxide with other oxides). Hence, an AE-metal-bearing precursor can be converted into a desired compound, while maintaining the precursor shape and dimensions. For example, the net volume changes for the formation of $\text{BaAl}_2\text{Si}_2\text{O}_8$, $\text{MgAl}_2\text{O}_4$, and $\text{Ba}_{4.7}\text{Pb}_{5.3}\text{TiO}_3$ are less than 0.5% via the SMP method as listed in Table 1.2.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>Product</th>
<th>$\Delta V/V_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \text{ Ba} + 1.68 \text{ Al} + 0.16 \text{ Al}_2\text{O}_3 + 2.0 \text{ SiO}_2$</td>
<td>$\text{BaAl}_2\text{Si}_2\text{O}_8$</td>
<td>$&lt;0.1%$</td>
</tr>
<tr>
<td>$1.0 \text{ Mg} + 1.0 \text{ Al}_2\text{O}_3$</td>
<td>$\text{MgAl}_2\text{O}_4$</td>
<td>$&lt;0.5%$</td>
</tr>
<tr>
<td>$0.47 \text{ Ba} + 0.53 \text{ Pb} + \text{ Ti}$</td>
<td>$\text{Ba}<em>{4.7}\text{Pb}</em>{5.3}\text{TiO}_3$</td>
<td>$&lt;0.1%$</td>
</tr>
</tbody>
</table>

Table 1.2: The volume changes of various ceramic compounds synthesized via SMP methods from AE-metal-bearing precursors [33, 34, 37, 44].

Thus, a malleable, AE-metal-bearing precursor can be compacted to a relatively high green density, formed into a desired shape by deformation processing or machining, and then converted into an all-ceramic body with a retention of shape and with relatively small dimensional changes. For some systems, the process can be carried out at relatively low processing temperatures (i.e., $\leq 900^\circ\text{C}$) [35, 41, 42].

To date, a variety of AE-bearing ceramics have been produced by this approach, including dielectric $\text{BaTiO}_3$, magnetic $\text{BaFe}_{12}\text{O}_{19}$, superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$, ionically-conducting $\text{BaCeO}_3$, and refractory $\text{MgAl}_2\text{O}_4$ and $\text{BaAl}_2\text{Si}_2\text{O}_8$ [33–45]. Metal-ceramic and ceramic-ceramic composites have also been produced by the selective oxidation or transformation of certain precursor components [33, 34, 37, 44].

b. Precursors to Monolithic HA

The phase content of the precursor must be properly adjusted to obtain the desired precursor formability (to allow for the fabrication of shaped precursors by deformation
processing), stoichiometry (to allow for the formation of phase-pure HA), and molar volume (to allow for the fabrication of HA components with low net shrinkage).

Consider the conversion of a mixture of four moles of calcium and three moles of $\beta$-Ca$_2$P$_2$O$_7$ into HA, as per the following net reaction.

$$4 \text{Ca} + 3 \beta\text{-Ca}_2\text{P}_2\text{O}_7 + 2 \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$$ (1.2)

The metallic calcium within this precursor can be oxidized at a relatively rapid rate at modest temperatures ($\leq 600^\circ\text{C}$) owing to the formation of a porous, non-protective CaO scale [46-49]. Post-oxidation annealing of such an oxidized precursor can then yield HA by the reaction of CaO with $\beta$-Ca$_2$P$_2$O$_7$ and H$_2$O(g).

The difference between the molar volume of HA and the combined molar volumes of Ca and $\beta$-Ca$_2$P$_2$O$_7$ within a 4Ca: 3$\beta$-Ca$_2$P$_2$O$_7$ precursor is only -8.8% ($4 \times 26.27 + 3 \times 81.39 = 349.25 \text{cm}^3/\text{mol}$). The molar volumes of Ca, $\beta$-Ca$_2$P$_2$O$_7$, and HA are 26.3, 81.4, and 318.5 cm$^3$/mole, respectively [50]). In other words, the conversion of a 4 Ca: 3 $\beta$-Ca$_2$P$_2$O$_7$ precursor into HA by the reaction shown in equation 1.2 should result in an 8.8% reduction in the solid volume. If the volume changes resulting from calcium oxidation and from HA conversion occur in a uniform manner throughout the specimen, then a final dense HA body should retain the shape and dimensions (to within 3.0%) of a dense precursor. Since the conversion of the Ca + $\beta$-Ca$_2$P$_2$O$_7$ precursor into HA results in a reduction in solid volume, the difference between the solid volume of HA and the Ca + $\beta$-Ca$_2$P$_2$O$_7$ precursor should result in increased porosity within the HA converted body relative to the precursor (if there is little change in the external volume of a converted HA body).

c. Advantages of SMP Over Conventional Processes

There are several advantages in the use of the SMP method compared to conventional processing. The key advantages are: the ability to produce (1) a large quantity of HA with desired composition (stoichiometric, Ca-deficient or enriched, carbonated, or fluorinated) and (2) desired shapes (dense or porous body with complex
shape) with (3) relatively simple process steps, while (4) being devoid of toxicity or environmental concerns due to the pyrolysis of the binder.

Since the precursor with desired Ca/P ratio can be mechanically alloyed with a yield higher than 98% (see section C.i. of this chapter), and the subsequent heat treatment is conducted with de-hydrated, de-carbonated O\textsubscript{2}, the synthesis of s-HA can be carried out with relative ease. Calcium serves the role of a non-fugitive inorganic binder in the precursor processing. An intimate mixture of Ca and Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{7} is produced during mechanical alloying by coating the malleable calcium onto the fine Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{7} particles. Utilization of the ductile calcium as a binder imparts considerable toughness to the green body, thus rendering the body machinable. Complete reaction and transformation into HA can be conducted within a few hours.

Since calcium remains in the system, no organic burn-off is required, so that problems associated with organic binder burnout are avoided. One advantage of using non-fugitive binders over organic binders is the low linear shrinkage upon sintering. The linear shrinkage upon sintering can be 10-20\% in conventionally-processed ceramics, since up to 50 vol\% of organic binder is used. In the SMP process, however, only the porosity created upon the oxidation of the AE metals needs to be removed by sintering. This corresponds to linear shrinkage of only a few percent, as observed upon sintering of SMP-derived HA bodies (see section C.v. of this chapter).

d. **SMP comprised of Ca+P or Ca+CaO+\beta-Ca\textsubscript{3}P\textsubscript{2}O\textsubscript{7} Mixtures**

While a precursor comprised of a mixture of calcium and red phosphorus, or of calcium and phosphorus pentaoxide, should be quite ductile, attempts to mechanically alloy such precursors were complicated by appreciable welding of calcium to the milling media and vial (i.e., powder yields of < 50\% were obtained after milling for 4 h). Furthermore, oxidation of these precursors resulted in weight loss, rather than the anticipated weight gain, owing to phosphorous. Particular care must also be taken in handling all-metallic Ca-P precursors to HA. Prolonged milling can lead to the formation of the intermetallic compound Ca\textsubscript{3}P\textsubscript{2}, that, in turn, can react with water vapor
in air to form calcium hydroxide and the toxic gas phosphine, \( \text{PH}_3(\text{g}) \), as shown in the following reaction.

\[
\text{Ca}_3\text{P}_2 + 6\text{H}_2\text{O}(\text{g}) \rightarrow 3\text{Ca(OH)}_2 + 2\text{PH}_3(\text{g}) \quad (1.3)
\]

The welding, phosphorous evaporation, and phosphine generation can be reduced by replacing phosphorus in the precursor with the phosphorus-bearing compound, \( \beta-\text{Ca}_2\text{P}_2\text{O}_7 \). \( \beta-\text{Ca}_2\text{P}_2\text{O}_7 \) powder is a hard oxide that can serve as a milling agent during mechanical alloying to contribute in breaking down the calcium flakes and, at the same time, inhibit the welding of calcium powder to the steel vial and balls. Thus, a precursor with a \( \text{Ca}:\beta-\text{Ca}_2\text{P}_2\text{O}_7 \) molar ratio of 4:3 has the appropriate stoichiometry for HA and could be mechanically alloyed without appreciable welding to the milling media or vial. An intimate mixture of \( \text{Ca}:\beta-\text{Ca}_2\text{P}_2\text{O}_7 \) precursor was achieved within 4 h of milling with powder yields of > 98%, as discussed in section C of this Chapter.

Moreover, \( \beta-\text{Ca}_2\text{P}_2\text{O}_7 \) is a relatively stable compound at temperatures below 1000°C (see Appendix A.ii). Thus, negligible phosphorous evaporation during oxidation of the precursor specimen (≤ 600°C) may be experienced. Ninety-nine percent of the weight gain expected for calcium oxidation can be achieved in the \( \text{Ca}:\beta-\text{Ca}_2\text{P}_2\text{O}_7 \) precursors (i.e., weight loss due to phosphorous evaporation can be minimal). The degree of \( \text{Ca}_3\text{P}_2 \) formation during milling, and of phosphine generation afterward, can be minimized by using \( \beta-\text{Ca}_2\text{P}_2\text{O}_7 \) in the place of \( \text{P} \) or \( \text{P}_2\text{O}_5 \).

Some of the ductile calcium in the \( \text{Ca} + \text{Ca}_2\text{P}_2\text{O}_7 \) precursor could have been replaced with lime, \( \text{CaO} \), in order to further reduce the reaction-induced volume change to a value less than 8.8%, as shown in the following reaction (the molar volume of \( \text{CaO} \) is 16.8 cm\(^3\)/mole [50]):

\[
x \text{Ca} + (4-x) \text{CaO} + 3 \text{Ca}_2\text{P}_2\text{O}_7 + x/2 \text{O}_2 + \text{H}_2\text{O} = \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2
\quad (1.4)
\]

However, such replacement would have come at the expense of precursor malleability. For example, although a precursor with a \( \text{Ca}:\text{CaO}:\beta-\text{Ca}_2\text{P}_2\text{O}_7 \) molar ratio of 0.75:3.25:3.00 would possess a volume very close (within 0.01%) to that of HA, such a
precursor would contain only 6.2 vol % calcium. The variation in the reaction-induced volume change, $\Delta V/V_0$, versus the "binder"-calcium content within the $4(Ca + CaO):3\beta$-$Ca_2P_2O_7$ precursors is shown in Figure 1.3. Because a $4Ca:3\beta$-$Ca_2P_2O_7$ precursor is comprised of 30 vol % ductile calcium, such precursor powders are more malleable and can be compacted into green bodies of relatively high density (see section C of this Chapter). The green disks and bars of the present work were uniaxially pressed to bulk densities in the range of 77-86% of the theoretical density. The pressed bars were also sufficiently robust to allow for machining on a lathe: for example, a 27.1 mm x 6.7 mm x 6.6 mm bar was turned down to a 6.4 mm diameter cylindrical rod using conventional hardened steel tooling (see Figure 1.16). Such machinability allows for the fabrication of HA precursors of relatively complicated shapes, which is the subject of future work.

vi. **Scope and Objectives**

In this thesis, studies were conducted on the synthesis of monolithic HA from a solid metal-bearing precursor consisting of $Ca + \beta$-$Ca_2P_2O_7$, as discussed in this chapter. In Chapter 2, the application of this SMP method to the fabrication of a HA/ASTM Co-Cr-Mo alloy composite, along with some mechanical tests, will be reported. The kinetics of HA conversion from $Ca + \beta$-$Ca_2P_2O_7$ will be discussed in Chapter 3.

The objective of this Chapter is to evaluate the synthesis of monolithic HA from Ca-bearing precursors by a powder metallurgical route that involves: (1) powder fabrication by mechanical alloying to produce an intimate mixture of $Ca + \beta$-$Ca_2P_2O_7$ with a reasonable yield. (2) compaction/machining of the precursor without a fugitive organic binder (to demonstrate the machinability of the formed precursor), and (3) HA formation and shape retention via oxidation and post oxidation annealing.
Figure 1.1: CaO-P2O5 (a) and CaO-P2O5-H2O (b and c) phase diagrams [26]. T₁ is the temperature for HA ⇌ 2[Ca₃(PO₄)₂] + Ca₄P₂O₉ + X₁ (H₂O) and T₂ is for HA + 2CaO ⇌ 3[Ca₄P₂O₉] + X₂ (H₂O).
(a) Powder preparation:
Produce intimate precursor mixture by milling of Ca/CaO/\(\text{Ca}_2\text{P}_2\text{O}_7\) mixture within hardened steel vial with the aid of four steel balls. Milling was conducted in a high energy vibratory ball miller (SPEX model 8000).

\[ P = 1312 \text{ MPa}. \]

(b) Deformation: Compacting/machining of the precursor powder mix into desired shapes (rectangular bar or circular disk).

Figure 1.2: Schematic illustration of the SMP process (to be continued on next page).
(c) Thermal processing: Oxidation of the calcium within the precursors and conversion of the precursors into HA in a moist O₂ /or ambient air atmosphere. The dosing pump and heating unit were utilized to generate moist O₂.

Figure 1.2 (continued): (c) Schematic illustration of the SMP process. Thermal processing was conducted within a silica tube enclosure. The silica tube enclosure was also used to transfer specimens to/from the argon atmosphere glove box and the tube furnace. The set up for introducing moist O₂ to the silica tube is also shown.
Net reaction for stoichiometric HA:

\[ x\text{Ca} + (4-x)\text{CaO} + 3\text{Ca}_2\text{P}_2\text{O}_7 \xrightarrow{\text{O}_2, \text{H}_2\text{O}} \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \]

Figure 1.3: The variation in the reaction-induced volume change, \( \Delta V_{\text{rxn}}/V_o \), versus the "Ca binder" content - Ca volume fraction within the 4 (Ca+CaO) : 3 \( \beta-\text{Ca}_3\text{P}_2\text{O}_7 \) precursors.
B. **EXPERIMENTAL PROCEDURE**

i. **PRECURSOR PROCESSING**

A powder metallurgical process was used to fabricate intimate powder mixtures of metallic calcium and calcium pyrophosphate, $\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$. To allow for reproducible (and safe) processing, all precursor handling operations (e.g., calcium machining, mixing, milling, pressing, bar machining) were conducted within an argon atmosphere glove box. The argon within the glove box was purified by passage through a powder bed of Drierite (W. A. Hammon Drierite Co., Xenia, OH) and Ascarite II™ (Thomas Scientific, Swedesboro, NJ) to remove residual water vapor and carbon dioxide, as well as through a Model MO-5 Dri-Train gas purification system (Vacuum Atmospheres Co., Hawthorne, CA) to remove residual oxygen. The oxygen content of the glove box atmosphere was maintained at $\leq 0.1$ ppm, as indicated by a zirconia oxygen sensor (Model TM-1B, Ametek, Inc., Pittsburgh, PA).

$\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$ powder was produced by heating $\alpha$-$\text{Ca}_2\text{P}_2\text{O}_7$ powder ($\approx 99.9\%$ purity, Aldrich Chemical, Inc., Milwaukee, WI, see Table 1.3) for 4 h at 950°C within a magnesia crucible in a flowing, pure oxygen atmosphere. The resulting powder was characterized with x-ray powder diffraction to confirm that the $\alpha$ to $\beta$ conversion was completed (see Figure 1.4). The $\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$ powders were then placed within a hardened steel vial (37.8 mm dia. x 57 mm) along with 2 hardened steel balls of 7 mm dia. and $\approx 20$ ml of hexane. After sealing the steel vial within the argon atmosphere glove box, the $\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$ powder was milled for 4 h in a high-energy, vibratory ball mill (Model 8000 Mixer-Mill, SPEX Industries, Edison, NJ). After milling, hexane was removed from the milled powders by filtration and evaporation in the glove box. The effect of milling time on the particle size of the $\beta$-$\text{Ca}_2\text{P}_2\text{O}_7$ powder was studied with a sedimentation/centrifugal particle analyzer (Shimadzu SA-CP4, Shimadzu Corp., Kyoto, Japan) and with BET analyses (Autosorb I, Quantachrome Corp, Boynton Beach, FL).
Table 1.3: Impurities in the calcium pyrophosphate (by Aldrich Chemical Co.)

A calcium ingot (Johnson Matthey, Inc., Ward Hill, MA, see Table 1.4 for composition) was machined on a lathe to produce calcium flakes of ≤ 1 mm thickness and ≤ 10 mm length. The metallic calcium flakes and oxide powder were mixed to obtain a Ca:β-Ca$_2$P$_2$O$_7$ molar ratio of 4:3 (i.e., appropriate for stoichiometric HA). It should be noted that since the calcium content in the ingot was only 96.18 at % rather than 100%, the actual molar ratio of Ca:β-Ca$_2$P$_2$O$_7$ within the precursor was 3.85:3 instead of 4:3. In another words, the Ca/P ratio within the precursor was 1.64 instead of 1.67 (for stoichiometric HA). However, since the HA lattice is reported to have a wide range of Ca/P, a 0.03 deviation in this ratio should not affect the final HA structure or HA formation.

Table 1.4: Impurities in the calcium ingot (by Johnson Matthey Co.)

The mechanical alloying for milling the Ca + β-Ca$_2$P$_2$O$_7$ precursor was conducted in the same manner as for milling the β-Ca$_2$P$_2$O$_7$ powders mentioned previously. except that 2 additional hardened steel balls were used (total of 4 balls. 2 balls = 14 mm dia.. 2 balls

<table>
<thead>
<tr>
<th>Element</th>
<th>Sr</th>
<th>Na</th>
<th>Mg</th>
<th>Cr</th>
<th>Li</th>
<th>Fe</th>
<th>Zn</th>
<th>Cu</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. (ppm)</td>
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<td>40</td>
<td>15</td>
<td>10</td>
<td>9</td>
<td>6</td>
<td>6</td>
<td>2</td>
<td>0.4</td>
</tr>
<tr>
<td>At. (ppm)</td>
<td>38</td>
<td>117</td>
<td>41</td>
<td>13</td>
<td>87</td>
<td>7</td>
<td>6</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

Note: 1. Ca$_3$P$_2$O$_7$ = 31.5 wt. % Ca, 24.4 wt. % P, and 44.1 wt. % O
2. Ca, P assay: Ca: 30%, P: 23% (by wt) or Ca: 50.2%, P: 49.8% (by atomic fraction)
= 7 mm dia.). The steel balls were weighed before and after mechanical alloying to detect any change resulted from the milling process.

The milled precursor powder was pressed into circular disks (13 mm dia. x 1-2 mm thick) or bars (30 mm x 7 mm x 5 mm) under an applied uniaxial stress of ≤ 1312 MPa within hardened steel dies. The pressure used in disk fabrication could significantly affect the porosity content in the samples. To better understand the effect of pressure on sample density, disks were formed with two values of applied pressure: 656 or 1312 MPa.

ii. Heat Treatments

The pressed specimens were placed on a magnesia boat and then sealed within a silica tube enclosure (see Figure 1.2c) inside the argon atmosphere glove box. The sealed silica enclosure was removed from the glove box and placed within a horizontal tube furnace for heat treatment.

a. Oxidation of calcium and reaction to form HA

Three isothermal anneals were conducted to allow for calcium oxidation, reaction to form HA, and sintering, respectively. A schematic of the thermal treatments used to oxidize and transform the Ca+β-Ca2P2O7 specimens into HA is shown in Figure 1.5. The rate of heating to the annealing temperature was chosen to be 5°C per min based on a series of macro-DTA experiments (see section C.vi). Prior to heating to the initial oxidation treatment at 350-600°C, the argon within the enclosure was replaced with dry oxygen by passing the oxygen through the silica enclosure for 30 m. Upstream of the silica enclosure, the oxygen was passed through a packed column of Drierite (W. A. Hammon Drierite, Xenia, OH), Ascarite II™ (Thomas Scientific, Swedesboro, NJ), and Molecular Sieves (Type 5A, Advanced Specialty Gas Equipment, South Plainfield, NJ) to remove any residual water vapor and carbon dioxide. To avoid the back-flow of air into the silica enclosure, oxygen was bubbled through a low-vapor pressure oil (Fisher Brand 19, Inland Vacuum Industries, Churchville, NY) after passing through the outlet port.
After the oxidation treatment, the furnace was cooled to room temperature and the silica enclosure was evacuated, back-filled with argon, and then transferred into the argon-atmosphere glove box. One sample was removed from the enclosure for subsequent characterization. The remaining specimens were then returned to the furnace for further heat treatment at 850°C and then 1100 to 1150°C in either ambient air or in a moist oxygen atmosphere. The moist oxygen atmosphere was achieved by passing oxygen and water into a homemade heating unit set at 160°C (see Figure 1.2c). The mixed moist O\textsubscript{2} was then directed to the inlet of the silica enclosure. Water was pumped into the heating unit by an electromagnetic dosing pump (Model P131-157s, LMI, Acton, MA) set at 0.3 cc per stroke and 15 strokes per min. The O\textsubscript{2} flow rate was set at 16 cc/min. the calculated P\textsubscript{H\textsubscript{2}O} was calculated to be 99.7%.

It should be noted that the P\textsubscript{H\textsubscript{2}O} shown in Figure 1.2c was calculated from the flow rates of liquid water and O\textsubscript{2} gas into the heating unit. The water pump was set at 0.3 cc/stroke and 15 strokes/m. which pumped 4.5 cc of water into the heating unit per minute (or 4.5 g/m or 0.2498 moles/m). If O\textsubscript{2} (g) and H\textsubscript{2}O are approximately ideal, then the moles of O\textsubscript{2} passing into the heating unit per minute is given by the following equations:

\[
PV = nRT
\]

\[(1 \text{ atm})(0.016) = n(0.082) (298): n = 6.5 \times 10^{-4} \text{ moles } \text{O}_2/\text{m} \]

Thus, the P\textsubscript{H\textsubscript{2}O} level can be obtained from the molar ratio of H\textsubscript{2}O versus O\textsubscript{2} as:

\[
P_{H_2O} = \frac{nH_2O}{nH_2O + nO_2} = \frac{0.2498}{0.2498 + 6.5 \times 10^{-4}} = 0.997
\]

b. Alternative Heat Treatment

An alternative heat treatment has also been used to synthesize HA-bearing bodies from Ca+β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7}-bearing precursors. With the heat treatment used in Chapter 2 (Figure
the formed precursor bodies can be heated directly to a temperature >900°C in argon to allow for Ca melting and partial sintering (rearranging the packing between the powders). The calcium within the precursor bodies is partially oxidized after this anneal, since the PO\textsubscript{2} in the Ar tank was usually 37 to 50 ppm. A subsequent annealing at 850°C conducted in moist O\textsubscript{2} can then convert the mixture of calcium/CaO and phosphate within the body into HA. This heat treatment takes less time than the one discussed on the previous pages, since the oxidation treatment at 350-600°C is eliminated.

The third route of making dense HA is a reaction-sintering treatment. The precursor body can be simply heated to 1150°C in air and held for 2 h followed by slow furnace cooling (3°C/m). Thus, calcium oxide can react with the β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7} to form HA while the powder compact is sintering. This route may take even less time than the routes mentioned previously. Two disk samples and a partially-machined rod were heated with this latter route to demonstrate the feasibility of the heat treatment and the shape retention of the SMP process. The heating rate used in this case was 5 or 20°C/min.

### iii. SPECIMEN CHARACTERIZATION

#### a. ICP Analyses

The Inductive Coupled Plasma (ICP) analyses were conducted on the precursor mixture to determine the stoichiometry of the precursor, as well as to detect any contamination introduced by the milling process. The ICP samples were prepared by dissolving the as-milled precursor powders of 0.0064 to 0.055g in six times by weight of LiBO\textsubscript{2} and fusion within a Pt crucible heated for 20 min. The sample was transferred from the crucible to a beaker containing ~50 ml of 12.5% HCl. This solution was then diluted to 50 ml in a volumetric flask in order to match the lowest dissolved LiBO\textsubscript{2} concentration (768 ppm in LiBO\textsubscript{2}).

A Perkin Elmer Sciex optima 3000 Inductively Coupled Plasma optical Emission Spectroscopy (ICP-OES) was used for quantitative analyses. Firstly, the calibration curves of Fe, Ba, Ti, Cr, Ca, and P were generated by analyzing the standard solutions of these elements diluted from single element stock solutions (10,000 ppm in concentration. 20
purchased from Radian International, Midland, MI). The samples were then analyzed under the same operating conditions. The Fe, Ba, Ti and Cr standards used were from 20 ppb to 250 ppb, while the Ca and P standards used were from 10 ppm to 50 ppm. The operating conditions were listed below:

1300 W Power, 15 L/min of plasma gas flow, 0.5 L/m of aux. Gas flow, 0.8 L/m of neb. gas flow, approx. 1ml/m of sample uptake rate (Peristaltic Pump), 60 s of read delay, and 5 replicates for each measurement.

b. XRD Analyses

X-ray diffraction (XRD) was used to characterize the phases in the precursor and reacted specimens. In order to minimize the reaction of the precursor powder with air, the precursor powder was pressed into a disk shape within the argon-atmosphere glove box and coated with a thin layer of x-ray transparent grease (high vacuum silicon grease. Dow Corning, Midland, MI) prior to the XRD analyses. The XRD analyses were conducted at room temperature using Cu-Kα radiation at a scan rate of 1°/min. Reacted specimens in both powder and pressed disk forms were analyzed by the XRD and the same results were obtained, indicating that the phase content was uniform throughout the pellet specimens, so that analyses conducted on the pellet surfaces were adequate.

c. TG Analyses

Thermogravimetric analyses (TGA) (Model TG-171. Cahn Instruments. Inc., Cerritos, CA) were conducted to evaluate the oxidation kinetics of disk-shaped specimens at 350-600°C in flowing, dry oxygen. The disk samples tested in TGA were 13 mm in diameter x 3 mm in thickness. The samples were heated at 5°C/m to the desired peak temperature and held for 20 to 100 h at this temperature until the sample was completely oxidized. The weight changes of the sample were recorded every 20s. After each run, the experiment was repeated using an inert Al₂O₃ sample of similar geometry with the same profile and atmosphere to compensate for the weight changes caused by buoyancy changes with temperature. The reference thermocouple was calibrated periodically using pure metal standards as described in Appendix B.
d. **Macro-DT Analysis**

Differential thermal analyses (DTA) were used to evaluate the heat evolution within a given specimen during oxidation. Disk-shaped specimens of 13 mm diameter x 5 mm thickness containing an embedded thermocouple were fabricated by uniaxial pressing of precursor powder around a thermocouple bead using the slotted die assembly shown in Figure 1.6a. Temperature measurements, obtained from the embedded thermocouple and a reference thermocouple located a few mm away from the specimen (see Figure 1.6b), were recorded as a function of time during heating to 600°C at a rate of 5-20°C/min in dry, flowing oxygen.

e. **Dilatometry**

In order to investigate the dimensional changes of the samples during heat treatment, an Orton dilatometer (Orton 1600D) was employed. The test was conducted with a bar sample of 25 mm x 6 mm x 4 mm in dimensions. The samples were first oxidized within the dilatometer at 600°C for 18 h in a dry, flowing O₂ atmosphere. Upon completion of the oxidation cycle, the furnace was further heated to 850°C with the end of the tube open to ambient air. The final densification treatment was conducted in ambient air at 1150°C for 2 h then cooled to room temperature with a rate of 3°C/min. A heating rate of 5°C per min was used in all three thermocycles.

f. **Microstructural analyses**

Microstructural and microchemical information was obtained by optical microscopy, scanning electron microscopy (SEM), and electron probe microanalyses (EPMA). For optical and SEM analyses, specimens were mounted in epoxy, cross-sectioned with a diamond wafering blade, and then polished with diamond pastes to a 1 micron finish. In order to evaluate the microstructure of the Ca+β-Ca₂P₂O₇ precursor after mechanical alloying and pressing, the precursor disks were also mounted and polished with a similar procedure. However, Kerosene was used as the lubricant for polishing the precursor disk to avoid contact of oxygen or moisture with the samples.
Some of the converted HA specimens were demounted from epoxy and thermally etched for 4 h at 950°C in air after polishing to reveal the grain structure. To obtain a conductive surface for SEM analyses, polished specimens were coated with carbon. SEM analyses were conducted with a field-emission-gun microscope (Model XL-30, Philips Electronics N.V., Eindhoven, The Netherlands) equipped with a Si/Li detector (Edax International, Mahwah, NJ) for qualitative energy-dispersive X-ray spectroscopy (EDS).

The average pore size and distributions were obtained by image analyses of the SEM photographs using a PowerPC Macintosh computer with NIH image 1.59 software downloaded from the worldwide web (NIH image is freeware developed by Wayne Rasband at NIH. http://rsb.info.nih.gov/nih-image/). A Wacom digitizer II (model UD-0608-R, Wacom Co., Ltd. Japan) was used to trace the grain boundaries and pores to enhance the image contrast.

Quantitative chemical analyses via wavelength dispersive spectroscopy (WDS) were conducted with an electron microprobe (Model SX 50, Cameca Instruments, Inc., Trumbull, CT) operating at a beam voltage of 10 kV, a beam current of 20 nA, and a focused spot size of a few microns. A Smapt standard (99.9% purity apatite, see Table 1.5) was used to calibrate the Ca and P peak intensities. At least five WDS measurements were made on a given phase to obtain an average composition.

<table>
<thead>
<tr>
<th>Standard</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Ca</th>
<th>Na</th>
<th>P</th>
<th>La</th>
<th>Ce</th>
<th>Nd</th>
<th>S</th>
<th>F</th>
<th>Cl</th>
<th>O</th>
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</thead>
<tbody>
<tr>
<td>Smapt</td>
<td>.16</td>
<td>.04</td>
<td>.04</td>
<td>38.04</td>
<td>.17</td>
<td>17.53</td>
<td>.34</td>
<td>.63</td>
<td>.22</td>
<td>.15</td>
<td>3.48</td>
<td>.4</td>
<td>38.64</td>
</tr>
<tr>
<td>Anorthite</td>
<td>20.56</td>
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<td>.48</td>
<td>13.6</td>
<td>.39</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: All the data shown in this table are in wt. %

Table 1.5: The concentration of standards used in WDS analyses. Smapt is the standard used for analyzing Ca and P, while Anorthite is that used for analyzing Si. Both standards were obtained from the Smithsonian, Washington, DC.
g. **Density and Porosity**

Specimen densities were determined after various processing steps from measurements of dry weight and dimensions, as well as from Archimede's method (i.e., using Ethylene Glycol, 99% with density of 1.1088 g/cc as the buoyant fluid and a paraffin wax coating on the specimens). The porosity level inside the specimen was then estimated from comparison of theoretical density and the calculated bulk density or Archimede’s density.

h. **Raman Spectrometry**

In order to detect the difference between the de-hydrated apatite and hydroxyapatite, two Raman spectrometers were used: Dilor XY (Instruments SA, Edison, NJ) operated with both green laser (514.5 nm) and red laser (785 nm); and CHROMEX 250is (CHROMEX, Albuquerque, NM) operated with red laser (785 nm) in the Laser lab directed by Prof. R. McCreery.
Figure 1.4: The XRD pattern of converted $\beta$-Ca$_2$P$_2$O$_7$.

Figure 1.5: Schematic illustration of the heat treatments used to oxidize and transform the Ca-$\beta$-Ca$_2$P$_2$O$_7$ precursors into HA.
Figure 1.6: (a) Slotted die assembly used to produce disk-shaped precursors containing an embedded thermocouple for differential thermal analyses, as shown in (b).
C. RESULTS

i. PRECURSOR CHARACTERIZATION

The transformation of $\alpha$-Ca$_2$P$_2$O$_7$ to $\beta$-Ca$_2$P$_2$O$_7$ was completed after 4 h at 950°C, as shown in Figure 1.4. The yield for this transformation was 99.3 ± 0.2%, which confirms that the purchased $\alpha$-Ca$_2$P$_2$O$_7$ powder was largely free of volatile impurities, and that $\alpha$- and $\beta$-Ca$_2$P$_2$O$_7$ do not undergo any volatile decomposition at 950°C.

The average particle size of the $\beta$-Ca$_2$P$_2$O$_7$ powder after the 4 h milling treatment was 4.0 $\mu$m and 1.05 $\mu$m via sedimentation and BET analyses, respectively (see Figure 1.7). The average particle size decreased with an increase in milling time. The $\beta$-Ca$_2$P$_2$O$_7$ powders after 4 h of SPEX-milling were also investigated with SEM operated under BSE mode (see Figure 1.8 a through c). The $\beta$-Ca$_2$P$_2$O$_7$ powders milled with a mortar and pestle for 10 m were also investigated for comparison (Figure 1.8 d through f). Agglomerates of $\beta$-Ca$_2$P$_2$O$_7$ particles with 1 to 10 $\mu$m diameters were observed in the SPEX-milled sample. The powder milled with a mortar and pestle appeared to be more flake-like in shape and the agglomerates were larger than for the SPEX-milled powder.

Weight measurements on the Ca+$\beta$-Ca$_2$P$_2$O$_7$ precursors and the steel balls before and after milling indicated that the powder yield was 98.8 ± 0.7% and no detectable weight change occurred for the steel balls. The Ca/P ratio obtained by ICP analyses of three precursor samples was 1.67, which was consistent with the targeted precursor powder ratio for stoichiometric HA. The impurity content of the precursor samples obtained from the ICP analyses after SPEX milling is shown in Table 1.6. It should be noted that the Ba content shown in these samples could be due to contaminant since no Ba were reported in the Ca ingot from Alfa Aesar.

The average particle size of the Ca+$\beta$-Ca$_2$P$_2$O$_7$ precursor mix was analyzed via both BET and sedimentation techniques (see Figure 1.9). The BET results indicated that the average particle size after 4 h of milling was 1.01 $\mu$m, while the sedimentation technique indicated a median agglomerate size of 6.3 $\mu$m. The effect of pressure on the porosity
level of the precursor disks is presented in Figure 1.10. As the pressure increased from 696 MPa to 1400 MPa, both the porosity level and the scatter in the porosity value among samples decreased.

<table>
<thead>
<tr>
<th></th>
<th>Ca (wt %)</th>
<th>P (wt %)</th>
<th>Ba (ppm)</th>
<th>Cr (ppm)</th>
<th>Fe (ppm)</th>
<th>Ti (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32.8</td>
<td>25.3</td>
<td>222</td>
<td>47</td>
<td>208</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>39.3</td>
<td>18.0</td>
<td>568</td>
<td>43</td>
<td>367</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>40.3</td>
<td>18.7</td>
<td>542</td>
<td>56</td>
<td>451</td>
<td>2</td>
</tr>
<tr>
<td>Average</td>
<td>37.47</td>
<td>20.67</td>
<td>444.00</td>
<td>48.67</td>
<td>342.00</td>
<td>8.67</td>
</tr>
<tr>
<td>±</td>
<td>4.07</td>
<td>4.03</td>
<td>192.70</td>
<td>6.66</td>
<td>123.41</td>
<td>5.86</td>
</tr>
</tbody>
</table>

Table 1.6: The averages and standard deviations of measured impurity concentrations by ICP analyses of three precursor samples.

The bulk densities of the as-pressed precursor disks and bars (pressed at 1312 and 660 MPa, respectively) were 2.25 ± 0.03 and 1.97 ± 0.07 g/cc, respectively (average of ten samples each). The precursor porosity contents associated with these bulk densities (theoretical precursor density = 2.64 g/cc) were 14.73 ± 1.06 % and 25.38 ± 2.73 %, respectively. An intimate mixture of calcium and β-Ca₃P₂O₇ was produced by mechanical alloying, as indicated by SEM/X-ray maps, that reveal a relatively uniform distribution of calcium and phosphorous (see Figure 1.11). Some regions of ≤ 5 μm in size on the X-ray maps show Ca enrichment and P depletion, which indicated the existence of Ca particles. The porosity content in the as-pressed precursor disk, as analyzed with the NIH Image software on two SEM images as shown in Figure 1.11, was 5.55 ± 1.13 %. This result is much lower than that obtained from the bulk measurement. The discrepancy is likely due to the smearing of ductile calcium that "fills" the pores during polishing process.
Figure 1.7: Particle size distribution of $\beta$-Ca$_2$P$_2$O$_7$ after milling (a) by BET (b) by sedimentation technique.
Figure 1.8: BSE images of $\beta$-Ca$_2$P$_2$O$_7$ powders after 4 h of SPEX-milling: (a) through (c), or after mortar and pestle milling for 10 m: (d) through (f).
Figure 1.9: Particle size distribution of the Ca+β-Ca$_2$P$_2$O$_7$ precursor after 4 h milling (a) by BET analysis (b) by sedimentation technique.
Figure 1.10: A plot showing the porosity level as a function of the uniaxial pressure applied to the precursor disks.
Figure 1.11: (a) BSE image of a polished cross-section of a precursor specimen (b), (c), and (d) X-Ray maps of Ca, P, and O elements, respectively. Some Ca enriched areas of $\approx 5 \mu m$ in size indicated the existence of Ca particles.
ii. **Oxidation Kinetics of Calcium by TGA**

The first step in the conversion of the Ca+β-Ca₃P₂O₇ precursors into HA was the oxidation of calcium, which was conducted at 500-600°C in the present study. Since the purity of the calcium ingot was 96.18 at %, complete oxidation of the Ca+β-Ca₃P₂O₇ precursors should have resulted in a weight increase of 6.69 %.

As shown in the results of TG analyses (Figure 1.12a), 1.67, 1.92, 2.25, and 2.58 h were required to heat to the oxidation temperatures of 350, 400, 500, and 600°C for the ≈ 2 mm thick disk-shaped specimens, respectively (marked with an " * " on Figure 1.12a). These times include the 30 min dwelling in dry O₂ atmosphere and the heating time (with the heating rate of 5°C/min until 20°C below the designated temperature, and 3°C/min for the remaining heating). The net time required for a complete oxidation (6.69% weight gain) of the ≈ 2 mm thick disks were calculated from the difference between the total time it took to reach a 6.69 % weight gain and the time it took to reach the oxidation temperature (marked as " O " and " * " in Figure 1.12a, respectively). The results were 3.13, and ≥ 140 h for complete oxidation at 600, 500 and 400°C, respectively.

A plot of isothermal weight changes versus time on a log-log scale is shown in Figure 1.12b. Trend lines were fit to these plots and k values calculated from the slopes of these lines were: 0.43, 0.25, 0.17, and 0.04 for 350, 400, 500, and 600°C, respectively. The 350°C oxidation followed a nearly parabolic rate law (slope ≈ 0.5), while the oxidation data at the other temperatures could not be easily interpreted. It should be noted that a significant amount of oxidation had taken place in these samples during heating to the desired temperatures (see Figure 1.12a). Thus, it is difficult to analyze the kinetic rate constants from these data.

The TGA data for an oxidized disk further heated at 850 and 1150°C in ambient air are shown in Figure 1.13. After the disks were oxidized at 600°C, further heating was conducted to 850°C at a rate of 5°C/min and then held at 850°C for 4 h. A 0.5% weight loss was observed during heating between 700 to 850°C, instead of a weight increase as anticipated for the incorporation of H₂O during the formation of HA. The disk was
further heated to 1150°C at 5°C/m and held for 2 h. Another weight loss (1.4%) was observed between 1000 and 1150°C, that, in this case, was caused by the dehydration of HA. Interestingly, the lost weight at 1150°C was completely regained by the disk-shaped specimen as it was cooled from 1150°C to room temperature, in ambient air. The total weight gain during the cooling cycle was 1.8%.

iii. PHASE EVOLUTION: X-RAY DIFFRACTION AT DIFFERENT STAGES (XRD)

The XRD patterns obtained from ~86% dense precursor disks before and after exposed independently (not sequentially) to a peak temperature of 350, 500, or 600°C for 1 to 4 days in dry O₂, are shown in Figure 1.14. The heating and cooling rates were 5°C/m and 3°C/m, respectively. As expected, diffraction peaks for Ca and β-Ca₂P₂O₇ were detected in the precursor. The diffraction peak near 2θ = 27.7° was more intense than expected for the [202] reflection of β-Ca₂P₂O₇, which is consistent with an overlap of the most intense [111] reflection for Ca [50].

The diffraction peaks for CaO and β-Ca₂P₂O₇ were detected in the specimens after exposure to a peak temperature of 350, 500 or 600°C in dry oxygen indicating that metallic calcium was oxidized while residual β-Ca₂P₂O₇ was not completely consumed. The X-Ray peaks associated with HA can be detected in the specimens exposed to a temperature as low as 350°C. These HA peaks were not as sharp as those from the specimens exposed to a temperature ≥850°C, which indicated that the HA formed at 350-600°C may not have been well-crystallized.

Once the calcium was completely oxidized at ≤600°C, subsequent heat treatments were conducted at 850°C to form more HA followed by annealing at 1150°C to allow for HA densification (see Figure 1.5). XRD patterns obtained from the disks exposed to a peak temperature of 850°C for 4 h or 1150°C for 1 h in the air or moist oxygen are shown in Figure 1.15. Although both β-TCP and HA were detected in the specimens heated at 850°C, the only diffraction peaks detected for the specimen exposed to the 1150°C heat treatment in moisturized oxygen were those associated with HA. Thus, pure HA was achieved after the specimen was heated at 1150°C for 1 h in a moist O₂ atmosphere.
However, decomposition of HA into CaO, α-TCP, whitlockite β-TCP, and β-TCP (both possess rhombohedral lattice structure) was observed when the specimen was fired at a temperature of 1200°C (see Figure 1.15).

iv. **Oxidation, Densification, and Shape Retention**

The dimensions and volumes of precursor and annealed disks and bars are summarized in Table 1.7 and Table 1.8 (please see Appendix C for individual data of Table 1.7). The annealing of these specimens were conducted within the Lindberg horizontal tube furnace. The data in Table 1.7 are averaged measurements from 2 to 5 specimens (see the column named "# of samp" in Table 1.7). Both disk-shaped and bar-shaped samples have achieved close to complete oxidization after annealing at 500 or 600°C for 1 d in O₂. But the complete oxidation of these samples can not be achieved at 350/400°C even after annealing for 3 d in O₂. These results are consistent with the findings from TGA.

Significant volume expansions were observed when the specimens were annealed at a temperature between 500 and 850°C. The volume expansion was as much as 9.9 % of the precursor volume (see Tables 1.7 and 1.8). On the other hand, volume shrinkages (densification) were observed when the specimens were annealed at 1150°C.

The porosity contents within the specimens were calculated by comparing the densities of the specimens to the theoretical densities of a 100% dense precursor, an oxidized precursor, and HA (2.642, 3.168, and 3.156 g/cm³ respectively). The change in porosity contents in various heat treatment states of the specimens, less the expected 8.8% shrinkage from the theoretical calculation (see section A.v.b of this chapter), are also provided in the last column of these tables (ΔP-8.8).

Optical micrographs of a machined bar before and after reaction are shown in Figure 1.16a and b. After an annealing at 1150°C for 1 h in ambient air, the linear dimensional changes of the machined regions were approximately 1%. It should be noted that even the shapes and dimension of chipped corners in the precursor specimen were maintained after the 1150°C heat treatment. This evidence supports the net-shape capability of the SMP process.
Dilatometry was conducted to investigate length changes during oxidation and post-oxidation annealing. The length of the bar continued to increase with time at 500°C (see Figure 1.17a). A 1.84% total length increase was observed after 50 h in the experiment. Another experiment was conducted in which the bar-shaped specimen was exposed to a three-stage heat treatment, namely oxidation at 600°C for 12 h in O₂ followed by annealing at 850°C for 4 h in air and subsequent heating to 1150°C in air then cooling to room temperature at a rate of 3°C/m. The heating rate for reaching these three temperatures were 5°C/m (see Figure 1.17a). It indicates from the result that the length of the bar increased by 2% and 3.5% after the 600°C and 850°C anneals, respectively. Shrinkage of the bar started when the bar was exposed to a temperature higher than 950°C. As the temperature increased above 1000°C, the rate of densification increased significantly. When the specimen was exposed to a peak temperature of 1150°C for 1 h, the length of the converted specimen was recovered to within 1.3% ± 1% relative to the precursor dimensions (see Table 1.8). This demonstrated the feasibility of fabricating low-shrinkage bodies of HA by the SMP method.

v. MICROSTRUCTURE-SEM/EDX AND IMAGE ANALYSES

BSE images and X-ray maps from the polished surface of a section of a bar fired at 1150°C for 1 h in moisturized oxygen are shown in Figure 1.18. X-ray maps did not show any preferential distribution of calcium, phosphorous, or oxygen in the sampled area.

The effect of pressure applied during precursor deformation was studied with analyses of fully-reacted disks. These disks were thermo-etched at 900°C for 4 h to reveal the grain structures. The porosity level within the disk pressed at 656 MPa (Figure 1.19b) was higher than that within the disk pressed at 1312 MPa (Figure 1.19a). Another image taken from a bar sample (pressed at 656 MPa) heated for 1 h at 1150°C also shows high porosity (Figure 1.19c). The image analyses conducted on this micrograph show that the porosity level is 32.0%, with the maximum pore diameter of ≈ 5 μm (Figure 1.19d). This porosity was consistent with the levels calculated from bulk density measurements (26.6 to 30.8% as shown in Table 1.7).
**Table 1.7: Dimensions and volumes of disk-shaped specimens before and after transformation.**

<table>
<thead>
<tr>
<th>Disk Sample State</th>
<th># of samples</th>
<th>Pressure (MPa)</th>
<th>Weight (mg)</th>
<th>Diam. (mm)</th>
<th>Thick. (mm)</th>
<th>Volume (mm³)</th>
<th>ΔV/Vp (%)</th>
<th>Porosity (vol %)</th>
<th>(ΔP-8.8) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>3</td>
<td>656±73</td>
<td>402±0.03</td>
<td>13.07±0.03</td>
<td>1.46±0.25</td>
<td>196.3±33.6</td>
<td>—</td>
<td>22.58±0.85</td>
<td>—</td>
</tr>
<tr>
<td>after 350°C, 3 d in O₂</td>
<td>“”</td>
<td>411±75</td>
<td>13.08±0.03</td>
<td>1.46±0.25</td>
<td>196.8±3.4</td>
<td>0.25±0.57</td>
<td>34.10</td>
<td>-2.72</td>
<td>—</td>
</tr>
<tr>
<td>Precursor</td>
<td>3</td>
<td>1312±15</td>
<td>342±0.02</td>
<td>13.06±0.02</td>
<td>1.12±0.05</td>
<td>150.6±6.7</td>
<td>—</td>
<td>13.86</td>
<td>—</td>
</tr>
<tr>
<td>after 350°C, 3 d in O₂</td>
<td>“”</td>
<td>350±16</td>
<td>13.09±0.02</td>
<td>1.13±0.04</td>
<td>151.6±5.4</td>
<td>0.66±0.79</td>
<td>27.22</td>
<td>4.56</td>
<td>—</td>
</tr>
<tr>
<td>after 850°C, 4h in air</td>
<td>“”</td>
<td>363±16</td>
<td>13.47±0.01</td>
<td>1.16±0.05</td>
<td>164.4±6.7</td>
<td>9.16±0.85</td>
<td>30.12</td>
<td>7.46</td>
<td>—</td>
</tr>
<tr>
<td>after 1150°C, 1 h in H₂O/O₂</td>
<td>“”</td>
<td>368±13</td>
<td>13.03±0.04</td>
<td>1.20±0.00</td>
<td>159.9±0.9</td>
<td>6.18±2.15</td>
<td>27.10</td>
<td>4.44</td>
<td>—</td>
</tr>
<tr>
<td>Precursor</td>
<td>5</td>
<td>656±44</td>
<td>340±0.02</td>
<td>13.05±0.14</td>
<td>1.25±0.14</td>
<td>167.1±19.7</td>
<td>—</td>
<td>23.06±1.06</td>
<td>—</td>
</tr>
<tr>
<td>after 500°C, 1 d in O₂</td>
<td>“”</td>
<td>358±43</td>
<td>1.324±.004</td>
<td>1.27±.14</td>
<td>175.5±20.4</td>
<td>5.03±1.27</td>
<td>35.62</td>
<td>3.76</td>
<td>—</td>
</tr>
<tr>
<td>after 850°C, 4h in air</td>
<td>“”</td>
<td>361±55</td>
<td>13.48±0.2</td>
<td>1.28±0.18</td>
<td>182.1±25.6</td>
<td>8.98±1.03</td>
<td>37.25</td>
<td>5.39</td>
<td>—</td>
</tr>
<tr>
<td>after 1150°C, 1 h in air</td>
<td>“”</td>
<td>327±2</td>
<td>13.08±0.04</td>
<td>1.19±0.05</td>
<td>159.1±5.8</td>
<td>-4.79±1.90</td>
<td>34.89</td>
<td>3.03</td>
<td>—</td>
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<tr>
<td>Precursor</td>
<td>2</td>
<td>1312±10</td>
<td>331±0.01</td>
<td>13.07±0.01</td>
<td>1.09±0.03</td>
<td>146.2±4.1</td>
<td>—</td>
<td>14.27±0.15</td>
<td>—</td>
</tr>
<tr>
<td>after 500°C, 1 d in O₂</td>
<td>“”</td>
<td>352±13</td>
<td>13.22±.000</td>
<td>1.12±.03</td>
<td>153.7±3.9</td>
<td>5.13±0.79</td>
<td>27.74</td>
<td>4.67</td>
<td>—</td>
</tr>
<tr>
<td>after 850°C, 4h in air</td>
<td>“”</td>
<td>353±11</td>
<td>13.46±0.01</td>
<td>1.13±0.06</td>
<td>160.7±0.79</td>
<td>9.92±1.18</td>
<td>30.35</td>
<td>7.28</td>
<td>—</td>
</tr>
<tr>
<td>after 1150°C, 1 h in H₂O/O₂</td>
<td>“”</td>
<td>338±29</td>
<td>13.07±0.10</td>
<td>1.17±0.08</td>
<td>156.2±8.1</td>
<td>6.84±2.33</td>
<td>31.52</td>
<td>8.45</td>
<td>—</td>
</tr>
</tbody>
</table>

*V_p refers to the bulk (solid + pore) precursor volume. ΔV refers to the difference in bulk volume between the annealed bodies and the precursors.

*ΔP refers to the percentage difference in the pore volume between the precursors and the annealed products.

*: The porosity data were calculated by comparing the densities of the specimen to the theoretical densities of precursor (CaO+Ca₃P₂O₇: 2.641 g/cc); complete oxidized specimen (CaO-Ca₃P₂O₇: 3.168 g/cc), and HA (3.156 g/cc).
Table 1.8: Dimensions and volumes of bar-shaped specimens before and after transformation.

<table>
<thead>
<tr>
<th>Bar Sample State</th>
<th>Pressure (MPa) at 1 atm</th>
<th>Weight (mg)</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thick. (mm)</th>
<th>Volume (mm$^3$)</th>
<th>$\Delta V/V_p$ (%)</th>
<th>Porosity (vol %)</th>
<th>$(\Delta P-8.8)^*$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>660</td>
<td>1,165</td>
<td>29.90</td>
<td>6.70</td>
<td>2.64</td>
<td>528.9</td>
<td>—</td>
<td>16.62</td>
<td>—</td>
</tr>
<tr>
<td>after 600°C, 1d in O$_2$</td>
<td>&quot;</td>
<td>1,215</td>
<td>30.67</td>
<td>6.87</td>
<td>2.75</td>
<td>579.4</td>
<td>9.55</td>
<td>33.81</td>
<td>8.39</td>
</tr>
<tr>
<td>after 850°C, 4h in H$_2$O</td>
<td>&quot;</td>
<td>1,213</td>
<td>30.81</td>
<td>6.89</td>
<td>2.78</td>
<td>590.1</td>
<td>11.57</td>
<td>34.87</td>
<td>9.45</td>
</tr>
<tr>
<td>after 1150°C, 2h in H$_2$O</td>
<td>&quot;</td>
<td>1,213</td>
<td>29.81</td>
<td>6.67</td>
<td>2.75</td>
<td>555</td>
<td>4.93</td>
<td>30.75</td>
<td>5.33</td>
</tr>
<tr>
<td>Precursor</td>
<td>1508</td>
<td>1,572</td>
<td>25.82</td>
<td>6.57</td>
<td>4.44</td>
<td>753.2</td>
<td>—</td>
<td>20.94</td>
<td>—</td>
</tr>
<tr>
<td>after 350°C, 1d in O$_2$</td>
<td>&quot;</td>
<td>1,606</td>
<td>25.84</td>
<td>6.59</td>
<td>4.46</td>
<td>759.5</td>
<td>0.84</td>
<td>33.25</td>
<td>3.51</td>
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<tr>
<td>after 850°C and 1150°C in air</td>
<td>&quot;</td>
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<td>6.52</td>
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<td>723.8</td>
<td>-3.90</td>
<td>26.57</td>
<td>-3.17</td>
</tr>
<tr>
<td>Precursor</td>
<td>1555</td>
<td>1,494</td>
<td>24.93</td>
<td>6.60</td>
<td>4.40</td>
<td>724.0</td>
<td>—</td>
<td>21.83</td>
<td>—</td>
</tr>
<tr>
<td>after 600°C, 1d in O$_2$</td>
<td>&quot;</td>
<td>1,601</td>
<td>25.29</td>
<td>6.68</td>
<td>4.40</td>
<td>743.3</td>
<td>2.67</td>
<td>32.01</td>
<td>1.38</td>
</tr>
<tr>
<td>after 850°C and 1200°C in air</td>
<td>&quot;</td>
<td>1,595</td>
<td>23.30</td>
<td>6.40</td>
<td>4.30</td>
<td>641.2</td>
<td>-11.44</td>
<td>21.16</td>
<td>-9.47</td>
</tr>
</tbody>
</table>

$V_p$ refers to the bulk (solid + pore) precursor volume. $\Delta V$ refers to the difference in bulk volume between the annealed bodies and the precursors. $\Delta P$ refers to the percentage difference in the pore volume between the precursors and the annealed products.

The EPMA conducted on a fully-converted HA sample (see Figure 1.5 for the heat treatment) indicated that the average Ca/P ratio of this specimen was $1.69 \pm 0.06$ (from 6 measurements), which was not far from that of stoichiometric HA (Ca:P = 1.67). The average of five WDX analyses on another specimen heated at 850°C for 4 h in moist O$_2$ indicated that the Ca/P ratio for the phase is $1.68 \pm 0.04$. It is thus confirmed that HA was the dominant phase after the heat treatment of 4 h at 850°C in either air or a flowing water vapor atmosphere. β-TCP was detected with XRD as a minor second phase after the 850°C heat treatment (see Figure 1.15). However, it is difficult to distinguish the β-
TCP phase from HA using BSE imaging. The problem lies in the similarity of their average atomic numbers: 11.36 for HA and 11.85 for β-TCP.

vi. M-DTA, EFFECT OF HEATING RATE ON IGNITION

Heating to temperatures ≥ 600°C at faster rates (e.g., 20°C/min versus 5°C/min) was found to result in thermal runaway (i.e., ignition). DT analysis conducted on disk-shaped precursors (Table 1.9 for weight and dimensional information) heated at 5 and 20°C/min to 600°C in dry oxygen are shown in Figure 1.20. While no appreciable temperature excursion was detected within the precursor heated at 5°C/min (see Figure 1.20b). a significant, sudden increase in temperature was observed at 350°C for the specimen heated at 20°C/min (see Figure 1.20a). Optical images of the sample heated at 20°C/min to 600°C, followed by heating at 850°C to form HA, are shown in Figure 1.21a and b.

Although cracks were not observed in the M-DTA sample as anticipated due to ignition, other experiments with 5 and 6 precursor bars (see Table 1.10 for dimensions and porosity) heated within the silica enclosure at 20°C/min to 600°C resulted in ignition and catastrophic fracture. The XRD analysis on the powder sample obtained from an ignited piece of a bar-shaped sample together with the XRD analysis on the disk-shaped specimen heated at 20°C/m in the DT experiment are shown in Figure 1.21c. HA is the major phase present in these samples together with minor amounts of CaO and TCP. It should be noted that Si and Ag powder had been applied on the DTA sample to serve as the external standards to calibrate the peak positions (Figure 1.21c).

Table 1.9: The weight and dimensions for the M-DTA experiment.

<table>
<thead>
<tr>
<th></th>
<th>Pressure (MPa)</th>
<th>Weight (mg)</th>
<th>Diameter (mm)</th>
<th>Thickness (mm)</th>
<th>Volume (mm³)</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>551</td>
<td>1,470</td>
<td>14.27</td>
<td>4.235</td>
<td>677.3</td>
<td>2.17</td>
<td>17.79</td>
</tr>
<tr>
<td>20°C/m to 600°C, 8 h in O₂</td>
<td>-</td>
<td>-</td>
<td>14.27</td>
<td>4.380</td>
<td>700.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*: The final weight of the sample was not available due to the presence of the thermocouple within the sample disk.
<table>
<thead>
<tr>
<th>Bar #</th>
<th>Weight (mg)</th>
<th>Length (cm)</th>
<th>Width (cm)</th>
<th>Thickness (cm)</th>
<th>Volume (cm³)</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1120</td>
<td>29.92</td>
<td>6.67</td>
<td>2.85</td>
<td>568.8</td>
<td>1.97</td>
<td>25.41</td>
</tr>
<tr>
<td>2</td>
<td>1121</td>
<td>29.97</td>
<td>6.68</td>
<td>2.87</td>
<td>574.6</td>
<td>1.95</td>
<td>26.10</td>
</tr>
<tr>
<td>3</td>
<td>1070</td>
<td>29.89</td>
<td>6.68</td>
<td>2.76</td>
<td>551.1</td>
<td>1.94</td>
<td>26.45</td>
</tr>
<tr>
<td>4</td>
<td>1072</td>
<td>29.96</td>
<td>6.70</td>
<td>2.62</td>
<td>525.9</td>
<td>2.04</td>
<td>22.79</td>
</tr>
<tr>
<td>5</td>
<td>1069</td>
<td>29.89</td>
<td>6.67</td>
<td>2.58</td>
<td>514.4</td>
<td>2.08</td>
<td>21.28</td>
</tr>
<tr>
<td>6</td>
<td>1053</td>
<td>29.95</td>
<td>6.56</td>
<td>2.68</td>
<td>526.5</td>
<td>2.00</td>
<td>24.25</td>
</tr>
<tr>
<td>7</td>
<td>1067</td>
<td>29.93</td>
<td>6.73</td>
<td>2.77</td>
<td>558.0</td>
<td>1.91</td>
<td>27.56</td>
</tr>
<tr>
<td>8</td>
<td>1104</td>
<td>29.93</td>
<td>6.74</td>
<td>2.74</td>
<td>552.7</td>
<td>2.00</td>
<td>24.34</td>
</tr>
<tr>
<td>9</td>
<td>1088</td>
<td>29.97</td>
<td>6.72</td>
<td>2.81</td>
<td>565.9</td>
<td>1.92</td>
<td>27.18</td>
</tr>
<tr>
<td>10</td>
<td>1097</td>
<td>29.99</td>
<td>6.74</td>
<td>2.73</td>
<td>551.8</td>
<td>1.99</td>
<td>24.70</td>
</tr>
<tr>
<td>11</td>
<td>1065</td>
<td>29.98</td>
<td>6.72</td>
<td>2.69</td>
<td>541.9</td>
<td>1.97</td>
<td>25.56</td>
</tr>
<tr>
<td>Average</td>
<td>1084</td>
<td>29.94</td>
<td>6.69</td>
<td>2.74</td>
<td>548.3</td>
<td>1.98</td>
<td>25.06</td>
</tr>
<tr>
<td>Std Dev</td>
<td>23</td>
<td>0.03</td>
<td>0.05</td>
<td>0.09</td>
<td>19.3</td>
<td>0.05</td>
<td>1.87</td>
</tr>
</tbody>
</table>

Table 1.10: The dimensions of the precursor bars that ignited during oxidation treatment.

BSE images and X-ray maps from the polished surface of an ignited HA transformed sample are presented in Figure 1.22. Significant porosity was observed in the SEM images. Some of these pores may have resulted from the rapid evaporation of calcium during ignition. X-ray maps did not show any preferential distribution of calcium, phosphorous or oxygen in the sampled area.

**vii. Sintering Prior to Reaction and Reaction Sintering**

Alternative routes for preparing dense HA have also been studied with dilatometry and TGA. A precursor bar (see bar A in Table 1.11 for dimensions) heated to 900°C in argon at a rate of 20°C/min showed a linear shrinkage of 1.47% when the furnace reached 880°C (see Figure 1.23a). The final dimension change was 1.7% after the bar was cooled to room temperature. TGA of a disk sample (see disk A in Table 1.11 for dimensions) indicated that the sample weight increased with time due to oxidation of calcium (see
Figure 1.23b). In total, 62% of the calcium within the disk-shaped precursor was oxidized within 3 h at 900°C in the argon atmosphere (which contained 40-70 ppm of O₂, total weight gain of 4.15% compared to 6.69% when all the calcium was oxidized). When a precursor disk was heated to 1150°C in ambient air at a rate of 20°C per min, the increase in weight was irregular (see Figure 1.23c). The weight of the disk continued to increase even when the furnace was cooled from 1150°C temperature to 750°C. A maximum weight increase of 6.84% was observed after the furnace was cooled to 750°C. The final weight change was 5.4% at room temperature.

<table>
<thead>
<tr>
<th></th>
<th>Weight (mg)</th>
<th>Length/Diameter (cm)</th>
<th>Width (cm)</th>
<th>Thickness (cm)</th>
<th>Volume (cm³)</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bar A</td>
<td>0.911</td>
<td>2.536</td>
<td>0.670</td>
<td>0.263</td>
<td>0.4469</td>
<td>2.0386</td>
<td>22.78</td>
</tr>
<tr>
<td>Disk A</td>
<td>0.222</td>
<td>1.308</td>
<td>---</td>
<td>0.083</td>
<td>0.1115</td>
<td>1.9905</td>
<td>24.60</td>
</tr>
</tbody>
</table>

Table 1.11: The dimensions of the bar and disk shaped precursors used in dilatometer and TGA experiments mentioned above (see Figure 1.23).

Two precursor bars were subjected to the alternative heat treatment shown in Figure 2.7. These specimens were first annealed at 1150°C for 4 h in Ar atmosphere to partially oxidize calcium and to allow for densification. Upon completion of the 1150°C annealing, the specimens were cooled to 850°C for additional 2 h of annealing in a flowing H₂O/O₂ atmosphere to allow for HA conversion. An average shrinkage of 3 vol% was observed in the heat treated bars as compared to the precursor dimensions (see Table 1.12). The XRD analyses also indicated that pure HA phase was achieved within the specimens after the 850°C annealing (see Figure 1.24a).

Disk-shaped specimens pressed at 656 and 1312 MPa were also subjected to a single cycle annealing at 1150°C for 1 h in ambient air. The heating and cooling rates were 5 and 3°C/min. respectively. The disk specimen pressed at 656 MPa showed a minor shrinkage in volume after HA conversion while the one pressed at 1312 MPa showed a
minor expansion (see Table 1.13). However, the porosity level within the former was higher than the latter in both the precursor and post heat treatment stages. XRD analyses on the machined bar and the disk-shaped specimens pressed at 1312 MPa and 656 MPa indicated that the HA was the major phase present with TCP the minor phase, after annealed at 1150°C for 2 or 1 h in ambient air (Figure 1.24b). In addition, the HA phase within the 656 MPa pressed disk (72% dense) shows less crystallization than that within the 1312 MPa pressed disk (85% dense).

<table>
<thead>
<tr>
<th>Bar Sample State</th>
<th>Weight (mg)</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thick. (mm)</th>
<th>Volume (mm³)</th>
<th>ΔV/V₀ (%)</th>
<th>Porosity (vol %)</th>
<th>(ΔP-8.8) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>1761</td>
<td>30.00</td>
<td>6.67</td>
<td>4.70</td>
<td>939.47</td>
<td></td>
<td>29.00%</td>
<td></td>
</tr>
<tr>
<td>after 1150°C, 4d in Ar</td>
<td>1685</td>
<td>29.80</td>
<td>6.64</td>
<td>4.53</td>
<td>895.37</td>
<td>-4.69%</td>
<td>40.60%</td>
<td>2.80%</td>
</tr>
<tr>
<td>after 850°C, 2 h in H2O</td>
<td>1745</td>
<td>29.69</td>
<td>6.57</td>
<td>4.52</td>
<td>880.71</td>
<td>-6.25%</td>
<td>37.46%</td>
<td>-0.34%</td>
</tr>
<tr>
<td>Precursor</td>
<td>2425</td>
<td>29.97</td>
<td>6.67</td>
<td>6.06</td>
<td>1211.39</td>
<td></td>
<td>24.17%</td>
<td></td>
</tr>
<tr>
<td>after 1150°C, 4d in Ar</td>
<td>2283</td>
<td>29.88</td>
<td>6.68</td>
<td>6.12</td>
<td>1221.54</td>
<td>0.84%</td>
<td>41.01%</td>
<td>8.03%</td>
</tr>
<tr>
<td>after 850°C, 2 h in H2O</td>
<td>2339</td>
<td>29.80</td>
<td>6.64</td>
<td>6.08</td>
<td>1202.07</td>
<td>-0.77%</td>
<td>38.59%</td>
<td>5.62%</td>
</tr>
</tbody>
</table>

Table 1.12: The weight, dimension, and porosity within the bar-shaped specimens after 1150°C and 850°C annealing. The bars were pressed at 662 MPa.

<table>
<thead>
<tr>
<th>Disk Sample State</th>
<th>Pressure (MPa)</th>
<th>Weight (mg)</th>
<th>Diam. (mm)</th>
<th>Thick. (mm)</th>
<th>Volume (mm³)</th>
<th>ΔV/V₀ (%)</th>
<th>Porosity (vol %)</th>
<th>(ΔP-8.8) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor</td>
<td>656</td>
<td>272</td>
<td>13.17</td>
<td>1.05</td>
<td>143.0</td>
<td></td>
<td>27.97</td>
<td></td>
</tr>
<tr>
<td>after 1150°C, 1 h in air</td>
<td>&quot;</td>
<td>280</td>
<td>13.07</td>
<td>1.02</td>
<td>136.8</td>
<td>-4.34</td>
<td>35.15</td>
<td>-1.62</td>
</tr>
<tr>
<td>Precursor</td>
<td>1312</td>
<td>279</td>
<td>13.13</td>
<td>0.92</td>
<td>124.6</td>
<td></td>
<td>15.16</td>
<td></td>
</tr>
<tr>
<td>after 1150°C, 1 h in air</td>
<td>&quot;</td>
<td>289</td>
<td>13.10</td>
<td>0.94</td>
<td>126.7</td>
<td>1.69</td>
<td>27.62</td>
<td>3.66</td>
</tr>
</tbody>
</table>

Table 1.13: The weight and dimensional data of disk-shaped specimens prior and post heat treatment at 1150°C in ambient air.
Figure 1.12: Oxidation kinetics of 86% dense Ca+β-Ca$_2$P$_2$O$_7$ Precursor disk with dimension 13 mm diameter x 2 mm thick. Experiments were conducted in dry, decarbonated O$_2$. The heating rates were 5°C/min for these experiments. (a) Linear scale plot showing the overall weight changes versus time, (b) The log-log plot of the isothermal weight change versus time after the furnace reached the designated oxidation temperature showing the k values.
Figure 1.13: TGA of a disk heated at 850°C for reaction to form HA and at 1150°C for sintering of the HA body. Heating was conducted in ambient air. Note the weight drops that occurred.
Figure 1.14: XRD patterns obtained from as-pressed and oxidized Ca$+$β-Ca$_2$P$_2$O$_7$ precursor disks (the heat treatments for the specimens shown in this figure were not sequential).
Figure 1.15: XRD patterns obtained from disks that had been exposed to air or moist oxygen at a temperature of 850, 1150, or 1200°C.
Figure 1.16: Optical images of: a) a machined Ca+β-Ca$_3$P$_2$O$_7$ precursor bar, b) the bar shown in a) after HA conversion at a peak temperature of 1150°C for 1 h in ambient air.
Figure 1.17: (a) Dilatometer test showing the length changes of two bar-shaped specimens. One was oxidized at 500°C in dry O₂, the other was exposed to a three stage heat treatment: oxidation at 600°C in dry O₂, annealing at 850°C in ambient air and then 1150°C in ambient air. (b) An enlarged view of the cooling curve of the second specimen compared to the calculated thermal expansion for hydroxyapatite.
Figure 1.18: (a) through (c) BSE images of polished cross-sections of a heat treated bar showing HA: (d), (e), and (f) X-Ray maps of Ca, P, and O elements, respectively (associated with the BSE image in c). The maps indicated that Ca, P, and O were uniformly distributed.
Figure 1.19: (a) & (b) BSE images of polished cross-sections of fully-converted disk-shaped specimens (Figure 1.5) pressed at 1312 and 656 MPa, respectively; (c) BSE image of a polished cross-section of a bar-shaped specimen pressed at 580 MPa, fired for 1 h at 1150°C showing high degree of porosity; (d) Image analyses conducted on (c) showing the distribution of porosity inside the specimen.
Figure 1.20: Differential thermal analyses of uniaxially-pressed Ca+β-Ca$_2$P$_2$O$_7$ precursor disks obtained by heating at: a) 20°C/min and b) 5°C/min to 600°C in flowing, dry O$_2$(g). Sample dimensions: 1.45 cm diameter x 3.0 cm thickness. The densities of the specimens were 17.79 % and 18.0 % of theoretical, respectively.
Figure 1.21: (a) and (b) Macrophotographs of the disk after a Macro-DTA test (20°C/min to 600°C) and 850°C annealing showing no cracks resulted from the ignition. (c) XRD of an ignited bar-shaped sample after 600°C.
Figure 1.22: (a) through (c) BSE images of a polished cross-section of an ignited specimen showing porous HA (d), (e), and (f) X-Ray maps of Ca, P, and O elements, respectively, associated with the BSE image in (c). The maps indicated that Ca, P, and O are uniformly distributed.
Figure 1.23: Heating at 900°C in argon allowed for sintering prior to complete oxidation of the calcium. (a) Length change of a bar-shaped precursor measured with the dilatometer. (b) Weight change of a disk-shaped precursor measured with the TGA. (c) Weight change of a disk-shaped precursor annealed at 1150°C in ambient air.
Figure 1.24: The XRD analyses conducted on the samples after alternative heat treatment routes; (a) A 71% dense, 30 mm x 6.67 mm x 4.7 mm bar-shaped specimen after 1150°C, 2 h annealing in Ar and after additional 850°C 2 h annealing in H$_2$/O$_2$. (b) A machined bar (see Figure 1.16) and 2 disk-shaped specimens (pressed at 1312 MPa and 656 MPa, see Table 1.13) after a single step annealing at 1150°C for 2 and 1 h in ambient air.
D. DISCUSSION

i. PRECURSOR CHARACTERIZATION

The particle size analyses of the precursor powder obtained by the BET and the sedimentation techniques showed different results: 1.01 µm average size and 6.3 µm median size, respectively. The BET analyses in this study are calculated with the assumption of spherical particles, which can account for part of this discrepancy (in reality the particles have non-spherical shapes, see Figure 1.8). Since BET analysis is based on surface area, while the sedimentation technique is based on the rate of particle settling, the discrepancy in the measurements could also be caused by (a) porous particles and/or (b) particle agglomeration. The ratio of median particle size obtained from the sedimentation technique over that from the BET technique can be regarded as an agglomeration factor of the powder if agglomeration was the main contributor for the discrepancy.

From the data discussed in the Results section, an intimate mixture of calcium and Ca₃P₂O₇ (see Figure 1.11) was achieved with consistently high (> 98%) yields and fine (6.3 µm median) particle sizes. These information indicates that the high energy ball milling method is an attractive means of producing precursors to stoichiometric HA.

ii. HA CONVERSION AND DENSIFICATION

The results of the ICP analyses, powder yields, and EPMA indicated that the welding of calcium within the precursor mix to the milling media and the wear of the steel balls by the powder, were negligible. The impurities incorporated upon mechanical alloying were also relatively small in amount. Hence, the precursor chemistry was appropriate for synthesizing phase-pure HA.

The observations of HA in the specimens oxidized at 350 to 600°C were quite unexpected. Not only does HA formation require a supply of OH⁻, but also the reaction to form HA usually occurs at a temperature ≥ 800°C (e.g., reaction temperatures ≥ 1000°C have been reported for the reaction of CaCO₃ or Ca(OH)₂ with Ca₃P₂O₇ to form HA [8]).
The standard enthalpies and standard free energies for the reaction of CaCO₃, Ca(OH)₂, or CaO with Ca₃P₂O₇ to form Ca₅P₂O₈ are shown in Figure 1.25 and Figure 1.26, respectively. From these figures, it is clear that the formation of TCP from CaO and Ca₃P₂O₇ is more favorable thermodynamically than TCP formation from the reaction of CaCO₃ or Ca(OH)₂ with Ca₃P₂O₇. Since HA is the most stable calcium phosphate under the conditions of the present work, HA formation will be more favorable than TCP (see Table 1.14 for the standard free energies of formation for HA and TCP at room temperature).

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH°   (kJ mol⁻¹)</th>
<th>ΔG°   (kJ mol⁻¹)</th>
<th>S°    (J mol⁻¹ K⁻¹)</th>
<th>C°     (J mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>-635.09</td>
<td>-646.48</td>
<td>38.21</td>
<td>42.11</td>
</tr>
<tr>
<td>β-Ca₃P₂O₇</td>
<td>-3338.80</td>
<td>-3395.22</td>
<td>189.24</td>
<td>187.76</td>
</tr>
<tr>
<td>α-Ca₅(PO₄)₃</td>
<td>-4109.0</td>
<td>-3875.5</td>
<td>240.91</td>
<td>231.58</td>
</tr>
<tr>
<td>β-Ca₅(PO₄)₃</td>
<td>-4120.8</td>
<td>-3884.7</td>
<td>236</td>
<td>227.82</td>
</tr>
<tr>
<td>Ca₁₀(PO₄)₆(OH)₂</td>
<td>-13477</td>
<td>-12677</td>
<td>780.7</td>
<td>769.9</td>
</tr>
<tr>
<td>CaHPO₄</td>
<td>-1814.39</td>
<td>-1681.18</td>
<td>111.38</td>
<td>110.04</td>
</tr>
<tr>
<td>H₂O</td>
<td>-285.83</td>
<td>-237.13</td>
<td>69.91</td>
<td>----</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>-986.09</td>
<td>-1010.95</td>
<td>83.39</td>
<td>87.62</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>-1208.36</td>
<td>-1236.10</td>
<td>93.05</td>
<td>81.87</td>
</tr>
</tbody>
</table>

Table 1.14: The standard thermodynamic properties of for selected compounds at room temperature. [5]

The formation of HA in a dry oxygen environment at 600°C can also be explained. Studies have shown that if HA is heated in dry oxygen, an ionized oxidation O(-I) occurs in the apatite product [55] (perOAp hereafter). The lattice parameters of HA decrease as the O(-I) content increased. The maximum obtained was 2.6 wt % O(-I), with lattice parameters of a = 9.36 and c=6.85 Å. PerOAp was found to be diamagnetic. It was thought to contain one diamagnetic peroxide (O₂⁻) on a vacancy on the c-axis per unit cell [55]. The reaction between oxygen in OxiHA and dry O₂ at 900°C is [55]:

\[ \gamma O₂⁻ + \frac{1}{2} \gamma O₂ \rightarrow \gamma O₂⁻ \]  \hspace{1cm} (1.7)
If the perOAp is heated in air (so that water is available), loss of $O_2^{2-}$ starts at 200°C, and is complete by 600°C. when $O_2^{2-}$ is entirely lost from the lattice [55].

Wang, et al [54] observed that the HA structure is thermally stable up to 1200°C in ambient air. Sintering at a temperature higher than 1200°C will result in HA decomposition into $\alpha$-tricalcium phosphate ($\alpha$-TCP) and tetracalcium phosphate. $Ca_3P_2O_9$ [8, 54]. Ruys also reported that HA decomposes at a lower temperature in vacuum than in a moisturized environment [56, 57], and that sintering of HA in an H$_2$O-deficient environment can produce nonstoichiometric, OH$^-$ deficient HA. The XRD analyses conducted on a 1200°C annealed specimen also indicated the decomposition of HA. However, the product was $\alpha$-TCP, $\beta$-TCP (whitlockite), and $\beta$-TCP instead of $\alpha$-TCP and $Ca_3P_2O_9$.

iii. **Dimensional Changes and Porosity Content**

From the results of the dilatometer test, out of the ≈ 3.5% expansion of the sample shown at 1150°C (Figure 1.17a), approximately 1.5% is accounted for by the thermal expansion that is reversible, while the other 2% is the actual dimensional change due to oxidation and phase transformation.

The thermal expansion of HA (prepared at 900°C) between 20 and 900°C is linear with $\Delta a/a = 13.5 \times 10^{-6}$ and $\Delta c/c = 12.7 \times 10^{-6}$ per °C. (determined from Figure 2 of [55]).

Dimensional change calculated from these equations were plotted along with the cooling portion of the dilatometry result (Figure 1.17b). Similar slopes were observed between the cooling of HA synthesized via SMP with the lines generated from the equations. This observation further confirms that the precursor bar had been completely reacted to form HA after 10 h at 600°C, 2h at 850°C and ≤ 1 h at 1150°C, followed by furnace-cooling. It should be noted that the curvature of the lines shown in Figure 1.17b was caused by the non-linear rate of temperature change during cooling.

It should be possible to retain the dimensions of the precursor specimens after the HA transformation by tailoring the fraction of $Ca_3P_2O_7$ in the precursor and
controlling the extent of sintering. This postulate is confirmed in this study. From the results shown in Table 1.8, the volume changes were consistent with the expected reaction-induced volume change and the different pore volumes of the precursor and fired bodies. The macroscopic (externally-measured) volume change of a bulk Ca+β-Ca₂P₂O₇ precursor body upon conversion into HA is given by

\[ 100 \cdot \Delta V/V_p = \Delta P + (100 \cdot \Delta V_{rxn}/V_p) = \Delta P - 8.8 \]  

(1.8)

where \(100 \cdot \Delta V/V_p\) refers to the percentage change in bulk (solid plus pore) volume. \(\Delta P\) refers to the percentage difference in the pore volumes of the precursor and of the final fired body, and \(100 \cdot \Delta V_{rxn}/V_p\) refers to the percentage change in solid volume induced by the transformation reaction. As discussed above, \(100 \cdot \Delta V_{rxn}/V_p\) for a 4Ca:3β-Ca₂P₂O₇ precursor is -8.8%. The calculated volume changes (shown under the column labeled “\(\Delta P\) -8.8”) in Table 1.7 and Table 1.8 were close (i.e. within a few percent for most of the fully-converted specimens) to the measured volume changes for the disk and bar-shaped specimens.

The reaction-induced volume shrinkage should result in an increase of 8.8% porosity in the HA body, if the HA body were to retain its original dimensions and volume (i.e., if no sintering occurs). Such an increase in porosity is not necessarily a problem. As reported by many authors [7, 58], significant porosity is required in implant devices to enable blood circulation, which is crucial for biofixation between the implant and the bone tissue. The required amount of porosity depends on the type of application. In some cases, up to 70-80% porosity is needed [58]. In the case of HA-coated bone implants, approximately 30% free volume, composed of 100 to 400 μm size pores, is desired [59].

Nevertheless, the presence of residual porosity does jeopardize the strength of the implant [60, 61]. Thus, a robust implant material should have tough, dense core with a controlled level of porosity at the surface. Since the present work shows that the increase in porosity upon HA transformation is consistent with the theoretical calculation, it is
possible to further tailor the desired pore content by adjusting the fraction of the precursor components and extent of sintering.

**iv. WEIGHT LOSS DURING POST-OXIDATION ANNEALING**

The cause of the weight loss observed by TGA between 700 to 850°C is still unclear. However, the weight loss at 1150°C is likely to be due to the dehydration of HA. Studies [52] have shown that HA could lose a substantial amount of its constitutional water, while the integrity of the lattice was maintained. The weight loss may start at a temperatures as low as 800°C. The recovery of lost weight after the sample was cooled from 1100 to 1000°C, as shown by TGA, confirmed that the dehydration process did not render any permanent structural change of the HA involved with the weight loss.

As stated by Zhou et al [53], the water content of HA is a function of the partial pressure of water vapor and temperature. Dehydration of HA in ambient air takes place at temperatures above 800°C [53, 54]. The dehydrated HA can be represented with the chemical formula \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_x\text{V}_x \), where \( V \) is an \( \text{OH}^- \) ion vacancy. The water content of \( \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_x\text{V}_x \) at equilibrium with water vapor of partial pressure \( p \) is a function of temperature \( T \) (K) [17]. The reaction is:

\[
2\text{OH} \leftrightarrow \text{O}_{\text{OH}}^* + \text{V}_{\text{OH}}^* + \text{H}_2\text{O}(g)
\]  

Thus, \( \frac{p_x}{(2-2x)^x} = K(T) \)  

where \( K(T) = 1.2 \times 10^6 \text{exp}(-\Delta H^*/RT) \)

where \( \Delta H^* \) is -251 KJ/mol. It is also reported that HA can lose up to 75% of its constitutional water in vacuum when heated at 1230°C without loss of the apatite structure [17]. Such dehydrated HA is called O.OHAp ([8]).

This change in water content might slightly modify the HA lattice parameters but not its general structure. The lattice parameters of dehydrated HA are given by [8]:

\[
61
\]
\[ a = 9.4197 - 0.0268 \times \]  

\[ c = 6.8805 - 0.0129 \times \]  

where \( x \) can be calculated from equation (1.10). The lattice parameters of fully dehydroxylated HA are reported to be \( a = 9.3929 \) and \( c = 6.8676 \) Å when \( x = 1 \) [55].

In order to detect the difference between O.OHAp and HA, samples synthesized in dry and moist \( \text{O}_2 \) were analyzed with Raman spectroscopy (see Figure 1.27). It is indicated that O.OHAp and HA have similar Raman scattering at 962 cm\(^{-1}\) (\( \nu_1 \) PO\(_4\) stretch).

\section{V. THERMAL RUNAWAY DURING CALCIUM OXIDATION}

It is preferable to use a fast heating rate in a kinetic study so that the sample can be brought to the desired temperature as soon as possible and the kinetics of oxidation or reaction can be monitored isothermally with little non-isothermal weight gain. However, due to the exothermic nature of calcium oxidation, a fast heating rate will cause thermal runaway, and might alter the reaction path. Results of the DTA experiments indicated that a precursor disk (14.23 mm dia x 4.24 mm thick, 82.61% dense, 1.47 gm weight) can be heated at 20\(^\circ\)C/min to 600\(^\circ\)C in the silica enclosure without cracking, even when the DTA measurement from the thermocouple embedded inside this sample indicate a 650\(^\circ\)C superheat (see Figure 1.20). On the other hand, when six precursor bars (29.94 mm x 6.7 mm x 2.6 mm, 74.48% dense, 6.15 g total weight) were heated at the same rate with the same setup, they underwent catastrophic cracking during the ignition.

Thermal runaway during calcium oxidation has been attributed to the relatively poor thermal conductivity associated with a porous calcium oxide scale formed on calcium and to the exothermic nature of the oxidation reaction (e.g., the standard enthalpy of reaction for calcium oxidation at 500\(^\circ\)C is -630 kJ/mole [46, 51]). The porous oxide scale formed on calcium is a consequence of the 36% smaller molar volume of CaO relative to Ca [50]. The conditions required for ignition to occur depend on the relative rates of heat generation and dissipation, which are determined by the mass and geometry of the sample, the \( \text{PO}_2 \) level, the heating rate, and gas flow rate. Thus, heating was conducted at
5°C/min through 600°C with a gas flow rate of ≥ 20 ml/m (silica enclosure diameter = 3.8 cm. volume = 550 cm³) to avoid such uncontrolled combustive oxidation.

In order to further understand the nature of calcium ignition, an estimate of the potential peak temperature that the sample could reach in an adiabatic condition was made.

The heat evolved for the oxidation of calcium at 600°K (323°C) per mole of calcium is calculated from Gibbs Free Energies provided in Barin [46, 51] to be 629.12 KJ (see Figure 1.25). In an adiabatic condition, the heat evolved from calcium oxidation will raise the temperature of the CaO and Ca₂P₂O₇ system to a value $Q$. $Q$ can be calculated from the specific heat of CaO and Ca₂P₂O₇ per the following equation:

$$\int mC_{p,\text{CaO}}dT + \int nC_{p,\text{Ca}_2\text{P}_2\text{O}_7}dT = 629.12\text{KJ}$$

(1.14)

Where $m$ and $n$ are moles of CaO and $\beta$-Ca₂P₂O₇ in the sample respectively. In the monolithic precursor of this study, $m = 4$ and $n = 3$. The specific heat for CaO is [51]

$$C_{p,\text{CaO}} = 50.417 + 4.184 \cdot 10^{-1}T - 0.849 \cdot 10^{-2}T^{-2}\text{KJ/mole}$$

(1.15)

While the specific heat of Ca₂P₂O₇ is [51]:

$$C_{p,\beta}\text{Ca}_2\text{P}_2\text{O}_7 = a + b \cdot 10^{-1}T + c \cdot 10^{-2}T^{-2}\text{ KJ/mole}$$

(1.16)

Where $a$, $b$, and $c$ are listed in Table 1.15.

The latent heat of phase transformation from $\beta$ into $\alpha$ Ca₂P₂O₇ and then from $\alpha$ Ca₂P₂O₇ into liquid phase are also provided in Table 1.15.

Inserting the values for the specific heats of CaO and Ca₂P₂O₇ and the latent heat of phase transformation, equation (1.7) becomes:
\[
\begin{align*}
&\int_{T_0}^{T} \left( 4 \cdot (50.417 + 4.184 \cdot 10^{-3} T - 0.849 \cdot 10^6 T^{-2}) \cdot dT \\
&+ \int_{T_0}^{T} \left( 3 \cdot (221.878 + 61.756 \cdot 10^{-3} T - 4.669 \cdot 10^6 T^{-2}) \right) dT + 3 \cdot 6.694 \\
&+ \int_{T_0}^{T} \left( 3 \cdot 318.612 \cdot 10^{-3} T \right) dT + 3 \cdot 100.834 + \int_{T_0}^{T} \left( 3 \cdot 405.011 \cdot 10^{-3} T \right) dT 
\end{align*}
\]

\[= 629.12 \text{KJ} \]

The temperature \( Q \) was then calculated to be 2550°C.

<table>
<thead>
<tr>
<th>Phase</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
<th>( \Delta H^0 ) of phase transformation (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>221.878</td>
<td>61.756</td>
<td>-4.669</td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>318.612</td>
<td></td>
<td></td>
<td>6.694</td>
</tr>
<tr>
<td>( L )</td>
<td>405.011</td>
<td></td>
<td></td>
<td>100.834</td>
</tr>
</tbody>
</table>

Table 1.15: The thermodynamic constants \( a, b, \) and \( c \) for specific heat of \( \beta, \alpha, \) and liquid phases of \( \text{Ca}_2\text{P}_2\text{O}_7 \).

Suppose that all of the \( \beta-\text{Ca}_2\text{P}_2\text{O}_7 \) has reacted with \( \text{CaO} \) to form TCP prior to any phase transformation (since the thermodynamic data for HA is not available, TCP is used in this calculation). The heat evolved for forming TCP at 600°C (323°C) per mole of calcium is calculated to be 778.30 KJ (i.e., enthalpy of reaction for \( \text{Ca} + \text{O}_2 + \text{Ca}_2\text{P}_2\text{O}_7 \rightleftharpoons \text{Ca}_3\text{P}_2\text{O}_8 \)). In an adiabatic condition, the heat evolved from TCP formation will raise the temperature of the \( \text{CaO} \) and TCP system to another value \( Q_1 \). \( Q_1 \) can be calculated from the specific heat of \( \text{CaO} \) and TCP per the following equation as well as the coefficients of specific heat for TCP (see Table 1.16):

\[
\int_{T_0}^{T} 0.25 \cdot C_{p,\beta} dT + \int_{T_0}^{T} 0.75 \cdot C_{p,L} dT = 778.3 \text{KJ} 
\]

\[\text{(1.18)}\]
In this case, $Q_1$ is calculated to be $3180{^\circ}C$. However, neither CaO nor TCP are solid at this temperature, nor are thermodynamic data for CaO and TCP available at this temperature.

<table>
<thead>
<tr>
<th>Phase</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\Delta H^0$ of phase transformation (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>201.836</td>
<td>163.511</td>
<td>-2.092</td>
<td></td>
</tr>
<tr>
<td>$\alpha$</td>
<td>330.536</td>
<td></td>
<td></td>
<td>15.48</td>
</tr>
</tbody>
</table>

Table 1.16: The thermodynamic constants $a$, $b$, and $c$ for specific heat of $\beta$ and $\alpha$ phases of TCP

The Macro-DTA results indicated an overheating of $650{^\circ}C$ under flowing $O_2$. Some of the heat generated from calcium oxidation and HA(or TCP) transformation was apparently dissipated from the sample. If the heating rate is reduced (so is the oxidation rate of calcium) until the heat dissipation rate becomes comparable to the rate of heat generation, an ignition problem can then be eliminated. A modest over-heating might enhance the rate of HA formation at a lower temperature. However, severe overheating (ignition) results in catastrophic cracking of the sample. Since porosity within the sample should prohibit the heat dissipation, a denser sample should have less of an ignition problem than a porous one under the same heating condition, as observed in the disk-shaped (82.21%) and bar-shaped (74.48%) samples mentioned previously.
Figure 1.25: Values of $\Delta H^\circ$ for CaCO$_3$, Ca(OH)$_2$, and CaO reaction with Ca$_2$P$_2$O$_7$ to form Ca$_3$P$_2$O$_8$. The standard enthalpy of reaction for the oxidation of Ca is provided for comparison.
Figure 1.26: Values of $\Delta G^\circ_{\text{reaction}}$ for CaCO$_3$, Ca(OH)$_2$, and CaO reaction with Ca$_2$P$_2$O$_7$ to form Ca$_3$P$_2$O$_8$. The standard free energy for the oxidation of Ca is provided for comparison.
Figure 1.27: Raman analyses of the HA synthesized with dry and moist O$_2$ (heat treatment cycle of Figure 1.5), referred to as O.OHAp and hydroxyapatite, respectively. The two samples show the same Raman vibration at 962 cm$^{-1}$ ($\nu_1$ PO$_4$ stretch).
E. CONCLUSIONS

Intimate mixtures of Ca+β-Ca$_2$P$_2$O$_7$ precursors to monolithic hydroxyapatite, Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, were prepared by high-energy mechanical alloying for 4 h with reasonably high yields (≥ 98%). The precursors were sufficiently malleable as to allow for compaction into disks or bars with relatively high green densities (77-86%, Tables 1.5 and 1.6) and for subsequent machining into cylindrical rods. Oxidation of the calcium at 600°C and subsequent firing at up to 1150°C yielded pure (by XRD) hydroxyapatite. Circular disks and rectangular bars of HA were produced with modest, and predictable net volume changes of ≤ 3.2%.

This study demonstrates the feasibility of synthesizing near-net-shaped, pure HA from a Ca-Ca$_2$P$_2$O$_7$ precursor via the SMP method. Application of this SMP method to the syntheses of HA-bearing composite materials is also feasible, as demonstrated in Chapter 2.

Further evaluation of reaction paths and kinetics using planar reaction couples is presented in Chapter 3.
F. REFERENCES


44. Viers, D., K. Rogers, and K.H. Sandhage. Fabrication of BaAl2O4 and Ba,Sr,Al2Si2O8-Based Composites from Solid Alkaline Earth Metal-Bearing Precursors. in 99th Annual American Ceramic Society Meeting. 1997. Cincinnati, OH.


CHAPTER 2

FABRICATION OF
HYDROXYAPATITE-BEARING COMPOSITES

A. INTRODUCTION

Materials used for load-bearing implant devices should have good tension/compression strength and resistance to fatigue, corrosion, and wear, in addition to compatibility with the biological environment. Although HA has a high degree of biocompatibility [1-6], monolithic HA doesn’t have the strength, impact resistance, and toughness needed for a load-bearing application (see Table 1.1 for the mechanical strength values reported for HA, and Table 2.1 for the required mechanical properties for load-bearing orthopedic devices). Thus, load-bearing implant devices (e.g., the stem of a hip joint, where strength, fatigue resistance, and fracture toughness are crucial) are usually made of a biocompatible alloy (e.g., CoCrMo, CoNiCrMo, FeCrNiMo, TiAlV, etc) with a porous metal or HA-bearing coating.

<table>
<thead>
<tr>
<th>Mechanical Properties</th>
<th>Y.S.(MPa)</th>
<th>UTS(MPa)</th>
<th>Fatigue strength (MPa)</th>
<th>Elongation(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Requirement</td>
<td>&gt;450</td>
<td>&gt;800</td>
<td>&gt;400</td>
<td>&gt;8</td>
</tr>
</tbody>
</table>

Note: Fatigue strength is based on 5 million loading cycles at a cyclic frequency of 5 to 10 Hz

Table 2.1: The mechanical requirements for load-bearing implant devices [9].

Implant devices consisting of HA-bearing coatings on a non-toxic alloy (e.g., Co or Ti-based) substrate, or of bulk, shaped HA-bearing components, have been reported by several authors [1-6]. Composite ceramics reinforced with fibers (e.g. C, SiC, etc) are attractive for their upgraded flexural strength and stress to failure relative to monolithic
HA bodies [4]. An apatite-wallastonite glass-ceramic with dispersed ZrO$_2$ particles is used in applications for pelvic bone and vertebrae replacements owing to the relatively high mechanical strength, 220 MPa [7, 8], achieved in such composites.

### Co-Cr-Mo Alloys

The cobalt-based superalloys have been in commercial use since the 1930's and have been subjected to several investigations. The Co-Cr-Mo alloys with chemical compositions that conform to ASTM F75 (Table 2.2) [10] are also known as Vitallium or Wironium. Since 1930's, numerous orthopedic implants, such as hip and knee prostheses, have been fabricated from investment castings of Co-Cr-Mo-C alloys [11]. A low carbon, wrought Co-Cr-Mo alloy (ASTM F799-96 [12]) for femoral heads of hip prostheses has also been fabricated by machining and subsequent ion implantation [13]. The ASTM specifications for mechanical properties of CoCrMo alloys prepared via casting, wrought processing, or spray atomization for surgical implant applications are provided in Table 2.3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast or Atomized</td>
<td>bal</td>
<td>27–30</td>
<td>5–7</td>
<td>&lt;1.0</td>
<td>&lt;0.75</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;0.35</td>
<td>---</td>
</tr>
<tr>
<td>Wrought or Forged</td>
<td>bal</td>
<td>26–30</td>
<td>5–7</td>
<td>&lt;1.0</td>
<td>&lt;0.75</td>
<td>&lt;1.0</td>
<td>&lt;1.0</td>
<td>&lt;0.35</td>
<td>&lt;0.25</td>
</tr>
</tbody>
</table>

Table 2.2: The Chemical compositions for various states of Co-Cr-Mo alloy per ASTM standards. (all the data are presented in wt% [8-11]).

<table>
<thead>
<tr>
<th>State</th>
<th>Y.S. (MPa)</th>
<th>U.T.S. (MPa)</th>
<th>Elongation min. (%)</th>
<th>Red. area, min. (%)</th>
<th>Hardness, Rc, Min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cast</td>
<td>450</td>
<td>655</td>
<td>8</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>Forged</td>
<td>827</td>
<td>1172</td>
<td>12</td>
<td>12</td>
<td>25</td>
</tr>
<tr>
<td>Wrought</td>
<td>Annealed</td>
<td>517</td>
<td>897</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Hot work</td>
<td>700</td>
<td>1000</td>
<td>12</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Warm work</td>
<td>827</td>
<td>1172</td>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 2.3: The mechanical properties for Co-Cr-Mo alloys prepared differently.
ii. **Conventional Preparation of Implant Substrates from Co-Cr-Mo Alloys**

CoCrMo alloy implants have been produced by investment casting, wrought processing, or HIPping.

a. **Investment Casting**

Investment casting can be an attractive process due to the versatility in forming metal to a variety of nearly-finished shapes and dimensions. The near-net shape feature is achieved by utilizing a refractory ceramic shell mold shaped from a wax replica of the part to be cast [14]. This advantage is particularly useful for fabricating metals of high work hardening coefficient and/or metal devices with intricate shapes [14] (e.g. artificial skeletal joint replacements). The use of investment casting can allow for tight dimensional tolerances without much machining [14].

The CoCrMo (or CoNiCrMo) alloys are usually cast at temperatures of 1350 to 1450°C depending on their exact compositions [15]. Relatively fine grain sizes are usually preferred, owing to the better fatigue and tension/compression strengths observed in fine-grained specimens over their coarse-grained counterparts. The final grain size within a cast body depends on the nucleation and growth rates of the solid phase from the melt. The nucleation and growth rates are affected by the temperature of the melt before pouring, and the cooling rate after pouring. Rapid cooling leads to a fine grain size, but it is limited by the requirement that the melt has to flow readily within the casting mold [14]. In addition, compositional inhomogeneity can occur within the cast body if a high-melting point composition solidifies first, followed by lower melting compositions [14].

The effects of casting temperature on castability (measured as the percentage of a grid pattern that was filled by metal) and mechanical properties have been extensively studied [16]. The castability of the Co-Cr-Mo-C alloys can be increased by nearly 90% when the casting temperature is increased by 150°C to 1635°C [16].

The phases existing in the as-cast and heat-treated materials have been extensively studied [14, 17-19]. A core of Co-rich austenite with interdendritic zones enriched in
Mo, Cr and C and block carbides of the \( M_{23}C_6 \) (\( M = Co+Cr+Mo \)) phase were found in the as-cast components [14, 17]. Kilner identified a Cr-rich \( M_{23}C_6 \) phase, a sigma phase (a Co-rich solid solution containing Cr and Mo), and a gamma matrix phase within the interdendritic zones. Sande [18] identified four phases in the as-cast material: a \( M_7C_3 \) (\( M = Co+Cr+Mo \)) phase in the form of long prismatic needles, a \( M_{23}C_6 \) phase, a Co-rich alloy in pearlite-like lamella colonies, and a Mo-rich sigma phase of irregular shape interspersed between the colonies. The carbide and intermetallic phases are brittle, and their shapes and distributions in the as-cast alloy limit its ductility to only 5-8% [20]. The volume fraction of hard, carbide-containing particles increases with the content of C and Cr. In a tension test, these particles cracked in a direction perpendicular to the tensile stress, and rendered a reduction in ductility [16].

Because of these factors, load-bearing, cast Co-Cr-Mo implants are given a high temperature anneal at 1200 to 1230°C to dissolve the \( M_{23}C_6 \) carbide and sigma intermetallic phases into solid solution [21]. A longer than 24 h treatment at the temperature followed by rapid cooling is usually needed to dissolution of all the \( M_{23}C_6 \) and intermetallic phases, and to avoid reprecipitation of these brittle phases [21].

A lower temperature (650 - 850°C) aging treatment after the solution treatment causes the precipitation of fine, distributed \( M_{23}C_6 \) carbides and consequent strengthening [19]. Hardness increased appreciably with aging above 650°C, with peak hardness being reached by aging for 723 hr at 760 to 815°C [22].

**b. Wrought Co-Cr-Mo Alloys**

The wrought Co-Cr-Mo material is a further development from as-cast Co-Cr-Mo alloys for manufacturing highly-stressed implant components. By means of hot forging, followed by a certain heat treatment, a higher density, a much smaller grain size, and a finer distribution of block carbides can be achieved within the alloy [9]. As a result, wrought alloys generally have higher strength, ductility, and resistance to fatigue and stress-corrosion cracking compared with their cast counterparts [9]. A dramatic increase in fatigue strength can be achieved by hot forging and rolling at 1175°C, followed by a 10% cold-rolling reduction and annealing at 1050°C for 40 min and then air cooling [9].
c. **HIPping**

As stated earlier, the lamella carbide and intermetallic phases within the investment cast component can reduce the resistance to fatigue fracture. Metal fatigue failure has accounted for most of the stem fractures among total hip joints retrieved from the field [23].

Hot isostatic pressing (HIPping) of as-cast Co-based alloy implants (1230°C, 105 MPa, 2 h in Ar) can eliminate microporosity, and thus improve mechanical properties [24]. However, HIPping can only heal the closed internal voids. Slow-cooling after HIPping usually results in the formation of lamella-M$_{23}$C$_6$, grain-boundary precipitates at around 1100°C. A 1 h solution treatment at 1230°C followed by rapid cooling to room temperature is needed to dissolve the carbides. This treatment can improve the ductility vastly from 5 to 17% (reduction in area) but not greatly affect the UTS and YS [24].

A powder metallurgy process that includes preparation of ultra clean powder of controlled size by atomization and classification, and subsequent consolidation of the powder by HIPping (1100°C, 100 MN/cm$^2$), has been developed. The resultant solid material can achieve near 100 percent density and a very fine grain structure [25]. Prostheses prepared by this process have the same biocompatibility and corrosion resistance as the conventional cast alloy but higher strength and fatigue resistance [25].

d. **Transformation induced plasticity (TRIP)**

A strain-induced phase transformation in Co-based alloys was first observed by Nishiyama in a Co-26Ni-8.7Cr alloy [26]. Graham and Youngblood [27] demonstrated that the amount of hcp phase formed during cold swaging of Co-Cr-Mo-Ni multiphase alloys increased rapidly with the amount of deformation. The yield strength observed during subsequent tensile tests increased linearly with the amount of strain-induced hcp phase.

The plastic deformation of wrought Co-27Cr-5Mo-0.05C alloy as a function of grain size was investigated at 298 K by Salinas-Rodriguez [11]. His study indicated that an increase in the grain size from 7 to 70 microns resulted in a 50% reduction in the yield strength and a 18% increase in the ductility without much effect on the tensile strength.
This increase in ductility was a result of the transformation-induced plasticity (TRIP) in the coarse-grained material, which enhanced the material's ability to deform uniformly by maintaining a high rate of strain hardening during deformation. A reduction in fcc grain size inhibits the rate of fcc-to hcp transformation as observed by Olson and Cohen [28] in steel. The ductility enhancement in steel was postulated to be associated with the suppression of tensile instabilities due to increased strain hardening rates by the formation of martensite [28].

e. **Wear resistance**

It was reported that the as-cast Co-Cr-Mo alloy has excellent wear resistance because of the existence of numerous carbide particles in its microstructure [19]. In the case of metal on a metal-bearing surface, the metallic volume wear after 1.5 million cycles in a hip simulator was about 1/150 times the volume wear of polyethylene. The low wearing rate could be due to lack of surface roughness or the structural transformation of the surface into an hcp polymorph (which is harder than the fcc phase) during sample fabrication by TRIP [29].

f. **Phases in Co-Cr-Mo alloy**

The phases reported to exist in the Co-Cr-Mo system are summarized in Table 2.4.

1. **Co-Cr-C diagram**

A phase diagram for Co-Cr-C system is provided in Figure 2.1a. The composition of Co-Cr-Mo alloy utilized in this study (i.e., the Co-Cr binary assuming that Mo is equivalent to Cr) is marked with an "★" on this Figure. Koster [30] reported that there are two eutectic reaction temperatures for the Co-(Cr+Mo)-C system:

1. ET1 (1335°C): L = sigma (CoCr(LT)) + M23C6 + Co rich solid solution, liquid composition: 40.4% Co. 57% Cr + Mo. 2.6% C by weight.

2. ET2 (1230°C): L = graphite + M7C3 + Co, liquid composition: 77.5% Co. 19% Cr + Mo. 3.5% C by weight.
Since the Co-Cr-Mo alloy studied here contains only 3.6 at % of Mo, the phases present in the Co-(Cr+Mo)-C system can also be found in the Co-Cr-C system as shown in Figure 2.1a. The two eutectic points, ET1 and ET2 discussed by Koster [30] in the Co-(Cr+Mo)-C are noted in the Co-Cr-C diagram (Figure 2.1a).

<table>
<thead>
<tr>
<th>Phase</th>
<th>lattice</th>
<th>unit cell (Å) a</th>
<th>b</th>
<th>c</th>
<th>Stable temp (°C)</th>
<th>JCPDS Card #</th>
</tr>
</thead>
<tbody>
<tr>
<td>ε-Co</td>
<td>hcp</td>
<td>2.514</td>
<td></td>
<td></td>
<td>&lt;450</td>
<td>05-727</td>
</tr>
<tr>
<td>α-Co</td>
<td>fcc</td>
<td>3.545</td>
<td></td>
<td></td>
<td>&gt;450</td>
<td>15-806</td>
</tr>
<tr>
<td>Cr</td>
<td>bcc</td>
<td>2.884</td>
<td></td>
<td></td>
<td>6-694</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>bcc</td>
<td>3.141</td>
<td></td>
<td></td>
<td>42-1120</td>
<td></td>
</tr>
<tr>
<td>Co-Cr (α)</td>
<td>tetragonal</td>
<td>8.810</td>
<td>4.560</td>
<td></td>
<td>9-52</td>
<td></td>
</tr>
<tr>
<td>Co3 Mo</td>
<td>hexagonal</td>
<td>5.125</td>
<td>4.113</td>
<td></td>
<td>29-488</td>
<td></td>
</tr>
<tr>
<td>Co3 Mo6</td>
<td>rhombohedral</td>
<td>4.762</td>
<td>25.617</td>
<td></td>
<td>29-489</td>
<td></td>
</tr>
<tr>
<td>Cr0.548 Co1.539 Mo0.912</td>
<td>rhombohedral</td>
<td>10.903</td>
<td>19.342</td>
<td></td>
<td>26-425</td>
<td></td>
</tr>
<tr>
<td>( Cr0.77 Co0.15 Mo0.08 )25 C6</td>
<td>cubic</td>
<td>10.844</td>
<td></td>
<td></td>
<td>37-1229</td>
<td></td>
</tr>
<tr>
<td>Cr23 C6</td>
<td>cubic</td>
<td>10.660</td>
<td></td>
<td></td>
<td>35-783</td>
<td></td>
</tr>
<tr>
<td>Cr7 C3</td>
<td>orthorhombic</td>
<td>7.0149</td>
<td>12.153</td>
<td>4.532</td>
<td>36-1482</td>
<td></td>
</tr>
<tr>
<td>Cr7 C3</td>
<td>hexagonal</td>
<td>13.980</td>
<td></td>
<td>4.523</td>
<td>11-550</td>
<td></td>
</tr>
<tr>
<td>Cr3 C2</td>
<td>orthorhombic</td>
<td>11.460</td>
<td>5.520</td>
<td>2.821</td>
<td>3-935</td>
<td></td>
</tr>
<tr>
<td>Mo3 C2</td>
<td>hexagonal</td>
<td>3.016</td>
<td>14.64</td>
<td></td>
<td>42-890</td>
<td></td>
</tr>
</tbody>
</table>

Table 2.4. Crystallographic information for Co, Cr, Mo and their intermetallic compounds and carbides. [14]

(2) **Co-Cr-Mo diagram**

A liquidus projection for Co-Cr-Mo system is shown in Figure 2.2a, while the isothermal projections at 1200, 927, and 627°C are shown in Figure 2.2b, Figure 2.3a and b respectively.

Based on these diagrams, if the Co-Cr-Mo melt (of the composition indicated by the symbol "Â") is cooled slowly from a temperature higher than 1440°C, fcc Co-rich phase (Co(HT)) will begin to solidify at the temperature of 1440°C while leaving the melt with a composition lower in Co. As the melt is cooled continuously to ~1390°C, co-
precipitation of sigma phase (CoCr(LT)) and Co-HT will take place. From ≤ 1390 to
~1350°C, more sigma phase forms, although Co-HT is resorbed into the melt. At the
temperature of 1335°C, the liquid will undergo eutectic decomposition into a Co-rich fcc
phase, the sigma phase, and Co-Mo₆. As the alloy is cooled further, some of the fcc Co
phase will transform to hcp phase (Co(LT)).

(3) fcc vs. hcp Co alloys

There are two polymorphs for Co and its solid solutions, a high-temperature fcc
phase and a low-temperature hcp phase [31] (see Figure 2.2 and 2.4). The composition of
the Co-Cr-Mo alloy used in this study was consistent with most of the Cr and Mo atoms
dissolved in a Co solid solution.

The Co-Cr and Co-Mo binary phase diagrams are provided in Figure 2.4a and b.
respectively. The Co-Cr system contains a eutectic decomposition at 1395°C. As a Co-
Cr melt with 31.13% Cr (the Cr content in the F75 alloy - marked with a dash line in
Figure 2.4a) is cooled from a temperature higher than 1460°C, the melt will completely
solidify into α-Co (HT, fcc phase) solid solution at a temperature below 1420°C. At
900°C, the fcc α-Co should transform completely into its low temperature allotrope, ε-Co
(hcp phase), although the transformation at this temperature might be sluggish.

It should be noted that, if the alloy behaves more like a 62.34% Co alloy (the Co
content in the F75 alloy, marked with another dash line in Figure 2.4a), the α-Co-solid
solution will precipitate the σ phase (Co-Cr) at 1040°C. The σ phase has 55 to 62 wt.%
Cr, and a tetragonal unit cell [32]. The precipitation of σ phase will reduce the Cr
content within the Co solid solution. In addition, ε-Co will form by a peritectoid reaction
of α-Co and σ-(Co-Cr) phases at 967°C.

The hcp ε-phase is generally favored for implant applications. Ducheyne [14]
reported that when the F75 alloy was annealed at a temperature lower than 890°C, bands
of hcp will form within the fcc matrix. These hcp bands provide sites for precipitation of
M₂₃C₆, which is an important part of the strengthening mechanism [14]. Buckley [33]
stated that when tested under the same condition, hcp Co alloy gives 50% lower friction
coefficients and exhibits lower wear rates than the fcc Co alloy polymorph. Salinas [11] also argued that since Co-based alloys have low stacking fault energy, plastic deformation by dislocation slip in the fcc alloy is relatively difficult. Thus, plastic deformation is usually accommodated by the formation of stacking faults, twinning, and localized slip along the stacking faults. The interactions between dislocations, dissociated dislocations and twins are the major sources of strain hardening. These interactions can cause cracking when the alloy is overstressed.

### iii. Implants with Porous Surface Coatings

Porous surface implants made of metal powder have recently received great interest. By constructing a porous structure on the surface of the implant, tissue ingrowth and biofixation can be enhanced. If the implant has a dense metal core, a high mechanical strength can be retained [34-36]. A porous surface can be fabricated by placing metal powder on the surface of the dense implant and then sintering the metal particles to the solid substrate.

The fabrication of a porous Co-Cr-Mo metal-coated alloy usually requires the use of a heat treatment temperature higher than the incipient (non-equilibrium) melting temperature of this alloy system. (>1300°C) [37]. This high temperature is needed to dissolve the interdendritic carbides. These microstructural changes are pertinent for enhancing the mechanical properties of the implant, although not much change in overall corrosion behavior has been noticed [37].

The fact that tissue ingrowth can be accomplished with implants prepared by sintering atomized Co-Cr-Mo powder on the cast (or wrought) Co-Cr-Mo substrate confirms the biocompatibility of the Co-Cr-Mo alloy. This biocompatibility is in contrast to the toxicity and allergic reaction caused by cobalt and its oxides alone, which suggests that the solute elements contained in the alloy yield a passive, biocompatible oxide film in the biological environment [9].

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iv. HA Coated Implants

As mentioned previously, the application of an HA coating on the surface of a strong substrate can produce implant devices with relatively high mechanical strength and biocompatibility.

The HA coating is conventionally obtained by plasma-spraying [38-43]. A pulsed-laser deposition method, used in the field of high-critical-temperature superconductive thin films, has also been adopted for coating of calcium phosphates on implants [41, 42, 44].

The advantages, a concern, and the criteria of HA coatings are summarized below.

a. Advantages

(1) Bone ingrowth

Studies from more than 60 retrieved HA-coated prosthetic components indicated that bone ingrowth on an HA coating can cover as much as 20% and 78% of the surface area after 3 weeks and 25 months of implantation, respectively [5]. Studies have also shown that an HA coating can enhance bone growth across a gap around an implant in various mechanical conditions, and convert a motion-induced fibrous membrane into a bony anchorage [45-48]. Thus, an HA coating can provide mechanical stability of the prosthesis, as has been demonstrated in a comparison between HA coated and non-coated or cemented prostheses [49].

(2) Sealing effect

The wear debris from polyethylene is a serious problem in arthroplasty. Such debris can lead to granuloma and focal osteolysis around the implant and eventually cause failure of the prosthesis. It has been reported that an HA coating can inhibit the migration of polyethylene particles along the bone-implant interface [5].

b. Concern: Degradability of HA in the biological environment

The rate of HA resorption in the biological environment has a great influence on implant fixation. The resorption rate is affected by the HA surface area, the HA
structure. and the environment. If the resorption rate is too fast, the HA coating can be degraded to a point where delamination, production of particles, and loss of mechanical fixation may occur [50]. A controlled, slow resorption process is preferred, since it allows the surrounding bone to replace the resorbed coating.

c. Specifications

Criteria for an HA coating that will yield biofixation is thought to include: ~50 μm in thickness, > 95% in purity, a Ca/P ratio of 1.67 and pore sizes ≥100μm [51.64]. The porosity of available HA coatings was reported to be from 5% to 20% [54]. The shear strength between HA and the substrate should be 22 to 29 MPa and the minimum tensile strength of HA should be 51 MPa [52] [53]. It should be noted that a thin coating of ~50 μm has found to result in a stronger fixation than a thick coating of 200 μm [47]. Also, a porous substrate underneath the HA coating is better for biofixation than a grit-blasted surface [54].

v. SMP processing of HA/Co-Cr-Mo alloy composite

In this study, the fabrication of a HA/Co-Cr-Mo alloy composite has been attempted using solid, metal-bearing precursors containing metallic calcium and Co-Cr-Mo alloy as well as the oxide phase, β-Ca2P2O7. The advantages of this route have been elaborated in the introduction section of Chapter 1. Since near net shaped, phase-pure HA can be synthesized from solid metal-bearing precursors (SMP) with relatively low cost processing, the feasibility for the fabrication of an HA/Co-Cr-Mo composite via the SMP method should be examined. The introduction of a Co-Cr-Mo alloy in an HA-bearing composite should not only improve the mechanical strength with respect to monolithic HA, but also reduce the amount of shrinkage anticipated in the conversion of the precursor into HA. On the other hand, calcium can serve as a metallic binder for the Co-Cr-Mo powder and enable the forming of high-density composite precursor bodies without utilizing any fugitive organic binder.
vi. OBJECTIVES

The long term goal of this research is to synthesize a functionally-graded composite that consists of a core of a strong Co-Cr-Mo alloy, an intermediate layer of co-continuous HA/Co-Cr-Mo alloy, and an external coating of porous HA. The purpose of the intermediate layer is to provide good bonding with an external porous HA layer (i.e. HA-to-HA bonding) and with the underlying dense Co-Cr-Mo alloy substrate (i.e., alloy-to-alloy bonding). The intermediate composite layer should provide a more graded transition from pure HA to pure Co-Cr-Mo alloy, so that mechanical separation of the porous HA from the dense Co-Cr-Mo substrate in vivo should be less likely.

The objective of this study is to investigate the feasibility of fabricating the intermediate layer, a dense HA/Co-Cr-Mo alloy composite, with reasonably high mechanical strength using the SMP method.
Figure 2.1: (a) Liquidus projection of Co-Cr-C (b) Phase diagram of Co-Cr-C at 800°C. The scales are in atomic % [55].
Figure 2.2: (a) Liquidus projection for Co-Cr-Mo (b) Co-Cr-Mo phase diagram at 1200°C (the scales are in atomic %). [55].
Figure 2.3: Co-Cr-Mo phase diagrams (a) at 927°C and (b) at 627°C (the scales are in atomic %) [55].
Figure 2.4: (a) Phase diagram of Co-Cr (b) Phase diagrams of Co-Mo [56]
B. EXPERIMENTAL PROCEDURE

i. PRECURSOR PROCESSING

Co-Cr-Mo alloy powder with a median particle size of 135 μm, was obtained from Stellite Coatings (Goshen, IN). The particle size distribution and SEM images are shown in Figure 2.5. The composition of the powder was provided by Stellite Co. in weight percentage. The atomic composition was calculated and the chemical formula for this alloy powder was found to be $\text{Co}_{34}\text{Cr}_{17}\text{Mo}_2$ (see Table 2.5 below). The composition of the alloy conforms to ASTM F75-92. The theoretical density of the 100% dense ASTM F75-92 alloy was measured with the Archimedes method to be 8.358 gm/cm$^3$. An analysis from EPMA of a sintered composite sample is also provided for comparison. This composition was an average of six measurements.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Mo</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder</td>
<td>63.94</td>
<td>28.17</td>
<td>6.07</td>
<td>0.54</td>
<td>0.42</td>
<td>0.35</td>
<td>0.32</td>
</tr>
<tr>
<td>Sample</td>
<td>62.34</td>
<td>31.13</td>
<td>3.64</td>
<td>0.53</td>
<td>0.43</td>
<td>0.37</td>
<td>0.65</td>
</tr>
<tr>
<td>Sintered Sample</td>
<td>62.06</td>
<td>33.10</td>
<td>4.32</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Chemical formula: $\text{Co}_{34}\text{Cr}_{17}\text{Mo}_2$ (derived from the atomic fractions of Co, Cr, and Mo)

Table 2.5: The chemical composition of Co-Cr-Mo powder provided by Stellite Coating compared to the EPMA result obtained from a sintered composite sample.

The same powder metallurgical process mentioned in Chapter 1 was used to produce powder mixtures of metallic calcium, $\beta$-Ca$_3$P$_2$O$_7$, and Co-Cr-Mo powder. As mentioned in Chapter 1, all precursor handling operations (e.g., calcium machining, milling, mixing, pressing) were conducted within the argon atmosphere glove box to allow for reproducible (and safe) processing.
An intimate precursor mixture of calcium and $\beta$-Ca$_2$P$_2$O$_7$ powders was produced as detailed in Chapter 1. This mixture and the Co-Cr-Mo powder (with the desired volume ratio) were then placed within a hardened steel vial along with ~20 ml of hexane, sealed within the argon atmosphere and then mixed for 1 h in the SPEX 8000 ball mill (without using any steel balls as milling media). After mixing, the hexane was removed from the powder by filtration and evaporation in the glove box.

The volume fraction of Co-Cr-Mo alloy within the mixture has a significant effect on the density and formability of the powder mixture, as well as on the mechanical behavior of the converted Co-Cr-Mo/HA bodies. To better understand this effect, precursor mixtures with 50/50, 75/25 and 90/10 volume ratio of Co-Cr-Mo/HA upon conversion were prepared for comparison. The volume fraction of each constituent in these powder mixtures and the calculated theoretical densities of these mixtures, in their precursor and HA-converted states, are provided in Table 2.6.

<table>
<thead>
<tr>
<th>Type</th>
<th>Ca</th>
<th>$\beta$-Ca$_2$P$_2$O$_7$</th>
<th>Co-Cr-Mo alloy</th>
<th>Precursor Density (g/cm$^3$)</th>
<th>HA converted Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>14.91</td>
<td>34.8</td>
<td>50.29</td>
<td>5.516</td>
<td>5.892</td>
</tr>
<tr>
<td></td>
<td>Vol %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Molar ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75/25</td>
<td>4.3</td>
<td>10.1</td>
<td>85.5</td>
<td>6.941</td>
<td>7.156</td>
</tr>
<tr>
<td></td>
<td>Vol %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Molar ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90/10</td>
<td>1.6</td>
<td>3.7</td>
<td>94.7</td>
<td>7.792</td>
<td>7.884</td>
</tr>
<tr>
<td></td>
<td>Vol %</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Molar ratio</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: 1. Theoretical densities of 100% dense HA and Co-Cr-Mo alloy are 3.16 and 8.358 g/cc, respectively.

2. These data for the Co-Cr-Mo alloy are calculated from the formula for this alloy, Co$_{74}$Cr$_{17}$Mo$_{2}$, and its molecular weight: 3079 g/mol.

Table 2.6: The volume percentages and molar ratios of Ca, $\beta$-Ca$_2$P$_2$O$_7$, and Co-Cr-Mo alloy used in the composite precursors.

A 0.5 g or 2.5 g batch of the precursor powder mixture was poured into the hardened steel dies of cylindrical or rectangular shape for pressing into circular disks (13 mm dia. |
x 1-2 mm thick) or bars (30 mm x 7 mm x 5 mm), respectively. The powder within the die was shaken for 3-5 m in both directions to ensure uniform powder distribution inside the die opening prior to insertion of the upper plunger into the die. The die assembly was then subjected to an applied uniaxial stress of 656-1230 MPa with an automatic press. Some Co-Cr-Mo powders were also pressed into bars using 4 wt% of PVA binder.

ii. **Heat Treatments**

The pressed specimens were placed in a magnesia boat and then sealed within a silica tube enclosure inside the argon-atmosphere glove box. The sealed silica enclosure was removed from the glove box and placed within a Lindberg horizontal tube furnace.

a. **Sintering of Co-Cr-Mo alloy powder**

The Co-Cr-Mo alloy powders were fired at temperatures of 850, 950, 1050, and 1150°C in an Ar atmosphere in order to investigate the phase transformation of the Co-Cr-Mo alloy as a function of the annealing temperature. The heating rate was 5°C/m while the cooling rate was 3°C/m. Three pieces of Ti foil were placed within the silica enclosure in the hot zone upstream of the samples to serve as an O₂ getter. One of the three pieces was 100 mm x 50 mm x 0.25 mm in dimension, while the other two were 50 mm x 20 mm x 0.25 mm. An Ametek Thermox (Pittsburgh, PA) TM-1B oxygen sensor was attached to the outlet of the silica enclosure to detect the P₀₂ level of Ar at room temperature and at 1150°C. The P₀₂ level within the silica enclosure at room temperature was 37 ppm. At 1150°C, the P₀₂ level was 4.37 x 10⁻²¹ atm and 1.32 x 10⁻⁹ atm with and without the Ti getter, respectively. At a P₀₂ of 4.4 x 10⁻²¹ atm at 1150°C, calcium could be oxidized, while the chromium and cobalt should not oxidize as demonstrated in the Ellingham diagram (Figure 2.6). To investigate the sintering behavior of the compacted Co-Cr-Mo alloy powder, the bars pressed from this alloy powder were also fired under the same condition together with the composite precursor bars.

b. **Reaction couples of HA-Cr₂O₃**
In order to detect any reaction between HA and CrO$_3$ (i.e., yielding a new oxide compound), reaction couples between these oxides were prepared. The HA powder ($\geq$ 96% pure, $<43 \mu$m size, purchased from Aldrich Chemical Co., Inc. Milwaukee, WI) and CrO$_3$ powder (J. T. Baker Inc., Phillipsburg, NJ, see Table 2.7 for the impurity contents), together with $\sim$ 20 cc of hexane, were mixed within a hardened steel vial for 1 h using the high-energy vibratory mill (without using any steel ball as milling agent). The mixed powder was subsequently pressed into disks and heated at 1100°C in pure, flowing O$_2$ for 7 h. The annealed specimen was mounted and polished to 1 $\mu$m finish for SEM investigation. Powder samples were also prepared from the annealed specimen and analyzed with XRD.

<table>
<thead>
<tr>
<th>Assay CrO$_3$</th>
<th>Insoluble matter</th>
<th>Cl</th>
<th>NO$_3$</th>
<th>SO$_4$</th>
<th>Fe, Al, &amp; Ba</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>100.3%</td>
<td>$&lt;0.002%$</td>
<td>$&lt;0.001%$</td>
<td>0.03%</td>
<td>0.003%</td>
<td>0.03%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

Table 2.7: The impurity content of CrO$_3$.

c. **Heat treatment of 50/50 Co-Cr-Mo/HA composites**

In order to search for a successful heat treatment for fabricating an equivolume HA/Co-Cr-Mo composite, a preliminary set of experiments was conducted.

Thermogravimetric analyses (TGA) (Model TG-171, Cahn Instruments, Inc., Cerritos, CA) were conducted to evaluate the oxidation kinetics of 50-50 composite precursors. Disk-shaped precursor specimens of 13 mm in diameter by 1 mm in thickness were heated in TGA at a rate of 20°C/m to a peak temperature of 500, 600, 950, or 1050°C in flowing, dry oxygen and held at the desired temperature for 12 h. The weight change of the specimens were recorded once every 20 s with the electrical microbalance.
In order to confirm that the Ca + β-Ca$_2$P$_2$O$_7$ + Co-Cr-Mo alloy composite precursor would convert into HA + Co-Cr-Mo alloy, rather than forming other oxide compounds, the 50/50 composite precursor disks were heated separately at 600, 850, 950, or 1050°C in air for 4 h with anneal rates of 20°C/min. A subsequent heat treatment at 1150°C for 10 h in flowing argon atmosphere (PO$_2$ was $1.32 \times 10^{-9}$ atm) was also conducted to densify the composite.

d. **Heat treatment of 75/25 Co-Cr-Mo/HA composites**

A series of experiments were conducted for finding the optimum heat treatments for the Co-Cr-Mo/HA composite precursors that would yield desirable mechanical and biological properties (see CHAPTER 4). Preliminary results suggested that the oxidation or hydration of the precursor prior to sintering of the Co-Cr-Mo alloy would impede the sintering process of the Co-Cr-Mo particles. Thus, a heat treatment that included annealing at 1150°C for 4 h in Ar with $4.37 \times 10^{-21}$ atm PO$_2$, followed by annealing at 850°C for 2 h in moist O$_2$, was used for this study. It was anticipated that a relatively dense body of Co-Cr-Mo + calcium phosphate + CaO should result from the first annealing, and that the calcium phosphate and CaO should be converted into HA after the 2nd annealing. The specimens were cooled to room temperature within the furnace at a rate of 3°C/min after each annealing treatment (See Figure 2.7).

The setup for this heat treatment is the same as that mentioned previously. Ti foils were used as an O$_2$ getter in the 1st annealing so that the oxidation of Co or Cr was avoided and sintering of Co-Cr-Mo would not be retarded. The setup for achieving moist oxygen is the same as that mentioned in Chapter 1B.ii. The calculated P$_{H_2O}$ is this set up was 99.7%. Bar-shaped samples with a dimension of 30 mm x 6 mm x 4 mm were used so that these specimens could be subjected to mechanical tests after various heat treatment steps.

iii. **SPECIMEN CHARACTERIZATION**

a. **Characterization of Co-Cr-Mo powder**

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The morphology of the Co-Cr-Mo powders was investigated by SEM operated in BSE imaging mode, while the crystallographic structure of the powder was analyzed with the XRD. For SEM investigation, the alloy powder was mounted on an aluminum stud with a conducting carbon tape. In the case of XRD analysis, the powders were mounted on a silicon substrate with x-ray transparent grease (high vacuum silicon grease, Dow Corning, Midland, MI).

b. **Density and porosity**

The density and porosity level within the precursor specimens after various processing steps were determined with the same method mentioned in Chapter 1 B.iii.g and C.iv. The densities were calculated from measurements of dry weight and dimensions as well as from Archimede’s method. The porosity levels were estimated from the comparison of these density measurements to the theoretical densities.

c. **Dilatometry**

The linear dimensional changes of the samples during heat treatment were also investigated with the same instrument mentioned in Chapter 1.B.iii.e. Rod-shaped specimens with 10 mm diameter x 25 mm length were heated at a rate of 20°C per min to 950°C in air and held for 10 h at the temperature. Another specimen in bar shape with dimensions of 19.6 x 6.7 x 5 mm³ was heated to 1150°C with the same rate and held for 12 h at this temperature. After anneal, the specimens were cooled in the furnace at a rate of 3°C per min.

d. **Microstructural and Microchemical Analyses**

Microstructural and microchemical information from the Ca+β-Ca₂P₂O₇+Co-Cr-Mo composite precursors and annealed bodies were obtained by optical microscopy, SEM, and EPM with the same methods mentioned in Chapter 1.B.iii.f. At least 5 analyses were conducted with the SEM/EDS on a given phase to obtain an average composition. The WDS analyses were calibrated with the analyses conducted on elemental and compound standards. An apatite standard SMAPT (see Table 1.5 for purity) was used for analyzing
Ca and P. The elemental standards of Co. Cr, and Mo with >99.9% purity were used for analyzing Co. Cr, and Mo contents, respectively. An Anorthite standard (see Table 1.5) was used for analyzing the Si content. At least 8 analyses were performed with the EPMA on a given phase to obtain an average composition.

e. **Macro-DTA**

In order to detect melting during annealing at 1150°C or 850°C, the M-DTA method mentioned in Chapter 1.B.iii.d was used. A 75/25 disk-shaped specimen with 5 g weight was prepared for M-DTA test as per the procedure described in Chapter 1.B.iii.d. The same heat treatment profile mentioned in section B.ii.d of this chapter (Figure 2.7) was employed. However, there was no Ti foil used as O₂ getter in this study. The temperature reading was taken every second during heatup and then switched to every 10 seconds when the temperature was 1150°C.

f. **Microhardness test**

In order to determine the toughnesses of the composite materials after heat treatment, micro-hardness tests were performed using a digital Micro Hardness tester (Buehler Micromet II, Lake Bluff, IL). The test was conducted with 1 kg force using a Vickers indentor. The dwell time after indentation was 25 s. Since the specimen contained Co-Cr-Mo particles of 135 μm median size, the indentation was made either inside the Co-Cr-Mo particles, at the interface of Co-Cr-Mo and HA matrix, or in the HA matrix.

g. **Four point bending test**

A common method to determine the fracture strengths of ceramic-bearing composites is the bending test, because of relative experimental ease. The flexural strength is defined as the maximum stress on the tension side of the bar at failure. This stress is calculated assuming simple beam theory [57].

The four point bending test according to ASTM C1161-94 was conducted on bar shaped specimens. The sample dimensions were approximately 2 mm x 1.5 mm x 25
mm. The surfaces of the samples were polished to 1 μm diamond finish, and all four long edges of each sample were chamfered to 45° (see Figure 2.8).

The bending test was conducted on an MTS machine with a 50-kN tension-compression load cell. The crosshead speed was 2 mm/min. The load and strain were recorded every 0.01 mm of cross head movement until the sample was fractured. The bending strength was calculated according to the equation: 
\[ S = \frac{3PL}{4bd^2} \] where \( P \) is the maximum load, \( L \) is the distance between the span (20 mm in this case), while \( b \) and \( d \) are the width and thickness of the test specimen, respectively (see Figure 2.8).

**iv. Calcium Infiltration**

A piece of Co-Cr-Mo bar pressed with binder was placed on a Mg boat in the silica enclosure with 2 times by weight of Ca shot (≤ 10 mm diameter, ≥ 99% metal basis, Alfa Aesar, Ward Hill, MA) packed around the bar (see Figure 2.9). A flow of 3% H\(_2\)/Ar (PO\(_2\) \(\approx\) 10\(^{-19}\) atm at 950°C) was directed into the silica enclosure with a flow rate of 0.4 cc/s. A piece of Ti foil was placed inside the silica tube as the O\(_2\) getter. The silica enclosure was then inserted inside a horizontal Lindburg tube furnace and heated to 950°C with a rate of 3°C/min and held for 30 min at the temperature. The specimen was then cooled to room temperature at 3°C/min in the furnace. A piece of the sample was cut from the infiltrated bar, polished to 1 μm finish, and investigated with the SEM.
Figure 2.5: (a), (b) Secondary electron images of ASTM Co-Cr-Mo powder and (c) particle size analyses. The median particle size is 135 μm.
Figure 2.6: The Ellingham Diagram showing the standard Gibbs free energy of formation of some selected oxides. The dashed lines correspond to the PO$_2$ levels in the argon atmosphere with and without a Ti getter (4.37 X 10$^{-21}$ atm and 1.32 x 10$^{-9}$ atm at 1150°C, respectively) [59].
Figure 2.7: Heat Treatment for Ca-β-Ca₂P₂O₇ - Co-Cr-Mo Precursor Bars with 75/25 Volume Ratio.

Figure 2.8: (a) Set-up for four point bending tests (b) A typical test result.
Figure 2.9: Schematic showing the set-up for Ca infiltration study.
C. RESULTS

i. CHARACTERIZATION OF CO-CR-MO POWDER

The SEM analyses of the as-received Co-Cr-Mo powder indicated that the powders were spherical in shape with a dendritic structure on the surface (see Figure 2.5), which is consistent with powders produced by spray atomization. The distribution of the particle sizes is also plotted in Figure 2.5c, which indicated that the median size was 135 \( \mu m \).

ii. HEAT TREATMENT OF CO-CR-MO

As shown in the SEM micrographs, the Co-Cr-Mo bar annealed at 1150\(^\circ\)C for 4 h (in order to sinter the Co-Cr-Mo alloy) consisted of a highly porous, but continuous network (see Figure 2.10a and b). Thus, partial sintering has been achieved by this treatment, although more densification is needed to improve the strength.

The XRD analysis on as-received Co-Cr-Mo powder using Si powder as an internal standard indicated that the powder possessed a high temperature structure (fcc) with a lattice parameter of 3.5802\(\AA\) (calculated from the [200] peak of the XRD pattern shown in Figure 2.10c), which is 1.0% larger than the fcc lattice parameter for the pure Co (3.5447\(\AA\)). A phase transformation from fcc to hcp was observed for the Co-Cr-Mo powder heated at a temperature \(\geq 850\)^\(\circ\)C in dry, flowing argon atmosphere with Ti getters (see Figure 2.10c).

Although the fcc is the stable phase at this temperature, the hcp polymorph could have formed from the fcc allotrope during the slow cooling cycle (approximately 3\(^\circ\)C/m) after the isothermal anneal (see section A of this chapter). Increases in the hcp lattice parameters relative to pure, hcp Co were also observed. The \(a\) and \(c\) parameters were 0.94 % and 0.41 % larger, respectively, than the parameters for pure Co (calculated from the [101], [100] and [002] peaks from the XRD pattern of f75 powders after 850\(^\circ\)C. 4 h anneal, see Figure 2.10c). These lattice parameters are summarized in Table 2.8. The XRD analyses also indicated that anisotropic hcp phases were present in the powders after 1050 and 1150\(^\circ\)C anneal.
Table 2.8: The lattice parameters of the fcc and hcp Co-Cr-Mo F75 alloys relative to pure fcc and hcp Co.

### iii. Reactions between HA and Cr₂O₃

The disk samples made of powder mixtures of HA/CrO₃ were red brown in color prior to annealing, but changed to a green color after the 1100°C, 7 h anneal in O₂. This indicated that CrO₃ has been converted to Cr₂O₃ during annealing. In addition, the annealed disk showed a highly porous microstructure. Some of this porosity could have resulted from the decomposition of Cr₂O₃ into vapor forms (CrO, CrO₂, or CrO₃). XRD analysis from the powder collected from the outer surface of the disk (Figure 2.11a) indicated that Cr₂O₃ and TCP were the major phases present in the sample. Formation of TCP could have resulted from dehydration of HA. However, there was no apparent formation of any Ca-Cr-P-O-bearing compound resulting from any interaction between Cr and the calcium phosphates from both XRD and SEM analyses (Figure 2.11).

### iv. Characterization of composite precursors

The powder yields of the mixing operation were > 99% for all three types of composite precursors (calculated from the ratio of the precursor powder weights before and after mixing with the high energy ball mill).

The precursor bars and disks were pressed to approximately 70% of the theoretical densities calculated from the theoretical density of Ca+Ca₃P₂O₇ and the density of F75 powders measured via Archimedes method (see Table 2.9). There is no significant difference in the as-pressed relative density among the three composite precursors. However, the porosity content measured by the NIH image software on a 75/25
composite precursor indicated a much lower porosity value, 5.68%. The discrepancy in porosity measurement could be caused by the smearing of malleable calcium that filled the pores on the surface of the specimen during polishing.

<table>
<thead>
<tr>
<th>Precursor Type</th>
<th>Sample #</th>
<th>Pressure (MPa)</th>
<th>Density (g/cm³)</th>
<th>Porosity (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50 disk</td>
<td>5</td>
<td>980.7 ± 4.3</td>
<td>4.244 ± 1.592</td>
<td>27.92 ± 8.72</td>
</tr>
<tr>
<td>75/25 disk</td>
<td>11</td>
<td>977.8 ± 1.6</td>
<td>4.945 ± 0.386</td>
<td>28.76 ± 5.56</td>
</tr>
<tr>
<td>75/25 bar</td>
<td>4</td>
<td>663.0 ± 0.0</td>
<td>4.899 ± 0.244</td>
<td>28.35 ± 3.18</td>
</tr>
<tr>
<td>90/10 disk</td>
<td>15</td>
<td>977.9 ± 1.4</td>
<td>5.583 ± 0.248</td>
<td>29.42 ± 3.52</td>
</tr>
<tr>
<td>Image analysis</td>
<td>75/25 disk</td>
<td></td>
<td></td>
<td>F75/Ca+Ca₂P₂O₇ = 74.78/20.26 (remainder = porosity)</td>
</tr>
</tbody>
</table>

Table 2.9: The bulk densities for 50/50, 75/25, and 90/10 Co-Cr-Mo/Ca-Ca₃P₂O₇ precursors.

The XRD analyses for phases present in the 50/50, 75/25, and 90/10 HA/Co-Cr-Mo composite precursor and the monolithic precursor are shown in Figure 2.12. Ag was used as the external standard to calibrate for any peak shift due to misalignment or sample geometry. As expected, Ca, β-Ca₂P₂O₇, and the fcc phase of the Co-Mo-Cr solid solution are the predominant phases in the precursors. As the volume fraction of Co-Cr-Mo alloy increases to 75% or more, the relative intensities of the peaks of Ca and β-Ca₂P₂O₇ decreased to levels that were almost not detectable.

A uniform mixture of Co-Cr-Mo alloy with calcium + β-Ca₂P₂O₇ was produced by mixing in the vibratory mill. This is indicated by the SEM image which shows a co-continuous mixture of Co-Cr-Mo alloy particles with the calcium/β-Ca₂P₂O₇ (See Figure 2.13a). The X-ray maps showed that Co, Cr, and Mo were distributed inside the Co-Cr-Mo particles as expected (See Figure 2.13b through e). It was also indicated by the BSE image that an intimate mixture of calcium and β-Ca₂P₂O₇ was achieved during the first
step of mechanical alloying, since the X-ray maps showed uniform distributions of Ca, P, and O throughout the Ca/β-Ca$_2$P$_2$O$_7$ area (See Figure 2.14a through c).

**V. Oxidation of the 50/50 Equivolume Co-Cr-Mo/HA Composite Precursor**

Calcium in the composite precursor could be completely oxidized within 1 h of isothermal anneal at 600°C (see the TGA analyses of the type 50-50 composite precursor disks shown in Figure 2.15a). The asterisk marks on the graphs indicate the onset of isothermal annealing. Significant oxidation of the Co-Cr-Mo alloy took place when the specimen was heated at a temperature above 950°C in the air, as the TGA results indicated more than 9 % wt gain. The specimen heated at 1050°C in the air exhibited even more weight gain (nearly 18 %). The oxidation of the Co-Cr-Mo alloy was accompanied with an expansion in dimension as shown in the Dilatometer results (see Figure 2.15b). A total of 2.4% increase in the linear dimension was observed after the composite bar was heated at 950°C for 10 h.

XRD analyses conducted on the 50/50 composite disks oxidized at 600, 850, 950, and 1050°C for 4 h in ambient air indicated that oxidation at a temperature between 850 to 1050°C in ambient air was sufficient to convert Ca/β-Ca$_2$P$_2$O$_7$ into TCP + HA (See Figure 2.16).

As expected, β-Ca$_2$P$_2$O$_7$, CaO, β-TCP, HA and fcc Co-Cr-Mo were the phases detected in the disk after the 600°C anneal. However, in the sample with 950°C anneal, all the β-Ca$_2$P$_2$O$_7$ and CaO have been convert into TCP and HA. Most of fcc Co-Cr-Mo alloy had also transformed to its hcp polymorph at 850°C. In addition, a new phase, identified as CaMoO$_4$ by XRD pattern (need be verified otherwise) was also present with significant amount within this sample. In the specimen annealed at 950°C, most of the β-TCP had been converted into HA, while the fcc Co-Cr-Mo alloy remained as fcc phase. P$_4$O$_{10}$ phase was also detected as the minor phase present within the sample annealed at 950°C. When the sample was annealed at 1050°C, almost all the β-TCP has converted to HA. In addition, the σ-CoCr phase, Co$_3$O$_4$, and Ca$_2$SiO$_4$ phases were detected rather
than the Co-Cr-Mo alloy or the Cr₂O₃ phases. This results indicated that annealing at 1050°C in ambient air will oxidize the Co-Cr-Mo alloy severely.

Nonetheless, the formation of HA as the predominant phosphate phase in the samples heated at 950°C without formation of other Ca-Cr-Mo-P-bearing compounds demonstrates the feasibility of fabricating the HA/Co-Cr-Mo-bearing composites with the SMP method.

**vi. Dimensional Change for the 75/25 Co-Cr-Mo/HA Composite Precursors After Heat Treatment**

Based on the results discussed in Chapter 4, the 75/25 HA/Co-Cr-Mo composite precursors exposed to a two-stage heat treatment were chosen for further investigation. The 1st state of the heat treatment was a 1150°C, 4 h sintering-anneal. This anneal should enable the formation of a continuous network of Co-Cr-Mo particles that can enhance the mechanical strength of the composite. The sintered composite samples were subsequently subjected to the 2nd state anneal for 2 h at 850°C in moist O₂ to allow for calcium oxidation and for reaction of Ca oxide with calcium phosphates within the specimen to yield HA.

In order to detect the sintering behavior of the composite precursor in the 1st state heat treatment, dilatometry was conducted on a bar-shaped precursor sample in an argon atmosphere using Ti foil as an O₂ getter (PO₂ was 4.37X 10⁻²¹ atm at 1150°C). The linear dimension of the specimen decreased by 2.3 %, 2.5 %, and 3.0 % after 2 h, 4 h, and 12 h, respectively, of isothermal annealing at 1150°C (see Figure 2.16b).

Macrographs of bar-shaped specimens at the precursor stage, after the 1150°C annealing, and after the final 850°C annealing are presented in Figure 2.17. The monolithic counterparts heated under the same conditions are also provided in this figure for comparison.

The typical (averaged) dimensional changes of the composite bar during these heat treatments are shown in Table 2.10 (see Appendix D for detail data). Since there is only 25 volume percent of Ca+Ca₃P₂O₇ within the composite, the theoretical shrinkage upon conversion of Ca+Ca₃P₂O₇ into HA only accounts for 2.2% of the overall volume. This
shrinkage in internal solid volume should contribute to the increase in porosity within the specimen upon HA conversion. Thus, the change in porosity content less 2.2% is calculated for reference (see the column named ΔP -2.2 (%)).

<table>
<thead>
<tr>
<th>Bar Sample State</th>
<th># of Sample</th>
<th>Weight (g)</th>
<th>Length (mm)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Volume (mm^3)</th>
<th>ΔVV_p (%)</th>
<th>Porosity (vol %)</th>
<th>(ΔP-2.2) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>6</td>
<td>2.049 ± 0.23</td>
<td>29.92 ± 0.02</td>
<td>6.66 ± 0</td>
<td>2.06 ± 0.22</td>
<td>410.9 ± 45.1</td>
<td>——</td>
<td>28.1 ± 1.5</td>
<td>——</td>
</tr>
<tr>
<td>1150°C, 4 h in Ar</td>
<td>&quot;</td>
<td>2.032 ± 0.23</td>
<td>29.93 ± 0.02</td>
<td>6.63 ± 0</td>
<td>2.05 ± 0.22</td>
<td>408.3 ± 44.2</td>
<td>-0.62</td>
<td>30.4 ± 1.4</td>
<td>-2.2</td>
</tr>
<tr>
<td>850°C, 2h in H_2O/O_2</td>
<td>&quot;</td>
<td>2.053 ± 0.23</td>
<td>29.92 ± 0.04</td>
<td>6.63 ± 0</td>
<td>2.04 ± 0.26</td>
<td>405.8 ± 53.7</td>
<td>-1.24</td>
<td>29.1 ± 2</td>
<td>-2.2</td>
</tr>
<tr>
<td>precursor</td>
<td>3</td>
<td>5.047 ± 0.24</td>
<td>30.00 ± 0.04</td>
<td>6.70 ± 0</td>
<td>4.78 ± 0.04</td>
<td>962.8 ± 19.4</td>
<td>——</td>
<td>24.4 ± 2.7</td>
<td>——</td>
</tr>
<tr>
<td>1150°C, 4 h in Ar</td>
<td>&quot;</td>
<td>5.022 ± 0.24</td>
<td>30.13 ± 0.03</td>
<td>6.75 ± 0</td>
<td>4.72 ± 0.03</td>
<td>961.6 ± 19.4</td>
<td>-0.13</td>
<td>27.0 ± 3.2</td>
<td>-2.2</td>
</tr>
<tr>
<td>850°C, 2h in H_2O/O_2</td>
<td>&quot;</td>
<td>5.074 ± 0.24</td>
<td>30.06 ± 0.04</td>
<td>6.76 ± 0</td>
<td>4.7 ± 0.04</td>
<td>955.6 ± 14.2</td>
<td>-0.75</td>
<td>25.8 ± 2.5</td>
<td>-2.2</td>
</tr>
</tbody>
</table>

'V_p refers to the bulk (solid + pore) precursor volume. ΔV refers to the difference in bulk volume between the annealed body and the precursor.

ΔP refers to the percentage difference in the pore volume between the precursor and the annealed product.

Table 2.10: Dimensions of bar-shaped specimens at various stages of heat treatment.

vii. XRD: Phase Conversion of 75/25 Co-Cr-Mo/HA Composite Precursor

XRD analyses were conducted on the 75/25 composite sample after a 4 h anneal in argon 1150°C (P_O2 was 4.37X 10^-21 atm), and after the final 850°C. 2 h anneal in moist O_2. The XRD peaks of the 1150°C annealed specimen were associated with HA. fcc and hcp Co-Cr-Mo have alloys. CaO. Co-Cr (sigma phase), (Cr_0.77Co_0.15Mo_0.08)_{23}C_6, Ca_2SiO_4, and β-TCP (see Figure 2.18). It should be noted that hcp HA. CaO and TCP were generated from the interaction between O_2, Ca, and β-Ca_2P_2O_7. The Co-Cr sigma phase is a low-temperature stable phase. The Ca_2SiO_4 peaks indicated that some interaction
between Ca and the alloy had taken place. The carbide \((Cr_{0.77} Co_{0.15} Mo_{0.08})_{23} C_6\) could have been precipitated during the slow cooling cycle.

An additional anneal at 850°C for 2 h in moist \(O_2\) did not show much change in the phosphate phases. However, most of the fcc Co-Cr-Mo had transformed into its hcp allotrope. In addition, the carbide phase was no longer detectable.

**viii. SEM/EDX: MICROSTRUCTURAL AND MICROCHEMICAL ANALYSES OF 75/25 COMPOSITE**

SEM/EDX as well as WDX analyses were conducted on the 75/25 composite specimens after annealing at 1150°C in gettered argon, and after additional annealing at 850°C in moist \(O_2\).

Neck formation between the Co-Cr-Mo particles, as an indication of the first stage of sintering, was observed in the specimen after 1150°C annealing (see Figure 2.19a). The Co-Cr-Mo particles were decorated with dark, irregular-shaped precipitates located within 20 \(\mu m\) from the outer edges of the particles (see Figure 2.19b and c). These dark particles were identified as \(Ca_2SiO_4\) by both the EDX and WDX analyses (see the EDX spectrum in Figure 2.19d and the EDX and EPMA analyses in Table 2.11). An interaction layer around the Co-Cr-Mo particles was also identified to be \(Ca_2SiO_4\) (as marked in Figure 2.19c and e and indicated in Table 2.11). It should be noted that, due to the beam sweeping of the EPMA, the Co and Cr elements were detected from the adjacent area while conducting the analysis on the \(Ca_2SiO_4\) phase. This problem was not present when the EDX analysis was conducted on the \(Ca_2SiO_4\) phase.

Some white precipitates, enriched in Cr and P, were present within the HA matrix (see Figure 2.20a and c). These precipitates possessed an atomic ratio of \(Ca:Co:Cr:P:O = 2:2:8:7:6\). Such analyses were consistent with mixtures of Co-Cr alloy with some \(Cr_2O_3\) and \(Ca_3P_2O_8\). Other white, coarse precipitates shown in Figure 2.20a and b was a Ca-Cr-O rich phase (CaCrO_3). This phase could be the product of the reaction between CaO and Cr at 1150°C.

EDX analyses have also been conducted at six locations each within the Co-Cr-Mo particles and HA-bearing matrix. The EDX analyses in the Co-Cr-Mo regions showed
Co:Cr:Mo:Si = 64:32:3.6:0.9, which was similar to the composition provided by the vendor for the as-received powders. The analyses in the HA area (See Figure 2.20d) revealed two Ca/P ratios. Six of the analyses indicated Ca/P = 1.68 while three others (taken from areas that were slightly brighter in the BSE image) showed Ca/P = 1.8-2.0. These results suggest that either some HA-bearing regions were enriched in Ca, or Ca₄P₂O₉ existed along with HA, although it was not detected by the XRD analyses. The composition analyses of various phases via EDX or EPMA are summarized in Table 2.11. Each Co-Cr-Mo alloy and HA composition was obtained from an average of five to eight measurements as noted with a quote in the "Instrument" column.

The BSE image and x-ray maps of Co, Cr and Mo from a specimen after 1150°C annealing are shown in Figure 2.21a through d. The maps of Ca, Si, O, and P taken from the same region are shown in Figure 2.22a through d. There was a Mo-enriched region located near the outer edge of the Co-Cr-Mo particles. The dark, irregular shaped precipitates previously identified as Ca₂SiO₄ were confirmed by the dop maps (only Ca, Si, and O are found in these regions).

After an additional anneal at 850°C, the dark Ca₂SiO₄ precipitates that decorated the edges of Co-Cr-Mo particles were still present (see Figure 2.23 and Figure 2.25). The X-ray maps of Co, Cr, Mo, Ca, Si and P taken from the region shown in Figure 2.23c are shown in Figure 2.24. These images exhibit five different phases: A) Ca₂SiO₄ shown as the dark precipitates. B) Co₇₇Cr₂₂Mo₄P₁₈Cx, P-enriched gray phase surrounding the Ca₂SiO₄. C) Mo-enriched σ (Co-Cr+Mo) shown as the bright phase. D) the Co-Cr-Mo alloy. and E) the lamellar M₃₃C₆/σ (Co-Cr+Mo) phase. The normalized chemical compositions of these phases (disregarding C and O) are shown in Table 2.12.

It should be noted that the Co₇₇Cr₂₂Mo₄P₁₈Cx phase contains nearly 44.65 atomic % of C based on EDX analyses.

ix. MACRO-DTA

Macro-DTA was conducted on a 75/25 Co-Cr-Mo/HA composite precursor disk (pressed around a thermocouple) to detect any melting during annealing at 1150°C and
850°C. The temperature reading taken while the sample was heated at 1150°C shows no clear endothermic reaction (Figure 2.26).

<table>
<thead>
<tr>
<th>Phase</th>
<th>Instrument</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Ca</th>
<th>P</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Cr-Mo</td>
<td>EPMA (8)</td>
<td>63.23</td>
<td>32.50</td>
<td>3.69</td>
<td>0.58</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>± 1.00</td>
<td>± 0.65</td>
<td>± 0.36</td>
<td>± 0.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-Cr-Mo</td>
<td>EDX (5)</td>
<td>63.69</td>
<td>31.76</td>
<td>3.60</td>
<td>0.95</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>± 0.71</td>
<td>± 0.41</td>
<td>± 0.28</td>
<td>± 0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca$_2$SiO$_4$</td>
<td>EPMA (1)</td>
<td>3.86</td>
<td>1.52</td>
<td>0.19</td>
<td>13.63</td>
<td>23.23</td>
<td>0.11</td>
<td>57.46</td>
</tr>
<tr>
<td>Ca$_2$SiO$_4$</td>
<td>EDX (1)</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>13.55</td>
<td>30.06</td>
<td>0.00</td>
<td>56.39</td>
</tr>
<tr>
<td>HA (dark)</td>
<td>EDX (6)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>24.25</td>
<td>14.42</td>
<td>61.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 1.49</td>
<td>± 0.82</td>
<td>± 2.29</td>
</tr>
<tr>
<td>C$_4$P</td>
<td>EDX (6)</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>28.07</td>
<td>15.15</td>
<td>56.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 4.17</td>
<td>± 1.75</td>
<td>± 5.84</td>
</tr>
</tbody>
</table>

Note: All the data are presented in atomic percent.

Table 2.11: Composition of various phases from EDX and EPMA.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Instrument (### of anal.)</th>
<th>Co</th>
<th>Cr</th>
<th>Mo</th>
<th>Si</th>
<th>Ca</th>
<th>P</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>Co$<em>2$Cr$</em>{22}$Mo$<em>4$P$</em>{18}$C$_x$</td>
<td>EDX (2)</td>
<td>37.15</td>
<td>30.62</td>
<td>5.48 ± 0.09</td>
<td>0.00</td>
<td>1.64 ± 2.32</td>
<td>25.09 ± 5.74</td>
</tr>
<tr>
<td>C</td>
<td>σ (Co-Cr+Mo)</td>
<td>EDX (4)</td>
<td>47.68</td>
<td>37.23</td>
<td>9.43 ± 0.42</td>
<td>0.00</td>
<td>0.59 ± 0.52</td>
<td>5.04 ± 0.62</td>
</tr>
<tr>
<td>D</td>
<td>Co-Cr-Mo</td>
<td>EDX (2)</td>
<td>85.37</td>
<td>30.73</td>
<td>3.41</td>
<td>0.00</td>
<td>0.27 ± 0.38</td>
<td>0.2 ± 0.29</td>
</tr>
<tr>
<td>E</td>
<td>M23C6</td>
<td>EDX (1)</td>
<td>12.40</td>
<td>75.13</td>
<td>0.00</td>
<td>0.71</td>
<td>1.51</td>
<td>10.24</td>
</tr>
</tbody>
</table>

Table 2.12: Composition of various phases in the bar specimen after 850°C 2 h anneal.
x. **Calcium Infiltration**

The calcium infiltration test was conducted to determine whether calcium would wet the Co-Cr-Mo alloy and thereby assist in the compaction of the Co-Cr-Mo particles within the Co-Cr-Mo/Ca-β-Ca₃P₂O₇ composite precursor.

The SEM/EDX analyses of the infiltrated specimen are shown in Figure 2.27. The infiltrated calcium filled the porosity between the Co-Cr-Mo particles, and the resulting capillary force enhanced the compaction of Co-Cr-Mo particles. Some necking of the Co-Cr-Mo particles can be seen in Figure 2.28a. This partial sintering is considered to have resulted from the capillary force of the liquid calcium. The original particles are drawn in dashed circles for reference (Figure 2.28a). There is also evidence that some dissolution occurred in the liquid calcium, since C and Si, the minor constituents within the Co-Cr-Mo alloy, had precipitated within the Ca region (Figure 2.27c and d). Ca₃SiO₇ was also found in some calcium-infiltrated areas (Figure 2.27b and f).

xi. **Mechanical Tests**

a. **Microhardness Test**

The results of microhardness tests are summarized in Table 2.13. As shown in this table, the hardnesses for Co-Cr-Mo particles after the 1150°C anneal are much higher than that for the HA matrix (RC 22.2 to 41.7 for the Co-Cr-Mo versus RB 38 or less for the HA). In addition, the Co-Cr-Mo particles within the final heat-treated specimen (after the 850°C anneal) are about twice as hard as their counterparts within the as-sintered (1150°C) specimen. Such an increase in hardness is consistent with the formation of the carbide phases seen in Figure 2.23 and Figure 2.25, as have been reported by several authors [14, 17-19].

There were no observable cracks produced by the indentor. Thus, an estimate for the fracture toughness of the composite bodies via the microhardness test could not be obtained.

b. **Four Point Bending**
In order to comply to the ASTM standard, the post-heat treatment bar samples were cut into four pieces longitudinally, polished on all faces, and chamfered along all of the four long edges. The set up for bend testing and a load-displacement curve from one of the tests are presented in Figure 2.8. A total of six bars were tested and their average bending strength was found to be 44.1 ± 32.3 MPa (see Table 2.14 for raw data). Two HA bars were also tested with the same procedure and their average bending strength was 29 MPa. These results suggest that the composite material did not achieve much higher strength than the monolithic HA.

<table>
<thead>
<tr>
<th>Measure -ment</th>
<th>1150°C, 4h in Ar</th>
<th>850°C 4h in moist O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inside a Co-Cr-Mo particle (RC)</td>
<td>Inside a Co-Cr-Mo particle (RC)</td>
<td>Inside a Co-Cr-Mo particle (RC)</td>
</tr>
<tr>
<td>Between Co-Cr-Mo and HA (RB)</td>
<td>Between Co-Cr-Mo and HA (RB)</td>
<td>Between Co-Cr-Mo and HA (RB)</td>
</tr>
<tr>
<td>HA matrix (RB)</td>
<td>HA matrix (RB)</td>
<td>HA matrix (RB)</td>
</tr>
<tr>
<td>1</td>
<td>28.5</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>23</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>28.1</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>32.2</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>30.2</td>
<td>74</td>
</tr>
<tr>
<td>6</td>
<td>32.6</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>27.7</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>41.7</td>
<td>82.3</td>
</tr>
<tr>
<td>9</td>
<td>28.5</td>
<td>77.2</td>
</tr>
<tr>
<td>10</td>
<td>22.2</td>
<td>55.5</td>
</tr>
<tr>
<td>Average</td>
<td>28.55</td>
<td>62.35</td>
</tr>
<tr>
<td>Std.Dev.</td>
<td>5.73</td>
<td>15.68</td>
</tr>
</tbody>
</table>

Table 2.13: Results of microhardness tests on the 75-25 composite.

<table>
<thead>
<tr>
<th>Sample #:</th>
<th>Com-1</th>
<th>Com-2</th>
<th>Com-3</th>
<th>Com-4</th>
<th>Com-5</th>
<th>Com-6</th>
<th>HA-1</th>
<th>HA-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width (mm)</td>
<td>1.81</td>
<td>1.7</td>
<td>2.18</td>
<td>2.17</td>
<td>2.26</td>
<td>2.28</td>
<td>2.44</td>
<td>1.60</td>
</tr>
<tr>
<td>Thick (mm)</td>
<td>1.29</td>
<td>1.19</td>
<td>1.83</td>
<td>1.17</td>
<td>1.8</td>
<td>1.92</td>
<td>2.25</td>
<td>2.54</td>
</tr>
<tr>
<td>Max load (Nt)</td>
<td>4.95</td>
<td>5.23</td>
<td>32.80</td>
<td>7.22</td>
<td>37.3</td>
<td>14.9</td>
<td>25.1</td>
<td>18.8</td>
</tr>
<tr>
<td>MPa</td>
<td>24.7</td>
<td>32.6</td>
<td>67.40</td>
<td>36.5</td>
<td>76.4</td>
<td>26.8</td>
<td>30.6</td>
<td>27.4</td>
</tr>
</tbody>
</table>

Table 2.14: Results of four point bend test on the 75-25 composite.
Figure 2.10: (a) and (b) SEM Images of a sintered Co-Cr-Mo bar, and (c) X-ray Diffraction Patterns of Co-Cr-Mo sintered at various temperature (cooling rate to room temperature was 3°C/m).
Figure 2.11: (a) XRD and (b) and (c) BSE images of disk-shaped samples of HA/Cr$_2$O$_3$ mixtures heated at 1100°C for 7 h in O$_2$. Cr$_2$O$_3$ and TCP are the only phases present after heat treatment.
Figure 2.12: X-Ray diffraction patterns of various composite precursors compared to the monolithic HA precursor.
Figure 2.13: BSE images and X-Ray maps of a 75/25 composite bar at the precursor stage.
Figure 2.14: X-Ray maps of the 75/25 composite bar at the precursor stage.
Figure 2.15: (a) Oxidation kinetics of 50/50 Ca-β-Ca$_2$P$_2$O$_7$ /Co-Cr-Mo precursor disks (72% dense, 13 mm diameter x 2 mm thickness) in ambient air. (b) Dimensional changes of a composite rod heated for 10 h at 950°C in ambient air. The rod was 10 mm in diameter x 25 mm in length. The anneal was conducted at a rate of 5°C/min, while cooling was at 3°C/min.
Figure 2.16: (a) X-ray diffraction patterns of 50/50 composite disks before and after heat treatment; (b) Linear dimension change for a 75/25 Co-Cr-Mo/HA bar specimen heated at 1150°C in Ar. The precursor bar was 30 x 6.7 x 4 mm in dimensions.
Figure 2.17: Optical images of 75/25 Co-Cr-Mo/HA composite precursor specimens (a through c) and a monolithic bar (d through f) at the precursor stage (a and d), after a 1150°C, 4 h anneal (b and e), and after a final 850°C, 2 h anneal (c and f).
Figure 2.18: (a) X-ray diffraction patterns for 75/25 Co-Cr-Mo/HA bars after sintering at 1150°C in gettered Ar showing formation of CaO, HA and $\beta$-C$_3$P from Ca and $\beta$-C$_3$P. (b) X-ray diffraction patterns for 75/25 HA/Co-Cr-Mo bars after annealing at 850°C in $O_2/H_2O$. 

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Figure 2.19: BSE images and EDX analysis of a 75/25 Co-Cr-Mo/HA specimen after 4 h annealing at 1150°C in Ar (a) a low magnification image showing partial sintering of Co-Cr-Mo particles; (b), (c), and (e) higher magnification images showing the Ca$_2$SiO$_4$ located near the edges of Co-Cr-Mo particles and at the Co-Cr-Mo/HA interfaces.
Figure 2.20: BSE Image and EDX analysis for 75/25 Co-Cr-Mo/HA specimen after 4 h annealing at 1150°C in Ar (a) an image showing Co-Cr-Mo particles within the HA matrix; (b) and (c) the EDX analyses on the coarse, irregular-shaped and fine, dispersed white precipitates, respectively; (d) an image of the HA matrix showing different contrast.
Figure 2.21: SEM Images and X-ray maps of Co, Cr, and Mo for 75/25 HA/Co-Cr-Mo bars after 4 h annealing at 1150°C in Ar.
Figure 2.22: X-ray maps of Ca, Si, P, and O for 75/25 HA/Co-Cr-Mo bars after 4 h annealing at 1150°C in Ar.
Figure 2.23: BSE images for 75/25 HA-F75 bars after final 2 h annealing at 850°C in moist O₂ (a) a low magnification view showing partial sintering between Co-Cr-Mo particles. (b) through (d) higher magnification images revealing various phases present near the outer edges of the Co-Cr-Mo particles.

A: Ca₂SiO₄
B: Co₀.₇₆Cr₀.₂₂Mo₀.₄₁ₐ₉C₁
C: σ (Co-Cr-Mo), enriched in Mo
D: Co-Cr-Mo alloy
E: Lamilla of M₂₃C₆ and Mo, Cr-rich phase
Figure 2.24: X-ray maps for 75/25 HA-F75 bars after final 2 h annealing at 850°C in Moist O₂, taken from the region shown in Figure 2.23c.
Figure 2.25: SEM Image(a) and EDX analyses (b and c) for 75/25 HA-F75 bars after final 2 h annealing at 850°C in moist O₂ showing the elements within different phases.
Figure 2.26: (a) M-DTA test of 75-25 precursor at 1150°C in argon atmosphere, $P_{O_2} = 1.32 \times 10^{-9}$. (b) is an enlargement of (a), showing the curves above 1000°C.
Figure 2.27: BSE images of calcium infiltrated Co-Cr-Mo alloy. (a) A low magnification image shows that Ca infiltrated through all the spacing between the Co-Cr-Mo particles within a pressed bar of Co-Cr-Mo alloy; (b) through (d) shows precipitation of Ca$_2$SiO$_4$, C, and Si particles from the alloy; (e) through (g) EDX analyses on the infiltrated Ca, Ca$_2$SiO$_4$ and Si, respectively.
Figure 2.28: BSE image and X-ray maps of a Ca infiltrated sample showing evidence that Co-Cr-Mo particles were sintered with the aid of liquid Ca.
D. Discussion

i. Free energy of formation

Thermodynamic analyses were conducted to make sure that the mixture of Co-Cr alloy with Ca+β-Ca₂P₂O₇ precursor would not undergo displacement reactions to yield oxide products of Co or Cr. The Gibb’s free energies of reaction for the reduction of β-TCP by Co or Cr to produce CoO, Co₃O₄, or Cr₂O₃, respectively, are presented graphically in Figure 2.30. All the free energy data are obtained from Barin [60] at standard state (1 atm). As shown in these graphs, Co or Cr should not reduce β-TCP at the annealing temperatures used in this study. Since HA is a more stable phase than β-TCP at the heat treatment temperatures used in this work, it is safe to assume that the reduction of HA by Co or Cr also should not occur.

ii. Reaction between HA/Cr₂O₃

The results of the HA/CrO₃ experiment indicated that TCP, CaO and Cr₂O₃ were the phases present after the 1100°C 7 h anneal in O₂. There was no formation of CaCr₂O₄ or CaCrO₄ resulting from this annealing treatment, indicating that TCP and Cr₂O₃ are compatible at 1100°C.

iii. Oxidation kinetics in ambient air

The weight gain of the composite precursor specimen in the TGA after 20 h of annealing at 600°C (1.65%) agreed with the calculated weight gain (1.67%) expected for oxidation of the metallic calcium inside the precursor mixture. Thus, no significant oxidation for Cr or Co was detectable at 500-600°C, although thin films of Cr₂O₃ could have formed at the interfaces between the Co-Cr-Mo particles and the phosphate matrix. The dramatic increase in weight of precursors heated at 950 and 1050°C in air indicated that the rate of Cr/Co oxidation had increased significantly with temperature.
iv. **Phase formation at 1150 and 850°C H/T**

The XRD results show that HA was the predominant calcium phosphate phase within the 75/25 composite specimens after 1150°C annealing in Ar. From the Ellingham diagram, oxidation of Ca at this $P_{O_2}$ ($4.37 \times 10^{-21}$ atm) is possible. Thus, it can be postulated that CaO had reacted with $\beta$-Ca$_2$P$_2$O$_7$ to form HA and TCP during the 1150°C heat treatment. HA formed under this condition is called Oxi-HA as stated in Chapter 1D.vi.

The results of SEM analyses on the fully heat treated sample indicated the presence of (A) calcium silicate, Co$_{27}$Cr$_{22}$Mo$_4$P$_{18}$C$_x$, (B) P-enriched gray phase surrounding the Ca$_2$SiO$_4$, (C) Mo-enriched $\sigma$ (Co-Cr+Mo) shown as the bright phase, (D) the Co-Cr-Mo alloy, and (E) the lamella $M_{23}C_6/\sigma$ (Co-Cr+Mo) phase. Among these phases, the $\sigma$ (Co-Cr+Mo) and the lamella $M_{23}C_6/\sigma$ (Co-Cr+Mo) phases had also been characterized by Sande [18]. Formation of Ca$_2$SiO$_4$ and the Co$_{27}$Cr$_{22}$Mo$_4$P$_{18}$C$_x$ phases could be due to the reactions between Ca, P of the calcium phosphates and the Co-Cr-Mo alloy. Since the reaction occurred within 20μm from the edges of the Co-Cr-Mo particles, which could establish chemical bounds between the HA and Co-Cr-Mo particles and thereby enhance the mechanical strength of the composite.

v. **Heat-treatment-hardened Co-Cr-Mo particles**

The microhardness test results indicated that the Co-Cr-Mo particles within the hydrated (850°C) specimens were twice as hard as their counterparts within the as-sintered (1150°C) specimens. As reported by Kilner [17] and Silence [19], the typical heat treatment for cast-F75 materials includes a prolonged solution treatment at a temperature of 1200°C to dissolve all the secondary phases, followed by a lower temperature (650 - 850°C) aging treatment to cause precipitation of the $M_{23}C_6$ carbides and consequent strengthening. The heat treatment used to fabricate the 75-25 composite in this study also had a high temperature step (1150°C, 4 h) that could serve as the solution treatment for the Co-Cr-Mo material, and a hydration cycle at 850°C that could
induce the precipitation of carbide phases in the Co-Cr-Mo grains and at grain boundaries. Thus, a strengthening of Co-Cr-Mo was achieved by this heat treatment.

**vi. Liquid phase assisted sintering**

The first annealing cycle for the 75-25 composite precursor was conducted at 1150°C, a temperature higher than the melting point of calcium. Thus, unoxidized calcium should be in liquid form at this temperature. Although the M-DTA result was inconclusive, the evidence from the calcium infiltration study (showing the precipitation of C and Si, which were also found in the composite specimen after 1150°C anneal) suggested that calcium was in liquid form at this temperature and components of the Co-Cr-Mo alloy had dissolved in the Ca solution.

It is believed that presence of liquid calcium enhanced the compaction of Co-Cr-Mo particles. As explained by Kingery et al [61, 62], for liquid-phase sintering to take place, it is essential to have (1) an appreciable amount of liquid phase, (2) an appreciable solubility of the solid in the liquid, and (3) wetting of the solid by the liquid. The driving force for densification is derived from the capillary pressure of the liquid phase located between the fine solid particles. The capillary pressure results in densification in a series of steps. First, upon formation of a liquid phase, there is a rearrangement of particles to give a more effective packing. This process can lead to complete densification with a sufficient amount of liquid. Secondly, at contact points between particles, high local stresses lead to selective dissolution, which allows for further rearrangement. A transfer of material away from the contact points occurs, allowing the center-to-center distance between particles to be decreased and densification to take place.

As mentioned earlier, metallic calcium should be present as liquid phase at 1150°C. At the 1150°C sintering stage, there could be as much as 7.5% in volume of liquid calcium involved in the sintering process (assuming all the calcium within the composite precursor had remained in liquid form). As demonstrated in Figure 2.27 and 2.28, the liquid calcium wet the Co-Cr-Mo particles. It is also demonstrated that Si and C were precipitated as single phases outside of the Co-Cr-Mo particles (Figure 2.27). Since the
Co-Cr-Mo particles were relatively large, liquid-phase-assisted sintering could not be completed within 4 h.

vii. Low Bending Strength of the Composite

The results of bending tests indicated that, although the bending strength of HA is comparable to the published value (29 MPa versus 15-35 MPa for a 60% dense HA, see Table 1.1), the 75/25 Co-Cr-Mo/HA composite did not have much higher strength (47 MPa) than its monolithic HA counterpart. However, these tests do not reflect the strength that a 75/25 composite could achieve. There are several characteristics of these particular test samples that need to be noted:

Firstly, the composite specimens were made with Co-Cr-Mo particles of 135 μm median size, while the thickness of the bend test samples were in the range of 1.2 to 1.5 mm. That is, the bar thickness were ≤ 10 times the size of an average Co-Cr-Mo alloy particle.

Secondly, the composite precursor bars were only 75% dense, and only partial densification was achieved upon annealing up to 1150°C.

However, this study serves as the base line for fabrication of a Co-Cr-Mo/HA composite. Further improvement of the mechanical strength by utilizing warm compaction and/or HIPping of the precursor powder to achieve a > 95% density is very probable.
Figure 2.29: (a) Ca-Co phase diagram [63]. (b) CaO-CoO phase diagram (c) CaO-Cr₂O₃ phase diagram [56]
Figure 2.30: Free energy of reaction between Co, Cr and phosphate compare to the oxidation of calcium at temperatures between 1000 and 1500°K.
E. Conclusions

1. High yields (>99%) of intimately-mixed powders of Ca + β-Ca$_2$P$_2$O$_7$ + Co-Cr-Mo alloy were obtained by mechanical alloying/mixing.

2. Shaped green bodies with relative densities of 75–80% were prepared by uniaxial pressing/machining.

3. Annealing at 1150°C for 4 h in Ar and 850°C for 2 h in moist O$_2$ yielded ~70% dense HA/Co-Cr-Mo composites with a maximum bending strength of 76.4 MPa. Partial sintering of Co-Cr-Mo was achieved at 1150°C.

4. The precursor with 25 Ca+Ca$_2$P$_2$O$_7$ +75 Co-Cr-Mo alloy can be transformed into a composite of HA + Co-Cr-Mo alloy with small (≤ 1.5 %) dimensional changes.

5. Based on the microhardness measurements, the 850°C annealing has strengthened the Co-Cr-Mo particles, which could be attributed by both the phase transformation of fcc Co-Cr-Mo into the hcp allotrope and the precipitation of M$_{23}$C$_6$.

6. Powder compact reaction couple of HA/CrO$_3$ annealed at 1100°C in air resulted in TCP and Cr$_2$O$_3$ phases. No Ca-Cr-P-bearing compounds were detected within the product. These results reassured the compatibility between HA and Cr$_2$O$_3$ (or between HA and the Co-Cr-Mo alloy since Cr is the most active element within the Co-Cr-Mo alloy).

F. Future Work

1. Utilize finer particle size of Co-Cr-Mo alloy and/or optimize heat treatments for desired density/strength of the Co-Cr-Mo alloy phase.

2. Optimize phase sizes/heat treatments so as to obtain the desired pore size.

3. Functionally grading the Co-Cr-Mo and Ca/Ca$_2$P$_2$O$_7$ in the precursor, to obtain a graded HA/Co-Cr-Mo alloy upon transformation.
G. References


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CHAPTER 3

KINETIC STUDIES OF THE FORMATION OF HYDROXYAPATITE
FROM CALCIUM OXIDE AND CALCIUM PYROPHOSPHATE

A. INTRODUCTION

i. BIOLOGICAL PERFORMANCE AND APPLICATIONS OF HA AND TCP

As described in Chapter 1 and Chapter 2, Hydroxyapatite (HA), Ca\(_{10}(PO_4)_6(OH)_2\), has received significant attention in the orthopedic implant industry [1] owing to its high degree of biocompatibility with biological systems. HA has a similar chemical composition and structure to the mineral components found in bones and teeth. Porous HA-bearing or HA-coated implant devices enable the ingrowth of tissues into the implants and biofixation between the tissues and the implants under physiological conditions [1]. HA powders have been prepared for dental fillings or for coatings on orthopedic devices. HA bodies have also been fabricated for applications in the middle ear.

β-Tricalcium phosphate (Ca\(_3\)P\(_2\)O\(_8\), β-TCP hereafter) is a solid precursor phase for the formation of HA (e.g. β-TCP can be reacted with CaO and H\(_2\)O to form HA). In the physiological environment, TCP is also a bioactive calcium phosphate. TCP ceramics are more active and biodegradable than HA in biological systems. Under physiological conditions, TCP will gradually be resorbed and substituted by newly grown bone with the HA structure, which is highly desirable in certain medical applications [2].

ii. SYNTHESIS OF HA VIA SMP METHOD

Previous work at OSU has demonstrated that near net-shaped HA-bearing bodies can be successfully synthesized from a precursor mixture of Ca and β-Ca\(_2\)P\(_2\)O\(_7\) or Ca + β-
Ca$_2$P$_2$O$_7$ + Co-Cr-Mo alloy via a solid, metal-bearing precursor (SMP) method (see Chapters 1 and 2).

The precursor for the synthesis of monolithic HA (Chapter 1) was an intimate mixture of Ca and \( \beta \)-Ca$_2$P$_2$O$_7$ prepared by high-energy mechanical alloying. The molar ratio of Ca to \( \beta \)-Ca$_2$P$_2$O$_7$ in such a precursor was 4:3, which was consistent with the stoichiometry of HA. The precursors to HA/Co-Cr-Mo alloy composites (Chapter 2) were blended mixtures of the mechanically-alloyed Ca + \( \beta \)-Ca$_2$P$_2$O$_7$ with spray atomized Co-Cr-Mo alloy powders in a volume ratio that would yield a composite body consisting of 25 vol% HA and 75 vol% Co-Cr-Mo alloy upon conversion. The malleable Ca-\( \beta \)-Ca$_2$P$_2$O$_7$ (or Ca+\( \beta \)-Ca$_2$P$_2$O$_7$+F75) powder mixture could be compacted, formed into desired shapes by uniaxial pressing and machining, and then converted into HA or HA/Co-Cr-Mo alloy composite bodies through a series of isothermal heat treatments.

In the case of monolithic HA, the precursor specimen could be exposed to flowing oxygen at \( \leq 600^\circ \text{C} \) to completely oxidize the calcium within the precursor. Post-oxidation annealing at \( \leq 1150^\circ \text{C} \) in a water-vapor-bearing atmosphere yielded (XRD) phase-pure HA (see Chapter 1).

Another heat treatment route has been developed to synthesize HA/Co-Cr-Mo composite bodies from Ca+\( \beta \)-Ca$_2$P$_2$O$_7$+F75 alloy precursors (Chapter 2). The precursor was first exposed to flowing argon at 1150°C for 4 h to allow for partial sintering of the Co-Cr-Mo particles within the composite precursor. This heat treatment yielded samples consisting of HA, CaO, \( \beta \)-TCP, and Co-Cr-Mo phases. The samples were further annealed in flowing, moist O$_2$ at a peak temperature of 850°C to allow for conversion of CaO and \( \beta \)-TCP into HA.

Although syntheses of HA by liquid phase methods (including sol-gel synthesis and hydrothermal synthesis) have been extensively studied [3] and the kinetics for these processes have also been reported [4], the rate of HA formation from solid state methods, particularly the transformation from Ca + \( \beta \)-Ca$_2$P$_2$O$_7$ or CaO + \( \beta \)-TCP precursors, has not been well studied.
The kinetics for the oxidation of calcium has been studied via TGA. The metallic calcium within a 2 mm thick Ca+β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7} precursor body can be completely oxidized within 3 h at 600°C (see Chapter 1). Since the oxi-apatite can be formed in a dry environment [3], the weight change from the intake of H\textsubscript{2}O can not be used to monitor the formation of the apatite. Thus, the kinetics for reaction of CaO and β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7}, or CaO and β-TCP, into HA can not be accurately determined via TGA. In this chapter, a model and the corresponding experimental design for evaluating the rate of HA formation at various temperatures in a flowing dry or moist oxygen environment are presented. Both powder compacts (spherical reaction couples) and planar reaction couples of CaO and β-TCP were used to determine the rate of HA formation.

### iii. Defects and Electrical Properties of HA

As is true in many other solids, point defects, line defects, and volume defects have been found in HA in the forms of vacancies, dislocations [5], and porosity.

At an elevated temperature, HA undergoes partial dehydration of its lattice hydroxide ions. This dehydration results in a time-dependent change in conductivity above 700°C [6]. The conduction was reported to be purely protonic by measurement with a hydrogen concentration cell [6]. The protonic conductivity increased to a high value of 10\textsuperscript{6} S/cm at the initial stage of dehydration then decreased with further dehydration. This change in conductivity was reversible. This observation indicated the importance of supplying H\textsubscript{2}O vapor during annealing [6].

### iv. Diffusion in HA

The diffusion coefficients for Ca\textsuperscript{2+} and PO\textsubscript{4}\textsuperscript{3-} measured in vapor-deposited fluoride apatite (FA) films between 1000 and 1800°K, and the diffusion coefficient for OD\textsuperscript{-} measured with IR spectroscopy in an FA crystal above 1250°K, have been reported [7-9] to be:

\[
\begin{align*}
\text{Ca}^{2+}: & \quad D_{\perp} = 1.28 \times 10^{4} \exp(-6.0 / kT) + 7.92 \times 10^{4} \exp(-1.15 / kT) \text{cm}^{2}/\text{s} \\
& \quad D_{//} = 9.3 \times 10^{6} \exp(-5.64 / kT) + 3.6 \times 10^{-3} \exp(-2.46 / kT) \text{cm}^{2}/\text{s}
\end{align*}
\]
PO$_4^{3-}$: \[
\begin{align*}
D_\perp &= 3.6 \times 10^{-12} \text{ cm}^2/\text{s} \\
D_{//} &= 1.2 \times 10^{-12} \text{ cm}^2/\text{s}
\end{align*}
\] at 1700°K \hspace{1cm} (3.2)

\[\text{OH}^-(\text{OD}^-): 2 \times 10^{11} \text{ cm}^2/\text{s}, \text{ for parallel or perpendicular direction at 1700°K} \hspace{1cm} (3.3)\]

where $\perp$ and $//\,$ represent the directions perpendicular or parallel to the $a$ $b$ plane of the unit cell.

Since FA and HA have similar crystal structures (hexagonal vs. pseudo-hexagonal structure), the self diffusion coefficients of these ions in HA should be similar to those in FA [6].

\textbf{v. HA FORMATION}

HA formation is generally preceded by the formation of one or more intermediate phases. The reported sequence of phases precipitated from a supersaturated aqueous solution is amorphous calcium phosphate followed by crystalline dicalcium phosphate dihydrate (CaHPO$_4$ \cdot 2H$_2$O) $\rightarrow$ octacalcium phosphate (Ca$_8$H$_2$(PO$_4$)$_6$.5H$_2$O) $\rightarrow$ HA [4]. In the solid-state synthesis of HA from CaCO$_3$ and (NH$_4$)$_2$HPO$_4$ powders, the intermediate phase was found to be $\beta$-TCP [10]. In that study, $\beta$-TCP formed at 750°C, prior to the formation of a carbonate-bearing HA at 1000°C. Another study using hydrothermal synthesis reported that $\beta$-calcium pyrophosphate ($\beta$-Ca$_2$P$_2$O$_7$) is a precursor phase for HA formation [11]. Synthesis of stoichiometric HA directly from $\beta$-Ca$_2$P$_2$O$_7$, H$_2$O and CaO was also reported [12].

Hench [13, 14] stated that a total of 12 reaction steps are involved in HA formation on a bioactive glass. The first five occur within the glass:

1. Exchange of Na$^+$ or K$^+$ with OH$^-$
   \[\text{Si-O-Na}^+ + \text{H}^+ + \text{OH}^- => \text{Si-OH} + \text{Na}^+ + \text{OH}^-\] \hspace{1cm} (3.4)

2. break Si-O-Si bond to form Si-OH.
$2 \text{(Si-O-Si)} + 2 \text{(OH)}^+ \Rightarrow \text{Si-OH} + \text{OH-Si}$  \hspace{1cm} (3.5)

3. Condensation & repolymerization of SiO$_2$-rich layer.

4. Migration of Ca and P$_2$O$_5$ through the SiO$_2$-rich layer, forming a CaO-P$_2$O$_5$ rich film and an amorphous layer.

5. Crystallization of the CaO-P$_2$O$_5$ film by absorbing OH$^-$, CO$_3^{2-}$, or F$^-$ from the solution.

The remaining seven steps occur at the tissue level, and will not be reviewed here.

vi. Kinetic Modeling: Evaluating the Rate-Limiting Step (RLS) from Planar Reaction Couples

As mentioned in Chapter 1, TCP forms as an intermediate phase during the synthesis of HA from a CaO+Ca$_3$P$_2$O$_7$ mixture. The CaO-P$_2$O$_5$-H$_2$O phase diagram [15] (see Figure 1.1b) also indicates that HA cannot be in local equilibrium with Ca$_3$P$_2$O$_7$. Thermodynamically, TCP should form between HA and Ca$_3$P$_2$O$_7$ as an interlayer phase.

The chemical reactions associated with stoichiometric TCP and HA formation are:

$$\text{Ca}_2\text{P}_2\text{O}_7 + \text{CaO} \Rightarrow \text{Ca}_3\text{P}_2\text{O}_8 \hspace{1cm} (3.6)$$

$$3 \text{Ca}_3\text{P}_2\text{O}_8 + \text{CaO} + \text{H}_2\text{O} \Rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \hspace{1cm} (3.7)$$

Let's assume that the following statements are true during phase formation in planar reaction couples:

- Product phases form as dense, adherent, continuous layers that are uniform in thickness, with flat interfaces parallel to the original interface.
- New phases only form at the interfaces.
- Diffusion of the ions occurs predominantly through the lattice of a product phase rather than via short circuit diffusion.
- The flux of ions in a product layer is independent of the location in the layer, at a given time (pseudo-steady-state assumption).
- A state of local equilibrium is achieved at each phase boundary.
Consider the reaction at a planar interface between porous CaO and β-TCP at a temperature higher than 800°C in a flowing H2O/O2 or dry O2 atmosphere. Initial growth of HA at the interface will take place heterogeneously by chemical reactions between these two solid phases and H2O. After a continuous layer of HA is formed, the new HA can grow at either/both CaO-HA or HA-TCP interfaces (see Figure 3.2). The rate of further growth of HA may be controlled by one or more of the following mechanisms:

1. Solid state diffusion of Ca^{2+} and OH^{-} ions through the HA layer, and reaction with TCP to from new HA at the HA-TCP interface via the following reaction:

\[ \text{Ca}^{2+} + 2 \text{OH}^{-} + 3 \text{Ca}_{3}\text{P}_{2}\text{O}_{8} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \]  

2. Solid state diffusion of P^{5+} and O^{2-} ions through the HA layer, and reaction with CaO and H2O to from new HA at the CaO-HA interface via the following reaction:

\[ 10\text{CaO} + 6\text{P}^{5+} + 15\text{O}^{2-} + \text{H}_2\text{O} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \]  

3. Chemical reaction (e.g., reaction 3.6 and 3.7) at an interface to form new HA.

**a. Possible Rate laws**

There are at least three possible kinetic expressions that may describe the rates of TCP and HA formation. These rate laws are discussed below.

1. **Linear rate law:**

When diffusion of the reactants is appreciably faster than chemical reactions at the temperature for HA formation, the formation rate may follow a linear rate law:

\[ r_l = \frac{d(\Delta \xi)}{dt} = k_l \]  

where \( \Delta \xi \) is the thickness of the HA layer and \( k_l \) is the linear rate constant.

The chemical reactions described in reactions 3.6 and 3.7 occur simultaneously at both the HA-TCP and the CaO-HA interfaces. Thus, the faster of the two will control the rate of HA formation.
The rate of chemical reaction may be controlled by a reaction step, such as the absorption rate of Ca$^{2+}$, O$^{2-}$, or PO$_4^{3-}$ onto the proper sites (which may resemble kinks at a free surface) at the HA-CaO or the TCP-HA interfaces, or the migration of these species along the interfaces to the proper sites to form the new HA phase.

(2) 2. **Parabolic rate law:**

If the diffusion of Ca$^{2+}$ or OH$^{-}$ ions inward through HA to the HA-TCP interface, or the diffusion of P$^{5+}$ and O$^{2-}$ (or PO$_4^{3-}$) ions outward through HA to the CaO-HA interface, is rate limiting, then the rate of thickening should be proportional to the flux of the migrating reactant species through the HA layer. In a quasi-steady state condition, the flux of a species through the HA layer is inversely proportional to the scale thickness. The reaction rate in such a case should be parabolic:

$$r_p = d(\Delta \xi / dt) = k_p / \Delta \xi \quad \text{or} \quad \Delta \xi = (2k_p)^{1/2} t^{1/2}$$

(3.11)

where $k_p$ is the parabolic rate constant.

(3) 3. **Logarithmic law:**

The rate of formation of a product layer sometimes decreases with time at a faster rate than that given by the parabolic rate law. In this case, the rate may either follow a direct logarithmic or inverse logarithmic law. The logarithmic rate law can apply to the case when the activation energy for ion migration increases as the film thickens due to a reduction in the number of rapid diffusion paths, or a reduction in the magnitude of an electric field across the film, or when the fraction of available surface sites for chemical adsorption decreases with time [16].

The logarithmic rate laws are:

for direct log law:

$$\Delta \xi = k_{log} \log(t + t_u)$$

(3.12)

for inverse rate law:

$$\frac{1}{\Delta \xi} = B - k_{invlog} \log(t)$$

(3.13)
Where \( k_{\text{log}} \) is the logarithmic rate constant, \( k_{\text{inlog}} \) is the inverse logarithmic rate constant, and \( B \) is a constant. In these cases, the rate constant can be directly obtained by plotting \( \Delta \xi \) or \( \frac{1}{\Delta \xi} \) versus log \( t \).

b. Rate controlling species and total rate of formation

Consider the formation of new layers of HA on both sides of an inert marker, say Pt, with thickness \( \Delta \xi_1 \) to the right side and \( \Delta \xi_2 \) to the left side of the marker. \( \Delta \xi_T \) is the total thickness of the HA layer. Let \( k_{p1} \), \( k_{l1} \) and \( k_{p2} \), \( k_{l2} \) be parabolic and linear rate constants associated with \( \Delta \xi_1 \) and \( \Delta \xi_2 \), respectively (see Figure 3.2).

Since the diffusion and chemical reactions take place in series, the parabolic and the linear steps can be combined as:

\[
\frac{1}{r_t} = \frac{1}{r_p} + \frac{1}{r_l}
\]

where \( r_t \), \( r_p \), and \( r_l \) refer to the total rate, the parabolic rate, and the linear rate of formation, respectively. By plugging in \( r_l \) and \( r_p \) from equation 3.8 and 3.9, the thickening rate to one side of the marker can be expressed as:

\[
\frac{d(\Delta \xi)}{dt} = \frac{\Delta \xi}{k_{p1}} + \frac{1}{k_{l1}}
\]

\[
\frac{d\Delta \xi_1}{dt} = \frac{k_{p1}k_{l1}}{\Delta \xi_1k_{l1} + k_{p1}}
\]

The total thickening rate is the sum of the rates of HA growth on both side of the marker, \( d\Delta \xi_1/dt \) and \( d\Delta \xi_2/dt \) (see Figure 3.2):

\[
\frac{d\Delta \xi}{dt} = \frac{d\Delta \xi_1}{dt} + \frac{d\Delta \xi_2}{dt} = \frac{k_{p1}k_{l1}}{\Delta \xi_1k_{l1} + k_{p1}} + \frac{k_{p2}k_{l2}}{\Delta \xi_2k_{l2} + k_{p2}}
\]

If the reaction follows a linear rate law, then this equation can be reduced to equation 3.8. For example, if \( k_{l1} \ll k_{p1} \), \( k_{l2} \ll k_{p2} \), and \( k_{l1} \gg k_{l2} \), then
\[
\frac{d\Delta \xi}{dt} = k_{ii} = \frac{d\Delta \xi}{dt}
\] (3.18)

On the other hand, if the HA conversion rate is limited by diffusion of one ionic specie through HA, then the reaction rate will be reduced to equation 3.9. By measuring the thickness of HA formed on both sides of the marker, \(\Delta \xi_1\) and \(\Delta \xi_2\), with respect to time, the rate limiting mechanism as well as the rate constants may be estimated.

If the growth of HA follows a diffusion-limited parabolic rate law, and if the diffusion rate of one ionic specie is orders of magnitude greater than the others, then the new HA will only form on one side of the marker. Since the diffusion rate of \(\text{Ca}^{2+}\) is reported to be much faster than that of \(\text{PO}_4^{3-}\) (or \(\text{P}^{5+}\) and \(\text{O}^{2-}\) ions) in HA [7-9], new HA is expected to grow predominantly at the TCP-HA interface (see Figure 3.2a).

**vii. Kinetic modeling: Predicting the RLS from spherical reaction couples**

Since the precursors discussed in chapters 1 & 2 were in powder form, a model with spherical geometry is more applicable to such precursors. A spherical geometry requires a different kinetic expression to reflect the variation in surface area between the inner and outer interfaces of a product layer and the changes in such surface areas with time.

If solid-state diffusion is the RLS, then the relation between the fraction of reaction \((\alpha)\), the original particle radius \((r)\), the unreacted particle radius \((a)\), the thickness of product layer \((d)\), and the volume of product formed per volume of reactant consumed \((z)\) are shown below [17]:

\[
\alpha = \frac{r_{m}^{3} - a^{3}}{r_{m}^{3}}
\] (3.19)

\[
\frac{d}{dr} = \left\{1 + (z - 1)\alpha\right\}^{k} - \left(1 - \alpha\right)^{k}
\] (3.20)

\[
\left[1 + (z - 1)\alpha\right]^{3} + (z - 1)(1 - \alpha)^{3} = z + 2(1 - z)\frac{kt}{r_{m}^{2}}
\] (3.21)
For low values of \( \alpha \).

\[
(\varepsilon \alpha)^2 = \frac{9d^2}{r_o^2} = 18k_p \frac{t}{r_o^2}
\]  

(3.22)

On the other hand, when a chemical reaction is the RLS. then based on the unreacted core model from Levenspiel [18]:

\[
\frac{t}{\tau} = 1 - \frac{r_n}{r_o} = 1 - (1 - \alpha)^\nu: \quad \tau = \nu V_m k (C_i)^n r_o
\]  

(3.23)

where \( \tau \) is the time it takes to complete the transformation. \( \nu \) is the ratio of the moles of reactant consumed per mole of product formed; \( V_m \) is the molar volume of the reacting particle. \( k \) is the reaction rate constant. and \( C_i \) is the concentration of species \( i \) involved in an nth order chemical reaction.
Figure 3.1: (a) An assembled planer reaction couple; (b) the cross-sectional view of the reaction couple; (c) the silica boat that the reaction couple was placed for annealing.
(a) Cross-sectional view of the CaO/\(\text{Ca}_3\text{P}_2\text{O}_8\) couple during reaction when \(\text{Ca}^{+2}\) and OH\(^{-}\) diffuse much faster than \(\text{P}^{+5}\) and \(\text{O}^{-2}\) (or \(\text{PO}_4^{-3}\)) in HA.

(b) Cross-sectional view of the CaO/\(\text{Ca}_3\text{P}_2\text{O}_8\) couple during reaction when \(\text{P}^{+5}\) and \(\text{O}^{-2}\) (or \(\text{PO}_4^{-3}\)) diffuse much faster than \(\text{Ca}^{+2}\) and OH\(^{-}\) in HA.

(c) Cross-sectional view of the CaO/\(\text{Ca}_3\text{P}_2\text{O}_8\) couple during reaction when new HA grows on both interfaces.

Figure 3.2: Schematics of Ca/\(\beta\)–Ca\(_3\)P\(_2\)O\(_8\) planar couples undergoing reaction in steam.
B. EXPERIMENTAL PROCEDURES

i. PREPARING THE PLANAR REACTION COUPLES

A polycrystalline β-TCP disk of 82 mm diameter by 6.9 mm thickness and with a density of 98.3% were produced by hot pressing β-TCP powders at a temperature of 1200°C for 1 h in vacuum with a gage pressure of 1500 psi. The β-TCP powder was ordered from Fluka Chemical Corp. (Ronkoma, NY) and possessed < 37 μm particle size and ≥ 98% purity (see Table 3.1 for the detailed information). The phase purity of the β-TCP in the disks was confirmed to be ~100% by XRD measurement (see Figure 3.3a). Square plates with a width of approximately 6 mm and a thickness of ~ 2 mm were cut from the hot-pressed disks with a low-speed diamond saw. Both large-area surfaces of these plates were then polished to a 1 μm diamond finish and cleaned with acetone in an ultrasonic cleaner for 5 m. Platinum foil (25 mm x 25 mm x 2 μm) with purity ≥ 99.85% was obtained from Alpha Aesar (Ward Hill, MA). Strips of 0.5 to 1 mm width were cut from the Pt foil with a razor blade.

<table>
<thead>
<tr>
<th>Species</th>
<th>β-TCP</th>
<th>Cl</th>
<th>SO₄</th>
<th>K</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration (wt %)</td>
<td>≥98</td>
<td>≤0.05</td>
<td>≤0.1</td>
<td>≤.01</td>
<td>≤.005</td>
<td>≤.005</td>
</tr>
<tr>
<td>Element</td>
<td>Pb</td>
<td>Cd</td>
<td>Fe</td>
<td>Cu</td>
<td>Co</td>
<td>Na</td>
</tr>
<tr>
<td>concentration (wt %)</td>
<td>≤.005</td>
<td>≤.005</td>
<td>≤.02</td>
<td>≤.005</td>
<td>≤.005</td>
<td>≤.1</td>
</tr>
</tbody>
</table>

Table 3.1: The purity of β-TCP, obtained from Fluka Chemical Corp., Ronkoma, NY.

Reagent grade calcium oxide powders with < 37 μm size and > 99% purity were obtained from Sargent-Welch (Buffalo Grove, IL). The impurity content of the CaO was analyzed with the ICP-MS and presented in Table 3.2.

155
Table 3.2: The purity of CaO from ICP-OES analyses.

CaO/TCP reaction couples of 13 mm diameter by 3 to 4 mm thickness were prepared by uniaxial pressing, with the following procedure. Firstly, approximately 0.5 g of CaO powder was placed inside the die and leveled with the plunger by hand. One strip of Pt was attached to each face of a polished β-TCP plate with the aid of some vacuum grease. The β-TCP plate was then placed on the leveled CaO powder and carefully centered within the die. Additional 0.6 g of CaO powder was then added on top of the β-TCP plate. The plunger was then inserted in the die and the die assembly was subjected to a pressure of 786 MPa with an automatic press.

The pressed CaO/β-TCP reaction couple (see Figure 3.1) was then annealed under isothermal conditions at temperatures between 700 to 1200°C for 1 to 48 h on a silica boat within a silica enclosure (see Figure 3.1c for the silica boat and Figure 1.a for the silica enclosure), which was inserted inside a horizontal tube furnace manufactured by Lindberg Inc (Watertown, WI). A flowing, moist oxygen atmosphere ($P_{\text{H}_2\text{O}} = 99.7 \%$) was directed to the inlet of the silica enclosure. The furnace was heated to 1150°C with a heating rate of 20°C per m. held for 1 to 100 h at this temperature, and subsequently cooled to room temperature at a rate of 3°C/m. The reaction couples were removed from the silica enclosure and prepared for microstructural analysis. It should be noted that due to the curvature at the bottom of the silica boat, the CaO disks only had two contact points with the boat (see Figure 3.1c), thus, reaction between silica and CaO was minimal.
ii. **Preparing the Powder Compacts**

Reaction couples with a spherical interface geometry were also prepared for kinetic study. Calcium was used in the reaction couple instead of CaO in order to achieve a better contact with β-Ca$_2$P$_2$O$_7$ particles (Ca is more ductile than its oxide, so that Ca can flow around and conform to the shapes of the β-Ca$_2$P$_2$O$_7$ particles). An intimate mixture of Ca + β-Ca$_2$P$_2$O$_7$ was prepared with the SMP powder metallurgy route as mentioned previously (see CHAPTER 1A.v.a). Disk-shaped specimens with approximately 10 mm diameter x 1 mm thickness, and 75.00 ± 1.68 % density, were obtained by uniaxial pressing at a pressure of 1333 MPa.

These disks were oxidized at 500°C for 4 h in flowing, dry O$_2$. One of the disk samples was ground into powder, blended with 0.1 weight fraction of Ag powder and analyzed with XRD. Since CaO possesses a smaller molar volume than Ca, the β-Ca$_2$P$_2$O$_7$ particles should have been surrounded by porous CaO after oxidation. These CaO/β-Ca$_2$P$_2$O$_7$ disks were then placed on a silica boat within the silica enclosure and thrust inside a horizontal Lindberg furnace held at 1150°C with moist O$_2$ flowing through the silica enclosure. The sample disks were removed from the furnace after 1.5 m, 3 m, 6 m, 10 m and 30 m of annealing and quenched to room temperature in air.

iii. **Specimen Characterization**

a. **Quantitative XRD Analysis**

In order to determine the degree of phase transformation inside the powder compact, spherical reaction couples were annealed for various amounts of time at 1150°C. After annealing, the disk samples were ground into powder with a mortar and pestle along with 0.1 weight fraction of Ag powder. XRD analyses were conducted at room temperature using Cu-K$_{α}$ radiation at a scan rate of 1°/min. The peak intensities of the CaO, Ca$_3$P$_2$O$_7$, TCP, and HA phases from XRD analyses were compared to calibration curves generated from standards containing these phases and Ag powder as an external reference as elaborated below.
An external calibration method [19-22] was adopted to generate calibration curves for quantitative evaluation of the amounts of β-TCP, and HA present within the disk samples (see Figure 3.4). These calibration curves were obtained from XRD analyses of powder mixtures of TCP/Ag, and HA/Ag with various weight ratios. Intensity ratios were correlated to weight ratios according to the following equation.

\[ I_{\beta-TCP}/I_{Ag} = K_{TCP} [W_{\beta-TCP}/W_{Ag}] \]  

(3.24)

where \( I_{\beta-TCP} \) is the intensity of the (0 2 1 0) diffraction peak for β-TCP (\( 2\theta = 31.0^\circ \)) \( I_{Ag} \) is the intensity of the (1 1 1) diffraction peak for Ag (\( 2\theta = 38.2^\circ \)). \( I_{rel} = 100\% \) \[23\]. and \( W_{TCP} \) and \( W_{Ag} \) are the weight fractions of TCP and Ag powder within the standard mixtures, respectively.

The calibration curve shown in Figure 3.4a was created by plotting the ratio of intensities \( I_{\beta-TCP}/I_{Ag} \) against the weight ratio, \([W_{\beta-TCP}/W_{Ag}]\). Least-squares fitting yielded the straight line shown in Figure 3.4a, the slope of which was used to obtain a \( K_{TCP} \) value of 0.110.

Intensities of diffraction peaks for HA and Ag was correlated to weight ratios of these phases with the following equation.

\[ I_{HA}/I_{Ag} = K_{HA} [W_{HA}/W_{Ag}] \]  

(3.25)

and \( I_{HA} \) is the integrated intensity of the (2 1 1) diffraction peak for HA (\( 2\theta = 31.8^\circ \)). \( I_{rel} = 100\% \) \[23\].

The calibration curve corresponding to HA is shown in Figure 3.4b. This curve was created by plotting the ratio of the intensity \( I_{HA}/I_{Ag} \) against \( W_{HA}/W_{Ag} \). Least-squares fitting of this data yielded the straight line shown in Figure 3.4b, the slope of which yielded a \( K_{HA} \) value of 0.200. These data are also summarized in Table 3.3.
Table 3.3: The slopes and $R^2$ values for the XRD calibration curves of $\beta$-TCP and HA.

<table>
<thead>
<tr>
<th>Phase</th>
<th>K (slope)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$-TCP</td>
<td>0.0891</td>
<td>0.9890</td>
</tr>
<tr>
<td>HA</td>
<td>0.1998</td>
<td>0.9939</td>
</tr>
</tbody>
</table>

b. SEM-EDX Analyses

The thicknesses of HA layers grown between the planar reaction couples were obtained with scanning electron microscopy (SEM). The planar reaction couples were mounted in epoxy, cross-sectioned with a diamond-wafering blade, and then polished with silicon carbide paper and diamond pastes down to a 1-μm finish. Kerosene was used as the polishing lubricant (instead of water).

BSE images (atomic number contrast mode) were used to study the morphology of the phases and the extent of HA-scale formation. The chemical compositions of the phases were obtained with an average of at least six EDX analyses on the SEM. The relative distributions of elements were evaluated with X-ray dot maps.

c. Raman Spectroscopy

Since $\beta$-TCP and HA have similar Ca/P ratios (1.5 versus 1.67), it was difficult to distinguish them by EDX or WDX analyses. However, these two phases have different Raman responses due to the differences in chemical bonding and crystal structure. Raman spectroscopy was employed to detect $\beta$-TCP and HA, as well as to confirm the formation of a HA layer between CaO and $\beta$-TCP in the planar reaction couples. Both green and red laser sources were used to analyze a hot-pressed TCP plate (see Figure 3.3 b and c). The green laser (514.5 nm) was further used for analyzing the extent of HA formation on the polished cross-section of the planar reaction couples. A line profile of 75 analyses was obtained through the reaction couple (total analyzed distance of 159
approximately 600 μm). Each analysis was integrated twice (2 s each), and was centered at the Raman shift of 1000 cm\(^{-1}\). Each CaO analysis was integrated twice (120 s each time) and two analyses were conducted with Raman shifts centered at 1000 and 1700 cm\(^{-1}\).

An advantage of Raman spectroscopy is the relatively simple specimen preparation that is required (i.e. the sample can be in powder, liquid, or bulk solid form). The shortcoming of Raman spectroscopy was its poor spatial resolution, 4 μm, which was governed by the resolution of the optical microscope attached to the instrument.
Figure 3.3: (a) XRD analysis of the hot-pressed TCP disk, (b) and (c) Raman spectrum from a wafer of the TCP disk using green Laser and Red Laser source, respectively.
Figure 3.4: Calibration curves for quantitative XRD analyses: (a) $\beta$-TCP and (b) HA.
C. RESULTS AND DISCUSSION

i. SPHERICAL REACTION COUPLES

a. Quantitative XRD analyses

The average weight and dimensions of the six spherical reaction couples prior to and after the oxidation heat treatment at 500°C are shown in Table 3.4. Complete oxidation of calcium within these samples had been achieved since each specimen gained ~6.7% of weight. It should be noted that these disks are smaller (10 mm dia. x 1 mm thick) than those utilized in the TGA analyses mentioned in Chapter 1 (13 mm dia. x 2 mm thick). Thus, the time required for completely oxidize these disks (4 h at 500°C) were much shorter than the results shown in Figure 1.12 (13 h at 500°C).

<table>
<thead>
<tr>
<th>Precursor disk</th>
<th>After 500°C, 4 h in O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (mg)</td>
<td>Diameter (mm)</td>
</tr>
<tr>
<td>164</td>
<td>10.2</td>
</tr>
<tr>
<td>145</td>
<td>10.2</td>
</tr>
<tr>
<td>166</td>
<td>10.2</td>
</tr>
<tr>
<td>163</td>
<td>10.22</td>
</tr>
<tr>
<td>167</td>
<td>10.22</td>
</tr>
<tr>
<td>166</td>
<td>10.22</td>
</tr>
<tr>
<td>avg</td>
<td>162</td>
</tr>
<tr>
<td>std</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 3.4: The weights, dimensions, and densities of disks before and after oxidation at 500°C.

The XRD analyses were conducted on the disks after oxidation, and after 1150°C annealing for 1.5 m, 3 m, 6m, 10 m, and 30 m (see Figure 3.5). After oxidation at 500°C, the disks contained CaO, β-Ca₃P₂O₇, and β-TCP, but not HA. However, after as short as
1.5 m of annealing at 1150°C in flowing moist O\textsubscript{2} atmosphere (P\textsubscript{H\textsubscript{2}O} = 99.7 %), essentially all the β-Ca\textsubscript{2}P\textsubscript{2}O\textsubscript{7} was converted to β-TCP and HA. Obviously, the reaction below happened quite rapidly when the disk was annealed at 1150°C.

\[ 4 \text{CaO} - 3 \text{Ca}_2\text{P}_2\text{O}_7 - x \text{H}_2\text{O} = 3(1-x) \text{Ca}_3\text{P}_2\text{O}_4 + (1-x) \text{CaO} - x \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \]  

(3.26)

Further reaction between the CaO, β-TCP, and H\textsubscript{2}O to form HA occurred at a slower rate at 1150°C. An annealing time longer than 30 m was needed for completion of this reaction. Quantitative analyses of the amounts of phases present in these samples are listed in Table 3.5. The percentage of HA and β-TCP within the disks are plotted against annealing time in a linear scale in Figure 3.6a.

<table>
<thead>
<tr>
<th>Time (m)</th>
<th>ITCP/IAg</th>
<th>IHA/IAg</th>
<th>Wt TCP</th>
<th>Wt HA</th>
<th>X TCP</th>
<th>X HA</th>
<th>XCaO</th>
<th>X CaP</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.1394</td>
<td>0</td>
<td>0.0271</td>
<td>0</td>
<td>0.168</td>
<td>0</td>
<td>0.528</td>
<td>0.304</td>
</tr>
<tr>
<td>1.5</td>
<td>0.2795</td>
<td>0.472</td>
<td>0.0549</td>
<td>0.041</td>
<td>0.641</td>
<td>0.149</td>
<td>0.209</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>0.2621</td>
<td>0.623</td>
<td>0.0447</td>
<td>0.047</td>
<td>0.621</td>
<td>0.203</td>
<td>0.176</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>0.1803</td>
<td>0.643</td>
<td>0.0346</td>
<td>0.055</td>
<td>0.559</td>
<td>0.274</td>
<td>0.167</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.0976</td>
<td>0.599</td>
<td>0.0184</td>
<td>0.050</td>
<td>0.473</td>
<td>0.400</td>
<td>0.127</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>0.0525</td>
<td>0.811</td>
<td>0.0103</td>
<td>0.071</td>
<td>0.267</td>
<td>0.569</td>
<td>0.164</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.5: The quantitative analyses for the phases present after different times of annealing at 1150°C (data are presented as normalized atomic fractions).

The rate of HA formation has also been fitted to the Carter’s model [24]. Carter stated that, the rate for phase formation in a spherical reaction couple is per the following expression when solid-state diffusion is the RLS:

\[ \frac{\{[1+(z-1)x]^{2/3} + (z-1)(1-x)^{2/3} -z\}/2(1-z)}{kt} = \frac{V_{HA}}{V_{Ca_2P_2O_7}} = \text{constant} \]  

(3.27)

where \( z \): the volume of product over the volume of reactant. \( V_{HA}/V_{Ca_2P_2O_7} \) in this case, is 0.9115. \( x \) is the molar fraction of HA formation at time \( t \).

e.g.: when \( t = 1.5 \), \( x = 0.149 \), plugging \( z \), \( x \) and \( t \) into equation 3.25:
\[
\left\{1+(0.9115-1)\times 0.149\right\}^{2/3} + (0.9115-1)(1-0.149)^{2/3} -0.9115\}/2(1-0.9115) = k \times 1.5
\]

thus. \(0.001217 = k \times 1.5\) \(\text{(3.28)}\)

The data from the other transformation time, 3, 5, 10, and 30 m, were also calculated according to eq. 3.25. These data were plotted against time as shown in Figure 3.6b. A straight line is fitted in this graph with \(R^2 = 0.9969\), which confirmed that HA formation was governed by solid-state diffusion. The slope of the line yielded \(k = 9 \times 10^{-4}\).

### ii. Raman Spectra with Green versus Red Laser

The Raman analyses on standard powder of CaO, \(\beta\)-TCP and HA using a red Laser source (785 nm) are shown in Figure 3.7a, b and c, respectively. Characteristic Raman shifts for these phases are marked on the curves for ease of identification.

A wafer of TCP used in the reaction couple analyses was also analysed with the Raman spectrometer using both green and red laser sources (Figure 3.3a) and with XRD (Figure 3.3b). The wafer consisted of pure TCP, as shown in the XRD analysis. However, the Raman shifts using green and red laser sources were very different. The spectrum taken with a red-laser source exhibited vibrations at 1319 and 1389 cm\(^{-1}\) that were absent in the one taken with a green laser source. On the contrary, major vibrations at 951, 971, and 1049 cm\(^{-1}\) in the spectrum taken with a green laser source were shown as minor peaks in the spectrum with red laser source.

### iii. Planar Reaction Couple

A CaO/\(\beta\)-TCP planar reaction couple with platinum inert markers (Figure 3.1) was annealed at 1150\(^\circ\)C for 5 days in a moist \(\text{O}_2\) atmosphere (\(P_{\text{H}_2\text{O}} \sim 99.7\%\)). The BSE images and X-ray maps taken from a polished cross section of this sample are shown in Figure 3.8. The entire TCP layer (440 \(\mu\)m) had been converted to HA after 5 days of annealing (as determined from EDX and Raman analyses). X-ray maps in this reaction couple show the distribution of Ca, Pt, P, and O in the HA area (see Figure 3.8 c, d, e, and f, respectively). It is also indicated that HA formed preferentially at the HA/\(\beta\)-TCP
interface (see Figure 3.8b). This observation suggested that \( \text{Ca}^{2+} \) and/or \( \text{OH}^- \) are the faster diffusing species inside HA, rather than \( \text{PO}_4^{3-} \) (or \( \text{P}^{5+} \) and \( \text{O}^{2-} \)).

A Raman profile was obtained from one CaO side of the reaction couple through the other side with a 10 \( \mu \text{m} \) interval in each step using green laser source with spot size 4 \( \mu \text{m} \) (Figure 3.9a). Both the contour plot (Figure 3.9b) and the 3-d plot (Figure 3.9c) indicated that HA was the only phase present in the dense region that was originally a TCP wafer. This result confirmed that 100\% conversion of TCP into HA had occurred.

The BSE image taken from the reaction couple after 1150°C annealing for 5 d in a moist \( \text{O}_2 \) environment indicated two calcium phosphate phases with different contrast. The average of six EDX analyses conducted on the brighter phase yielded a Ca/P ratio of 1.68 ± 0.03 (which should be the HA phase) while the darker phase yields Ca/P of 1.85 ± 0.11, which could be Ca-enriched HA.

BSE images of polished cross sections of CaO/TCP reaction couples annealed at 1150°C for 1 and 4 h in moist \( \text{O}_2 \) are shown in Figure 3.10a and b, respectively. The Raman profile across the cross sectional surface of the 4 h-annealed reaction couple is also shown in Figure 3.10c. The thickness of HA layer in this latter sample estimated from the Raman analyses was 170 \( \mu \text{m} \).

A CaO/β-TCP reaction couple was also annealed at 1150°C in a dry \( \text{O}_2 \) atmosphere. The BSE image of a polished cross section surface of this reaction couple is shown in Figure 3.11a. The CaO/TCP reaction couple shown in Figure 3.11b has also been analyzed with Raman spectroscopy (Figure 3.12). In this analysis, the laser beam was programmed to move a total of 25 \( \mu \text{m} \) in 10 steps from the CaO side towards the β-TCP side. The HA peaks start to appear after the third step, and remain through the rest of the scan. This result indicated that the HA layer between CaO/β-TCP reaction couple was at least \( 7 \times 2.5 = 17.5 \) \( \mu \text{m} \) thick.

**iv. The Growth of HA**

As stated by Van Loo, the shortest repeating distance of a product phase in a planar reaction couple is often aligned parallel to the direction of diffusion [17]. Consider the
diffusivities of the three species parallel to the c-axis of HA. From equations 3.2 through 3.4, \( \text{PO}_{4}^{3-} \) is the slowest diffusing specie in HA, while \( \text{Ca}^{2+} \) is the fastest. Thus, if solid-state diffusion is controlling the rate of HA formation, this rate should be controlled by the fastest moving specie, \( \text{Ca}^{2+} \). This postulate was confirmed by the fact that Pt markers were found between CaO and the HA layer. This indicated that the growth of HA occurred by the outward diffusion of \( \text{Ca}^{2+} \) from CaO rather than the counter diffusion of \( \text{PO}_{4}^{3-} \). Since the diffusion rate of \( \text{Ca}^{2+} \) parallel to the C-axis in the hexagonal unit cell of HA is faster than the diffusion rate perpendicular to the C-axis, the growth of HA should be aligned along its C-axis. This phenomenon was also found in a study of the growth of an HA seed in an aqueous solution: that is, the growth was predominantly in the c-axis direction [3].

Pole figure analyses were conducted to evaluate the orientation of the HA layer grown at the CaO/TCP interface in a planar reaction couple. After the reaction couple was annealed at 1150°C for one day in moist \( \text{O}_2 \), the sample was delaminated at the HA/TCP interface due to density gradient. The half of the sample with HA film on CaO was used for this analyses. Firstly, a \( \theta-2\theta \) scan was conducted on the HA film. The (211) peak of HA was enlarged, the (222) peak did not change, while the (300) peak disappeared relative to XRD powder patterns (see Figure 3.13). The (211), (222), and (002) pole figures together with the 3-d mesh plots are shown in Figure 3.14 through Figure 3.16. These pole figures indicated that the HA layer was highly textured and there were 6 times as many HA grains with (211) planes parallel to the surface of the HA layer as the grains with (211) planes facing the other directions (see Figure 3.14). The pole figure taken with (222) planes indicated that there are 10 times as many grains with (222) planes parallel to the top surface than the grains with (222) planes facing the other orientations (see Figure 3.15). On the other hand, the (002) pole figure indicated that there were 14 times as many grains with the (002) planes facing an angle from the top surface of the HA layer than the grains facing the other orientation (see Figure 3.16).

These results indicated that the HA layer grew preferentially with the (211) or (222) planes parallel to the surface with the (002) planes facing at an angle with the surface.
The fact that the (300) peak was missing indicated that the (300) planes could be perpendicular to the surface.

It should also be noted that, since HA grows in an aggregated manner, the bond between the HA and β-TCP was not strong. Thus, gaps usually opened up between HA and β-TCP, especially during a rapid quench, or during the metallographic sample preparation process.
Figure 3.5: XRD analyses on powder compact samples
Figure 3.6: Rate of HA formation at 1150°C (a) Linear Scale of HA formation versus time (b) The calculation based on Carter’s model.
Figure 3.7: Raman spectra (red laser) taken from CaO, TCP. and HA powders, respectively, of >99 % phase purity.
Figure 3.8: BSE images of a CaO/β-TCP reaction couple annealed at 1150°C for 5 days in moist O₂.
Figure 3.9: (a) BSE image of a CaO/β-TCP reaction couple annealed at 1150°C for 5 days in moist O₂. (b) and (c) projection contour plot and 3-d plot of Raman spectra taken from this sample using a green laser source.
Figure 3.10: (a) & (b) BSE images of CaO/β-TCP reaction couples annealed at 1150°C for 1 h & 4 h in moist O₂ respectively (c) Contour plot of Raman spectra for the 4 h annealed sample using a green laser source.
Figure 3.11: BSE images of CaO/ \( \beta \)-Ca\(_3\)P\(_2\)O\(_8\) reaction couples annealed at (a) 1150°C for 5 days in dry \( O_2 \) and (b) at 1150°C for 1 day in moist \( O_2 \).
Figure 3.12: Raman Spectra across the Interface of the CaO- $\beta$-Ca$_3$P$_2$O$_8$ reaction couple shown in Fig. 3.11b using a red laser source.
Figure 3.13: The θ-2θ XRD spectra for (a) an HA layer grown on a CaO substrate, and (b) the CaO substrate.
Figure 3.14: (a) The (211) pole figure showing the anisotropic orientation of a HA film grown between CaO and TCP, and (b) the 3-d mesh plot showing the relative intensities for the (211) poles pointing to different angles.
Figure 3.15: (a) The (222) pole figure, and (b) the 3-d mesh plot showing the relative intensities of the poles pointing at different angles.
Figure 3.16: (a) The (002) pole figure and (b) the 3-d mesh plot.
D. Conclusions

It is concluded that the formation of HA from $\text{Ca}_2\text{P}_2\text{O}_7$, CaO, and $\text{H}_2\text{O}(g)$ is controlled by the solid-state diffusion of $\text{Ca}^{2+}$ and/or $\text{OH}^-$ through the HA layer. The formation rate in powder reaction couples fits the Carter model for solid-state, diffusion-controlled kinetics.

Oxidation of calcium within a Ca-$\text{Ca}_2\text{P}_2\text{O}_7$ precursor with a dimension of 10 mm dia. x 1 mm thick can be completed within 4 h of annealing at 500°C in a flowing $\text{O}_2$ atmosphere.

The growth of the HA layer between the CaO/TCP planar reaction couple was highly textured. There were 10 to 20 times more HA grains with (211) and (222) plans parallel to the planar interface between HA and TCP, but there were less or none HA grains with the (300) or (002) planes parallel to the HA/TCP interface.


23. JCPDS_Cards:  #23-130 for Ca. #9-346 for Ca$_2$P$_2$O$_7$. #9-169 for Ca$_3$P$_2$O$_8$. #9-342 for Ca$_{10}$P$_4$O$_{16}$(OH)$_2$.
CHAPTER 4

HEAT TREATMENT FOR HA/CO-CR-MO COMPOSITE

A. INTRODUCTION

In chapter 2, the heat treatment chosen for converting Ca-Ca₅P₂O₇/Co-Cr-Mo alloy precursors into HA/Co-Cr-Mo alloy composites consisted of a two-cycle treatment that included a sintering anneal at 1150°C and an HA formation anneal at 850°C in moist O₂. This chapter outlines the experiments and results leading to this treatment.
B. Experimental Procedures

i. Precursor Processing

As mentioned in chapter 1, all precursor handling operations (e.g., calcium machining, milling, mixing, pressing) were conducted within an argon atmosphere glove box to allow for reproducible (and safe) processing.

The particle size of the Co-Cr-Mo alloy can significantly affect the compacted density of the precursor powders and the final mechanical strength of converted HA/Co-Cr-Mo bodies. In order to investigate the possibility of utilizing the SPEX mill to prepare fine Co-Cr-Mo particles, the coarse, as-received Co-Cr-Mo particles were placed in a hardened steel vial (37.8 mm dia. x 57 mm) with 4 hardened steel balls (2 x 15 mm dia., 2 x 7 mm dia.) and ~20 cc of hexane. After sealing the steel vial within an Ar atmosphere glove box, the powder mixtures were milled for various times using the same SPEX 8000 high-energy, vibratory ball mill described in chapter 1. After milling, the hexane was removed from the milled powders by filtration and evaporation. The Co-Cr-Mo particles were then sieved to determine the size distribution of the particles. The Co-Cr-Mo powders shown in Figure 4.1a, b and c were obtained after 6, 12, and 24 h of milling, respectively. The distributions of the particle sizes as received and after 6, 12, or 24 h of milling are shown in Figure 4.1d.

Particles of size less than 325 mesh (< 44 μm) were used for the preparation of a composite precursor. The same powder metallurgical process mentioned in Chapter 2 was used to produce powder mixtures of metallic calcium, β-Ca$_3$P$_2$O$_7$, and Co-Cr-Mo powder. Intimate precursor mixtures of calcium and β-Ca$_3$P$_2$O$_7$ powders were produced as mentioned in chapter 1. This Ca/β-Ca$_3$P$_2$O$_7$ mixture and the Co-Cr-Mo powder were then mixed to the desired volume ratio with the same method described in Chapter 2.

The volume fraction of Co-Cr-Mo alloy within the mixture plays a paramount role in the density and formability of the powder mixture as well as the mechanical behavior of the converted HA/Co-Cr-Mo bodies. To better understand this effect, precursor mixtures with 50/50 and 75/25 volume ratio of Co-Cr-Mo/HA upon conversion were prepared for
comparison. The volume fraction of each constituent in these powder mixtures and the calculated theoretical densities of these mixtures in their precursor and HA-converted state are provided in Table 2.6.

The mixed precursor powder was pressed into circular disks (13 mm dia. x 1-2 mm thick) or bars (30 mm x 7 mm x 5 mm) using the same procedures mentioned in Chapter 2.

ii. FACTORIAL EXPERIMENT

The results of preliminary experiments conducted on 50/50 Co-Cr-Mo/HA composite precursors mentioned in Chapter 2 indicated that HA could be obtained when the precursor disks were heated to a temperature between 600 and 1050°C for four hours in air. However, the need for the initial oxidation treatment was not clear. In addition, previous work indicated that the sintering treatment resulted in an interaction between the Co-Cr-Mo and the HA matrix. The exact effect of such interaction on mechanical strength was not clear. Thus, a $2^4$ factorial design was adopted to search for important parameters for fabricating HA/Co-Cr-Mo composites. The four parameters were four isothermal anneals conducted to oxidize calcium, to convert CaO & calcium phosphate into HA, to sinter the HA/Co-Cr-Mo composite, and to convert the remaining $\beta$-TCP+CaO. formed during the sintering treatment, into HA. Table 4.1 shows the parameters and levels of this design. The heating rate to the annealing temperature was 20°C per min. The experimental setup for conducting these heat treatments was the same as described in Chapters 1 and 2.

After the oxidation treatment, the furnace was cooled to room temperature at 3°C/m and the silica enclosure was evacuated, back-filled with argon, and then transferred into the argon-atmosphere glove box. Samples were removed from the enclosure for measurement of weight and dimensions. One of the samples was kept for further characterization, while the others designated to receive further heat treatment were replaced in the silica enclosure and the enclosure was returned to the furnace.
### Table 4.1: Factorial design for the fabrication of HA/Co-Cr-Mo composite.

<table>
<thead>
<tr>
<th>Level 1</th>
<th>500°C, 18 h in O₂</th>
<th>850°C, 4 h in moist O₂</th>
<th>1050°C, 4 h in Ar</th>
<th>850°C, 2 h in moist O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 2</td>
<td>no</td>
<td>no</td>
<td>950°C, 4 h in Ar</td>
<td>no</td>
</tr>
</tbody>
</table>

### iii. Specimen Characterization

X-ray powder diffraction (XRD) analyses and SEM-EDX analyses were conducted as discussed in Chapters 1 and 2.
Figure 4.1: Milling of ASTM F75 powder; (a) to (c) secondary electron micrographs of the particles milled for 6, 12, and 24 h respectively; (d) the particle size distributions of these milled powders.
C. RESULTS AND DISCUSSION

i. MICROSTRUCTURAL EVALUATION OF 50/50 COMPOSITE

As mentioned in Chapter 2, HA, β-TCP and Co were the phases detected in the 50/50 composite samples heat treated between 850 and 1050°C in the air (See Figure 2.16).

The SEM micrographs of the 50/50 composite after various heat treatments are shown in Figure 4.2. Little interaction between calcium, phosphate, and Co-Cr-Mo particles was detected in the precursor specimen and its counterpart annealed at 850°C for 4 h in air (Figure 4.2a and b). However, after the sample was fired at 1150°C, appreciable migration of calcium and phosphorus into the Co-Cr-Mo particles as well as migration of Co and Cr into the HA matrix was detected. (Figure 4.1c through f).

ii. COMPOSITE MADE OF FINE CO-CR-MO POWDER

A 50/50 mixture of Ca+β-Ca$_2$P$_2$O$_7$ and fine powder Co-Cr-Mo (< 44 µm) was prepared, compacted to a disk shape, and then subjected to a series of isothermal heat treatment: 500°C, 10h annealing in O$_2$ followed by 850°C, 8 h annealing in Ar and additional 850°C 2h annealing in H$_2$O/O$_2$. The XRD analyses on the sample at precursor state and after each isothermal annealing indicated that HA and TCP were the predominant phosphate phase present in the specimen after 2 h after the 850°C annealing (both in Ar and in H$_2$O/O$_2$)(see Figure 4.3a). As mentioned in Chapter 2, transformation of fcc to hcp allotrope of Co-Cr-Mo were observed in the specimen after 850°C annealing. The BSE image of the specimen after the final annealing showing that the HA area were highly porous (see Figure 4.4).

When the fine Co-Cr-Mo powder composite precursor was subjected to a 950°C, 12 h annealing in Ar, formation of CaO, HA and β-TCP from the reaction of Ca and β-Ca$_2$P$_2$O$_7$ was observed (Figure 4.3b). It should be noted that coarse Co-Cr-Mo alloy powders with a median particle size of 150 µm were used in all the other experiments conducted in this chapter.
iii. **Results of Factorial Experiment with 75/25 Composite**

A $2^4$ factorial experiment was carried out to search for important process parameters for producing a HA/Co-Cr-Mo composite. Tables 4.1 and 4.2 list the treatment of the samples and the resulting densities. Typical dimensional changes for disk and bar samples are shown in Tables 4.3 and 4.4 (please also refer to Appendix F for summary of the data). The porosity data listed here are calculated from the ratio of the bulk densities to the theoretical densities of the composite at precursor and post HA conversion states. The X-ray diffraction patterns from disks samples after various heat treatments are shown in Figure 4.5 through Figure 4.6. From these XRD results, β-TCP and HA are the predominant phosphate phases present in all of these specimens.

<table>
<thead>
<tr>
<th>ID</th>
<th>Type</th>
<th>Oxidation temperature (°C)</th>
<th>Conversion condition</th>
<th>Sintering temperature (°C)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>82gp1</td>
<td>75/25</td>
<td>500</td>
<td>850°C/4h air</td>
<td>950</td>
<td>6</td>
</tr>
<tr>
<td>82gp2</td>
<td>75/25</td>
<td>500</td>
<td>850°C/4h air</td>
<td>1050</td>
<td>5.52</td>
</tr>
<tr>
<td>82gp4</td>
<td>75/25</td>
<td>500</td>
<td>no</td>
<td>950</td>
<td>5.6</td>
</tr>
<tr>
<td>82gp5</td>
<td>75/25</td>
<td>500</td>
<td>no</td>
<td>1050</td>
<td>5.53</td>
</tr>
<tr>
<td>82gp11</td>
<td>75/25</td>
<td>no</td>
<td>850°C/4h air</td>
<td>1050</td>
<td>5.04</td>
</tr>
<tr>
<td>82gp13</td>
<td>75/25</td>
<td>no</td>
<td>850°C/4h air</td>
<td>950</td>
<td>5.05</td>
</tr>
<tr>
<td>82gp21</td>
<td>75/25</td>
<td>no</td>
<td>no</td>
<td>950</td>
<td>4.62</td>
</tr>
<tr>
<td>82gp24</td>
<td>75/25</td>
<td>no</td>
<td>no</td>
<td>1050</td>
<td>5.26</td>
</tr>
</tbody>
</table>

Table 4.2: Results of factorial design.

SEM investigations of the polished surfaces of these specimens were also conducted. There was no sign of interaction between the Co-Cr-Mo particles after the specimen was fired at 500°C in dry O₂, nor were there any detectable chromium oxide layers at the interfaces (see Figure 4.7).
<table>
<thead>
<tr>
<th>State</th>
<th>Diameter (cm)</th>
<th>Thickness (cm)</th>
<th>Density (g/cm³)</th>
<th>ΔV/V (%)</th>
<th>Porosity* (Vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>1.312</td>
<td>.089</td>
<td>4.94</td>
<td>—</td>
<td>28.83</td>
</tr>
<tr>
<td>500°C O₂</td>
<td>1.315</td>
<td>.092</td>
<td>4.53</td>
<td>5.0</td>
<td>36.70</td>
</tr>
<tr>
<td>1050°C Ar</td>
<td>1.317</td>
<td>.0987</td>
<td>4.17</td>
<td>12.5</td>
<td>41.73</td>
</tr>
<tr>
<td>850°C H₂O</td>
<td>1.320</td>
<td>.094</td>
<td>4.37</td>
<td>7.7</td>
<td>38.93</td>
</tr>
<tr>
<td>precursor</td>
<td>1.315</td>
<td>.092</td>
<td>4.70</td>
<td>—</td>
<td>32.29</td>
</tr>
<tr>
<td>1050°C Ar</td>
<td>1.315</td>
<td>.089</td>
<td>4.85</td>
<td>-3.6</td>
<td>32.22</td>
</tr>
<tr>
<td>850°C H₂O</td>
<td>1.315</td>
<td>.089</td>
<td>5.72</td>
<td>-3.3</td>
<td>20.07</td>
</tr>
<tr>
<td>precursor</td>
<td>1.312</td>
<td>.085</td>
<td>5.12</td>
<td>—</td>
<td>26.24</td>
</tr>
<tr>
<td>950°C Ar</td>
<td>1.311</td>
<td>.093</td>
<td>4.70</td>
<td>9.6</td>
<td>34.32</td>
</tr>
</tbody>
</table>

Table 4.3: Dimensions and volumes of disk-shaped specimens at various stages of transformation.

<table>
<thead>
<tr>
<th>State</th>
<th>Length (cm)</th>
<th>Width (cm)</th>
<th>Thick (cm)</th>
<th>Density (g/cm³)</th>
<th>ΔV/Vₚ (%)</th>
<th>Porosity (Vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>precursor</td>
<td>3.006</td>
<td>.665</td>
<td>.519</td>
<td>5.34</td>
<td>—</td>
<td>23.07</td>
</tr>
<tr>
<td>500°C O₂</td>
<td>3.018</td>
<td>.677</td>
<td>.522</td>
<td>5.23</td>
<td>2.73</td>
<td>27.22</td>
</tr>
<tr>
<td>1050°C Ar</td>
<td>3.021</td>
<td>.673</td>
<td>.528</td>
<td>5.11</td>
<td>3.57</td>
<td>28.59</td>
</tr>
<tr>
<td>850°C H₂O</td>
<td>3.019</td>
<td>.671</td>
<td>.525</td>
<td>5.20</td>
<td>2.61</td>
<td>27.33</td>
</tr>
<tr>
<td>precursor</td>
<td>2.988</td>
<td>.669</td>
<td>.483</td>
<td>5.34</td>
<td>—</td>
<td>23.07</td>
</tr>
<tr>
<td>1150°C Ar</td>
<td>3.012</td>
<td>.67</td>
<td>.457</td>
<td>5.54</td>
<td>-4.59</td>
<td>22.58</td>
</tr>
<tr>
<td>850°C H₂O</td>
<td>3.013</td>
<td>.67</td>
<td>.484</td>
<td>5.27</td>
<td>1.09</td>
<td>26.36</td>
</tr>
<tr>
<td>precursor</td>
<td>3.004</td>
<td>.673</td>
<td>.474</td>
<td>5.43</td>
<td>—</td>
<td>21.77</td>
</tr>
<tr>
<td>1050°C Ar</td>
<td>3.016</td>
<td>.674</td>
<td>.477</td>
<td>5.34</td>
<td>1.19</td>
<td>25.38</td>
</tr>
<tr>
<td>850°C H₂O</td>
<td>3.002</td>
<td>.683</td>
<td>.472</td>
<td>5.379</td>
<td>0.88</td>
<td>24.83</td>
</tr>
</tbody>
</table>

Table 4.4: Dimensions and volumes of bar-shaped specimens at various stages of transformation.

There was little interaction between the phosphate matrix and the Co-Cr-Mo alloy after a subsequent heat treatment at 850°C for 4 h in moist O₂ (see Figure 4.8a, b, and c). More significant reaction was detected in the disk subjected to a further heating at 1050°C for 12 hours in an argon atmosphere (see Figure 4.8d and e). Calcium silicate
precipitates were detected around the edges of Co-Cr-Mo particles (see Figure 4.8d), while particles enriched in Cr and Co were found in the HA matrix (see Figure 4.8e).

Skipping the 850°C treatment did not make much difference in the reaction between the Co-Cr-Mo alloy and the phosphate matrix. Disk specimens fired at 500°C for 16 h followed by 950 or 1050°C in Ar show the same kind of interaction between Co-Cr-Mo and HA (Figure 4.9). Calcium silicate particles were detected around the edges of Co-Cr-Mo particles, while particles enriched in Cr and Co were found in the HA matrix. However, there was slightly more interaction found in the specimens heated at 1050°C than their counterparts heated at 950°C in argon atmosphere.

Skipping the 500°C oxidation treatment did not make much difference in microstructure when the sintering temperature was 950°C (see Figure 4.10 a, b, and c). Further heating at 850°C in moist O₂ increased the reaction between the Co-Cr-Mo alloy particles and the phosphate matrix (see Figure 4.10 d, e, and f).

However, the degree of sintering between the Co-Cr-Mo particles and the interaction between Co-Cr-Mo and the phosphate matrix increased significantly when the specimen was heated directly to 1050°C for 12 h in argon (see Figure 4.11 a through d). The necking between the Co-Cr-Mo was more extensive than those found in the previous samples. Formation of calcium silicate at the edges of Co-Cr-Mo particles and precipitation of Co, Cr–enriched particles in the HA matrix were also evident (see Figure 4.11c and f).

It should be noted that the specimens that were fired in O₂ or moist O₂ at a temperature ≥ 500°C prior to the firing at a temperature higher than 850°C in argon were mechanically weak. They could easily be broken with bare hands. Their counterparts fired at a temperature ≥ 1050°C in argon directly from the precursor stage, on the other hand, exhibit greater mechanical strength (i.e., these specimens could not be broken with bare hands).
Figure 4.2: SEM Images of a 50/50 composite disks (a) at precursor stage. (b) after fired at 850°C for 4 h in air. (c) after further heating at 1150°C for 10 h in argon (d) through (f) are the X-ray maps of (c).
Figure 4.3: (a) XRD analyses of the 50/50 composite with fine (< 44 μm) F75 powder at precursor state: after 500°C, 10h annealing in O₂; after additional 850°C 8 h annealing in Ar: and after subsequent 850°C 2h annealing in H₂O/O₂, (b) The precursor and after annealing at 950°C in Ar. The latter shows formation of CaO, HA and β-TCP from Ca and β-Ca₂P₂O₇.
Figure 4.4: (a) and (b) SEM images of a composite disk after firing at 500°C for 10 h in O₂, 850°C, 8 h in argon, and 850°C, 2 h in moist O₂.
After 500°C 16 h in O₂, 850°C 4h in H₂O, 950°C 12 h in Ar

After 850°C 4h in H₂O, 950°C 12 h in Ar

After 500°C 16 h in O₂, 950°C 12 h in Ar

After 950°C 12 h in Ar

2-Theta

Figure 4.5: X-ray Diffraction Patterns of 75/25 composites after various heat treatment at 500, 850, 950°C
Figure 4.6: X-ray Diffraction Patterns of 75/25 composites after various heat treatment at 500, 850, 1050°C
Figure 4.7: SEM image and X-ray maps after 500°C oxidation
Figure 4.8: SEM image of 75/25 composite disks. (a), (b) and (c) after 500°C 16 h in O₂+ 850°C 4 h in moist O₂ (d) and (e) after additional 1050°C 12 h in Ar
Figure 4.9: SEM images of 75/25 composite disks. (a), (b) and (c) after 500°C for 16 h in O₂ + 950°C for 12 h in Ar; (d), (e) and (f) after 500°C for 16 h in O₂ + 1050°C for 12h in Ar.
Figure 4.10: SEM images of 75/25 composite disks. (a), (b) and (c) after 950°C 4 h in Ar (d), (e) and (f) after 950°C for 12 h in Ar + 850°C for 2 h in moist O₂.
Figure 4.11: SEM images of 75/25 composite disks. (a), (b), (c) and (d) after 1050°C for 12 h in Ar. (e), (f) and (g) after 1050°C for 12 h in Ar + 850°C for 2 h in moist O₂.
D. Conclusions

It is concluded that:

1. A HA/Co-Cr-Mo alloy-bearing composite will form after the precursor is heated to a temperature above 850°C in ambient air or moisturized environment. Heating at 500 or 600°C in O₂ in order to oxidize the calcium will inhibit the sintering process for the Co-Cr-Mo alloy particles when the specimens are fired further at a temperature higher than 850°C in argon.

2. Annealing of the composite precursors directly at 1150°C for 4 hour in argon and 850°C for 2 hour in moist O₂ yielded HA/Co-Cr-Mo alloy-bearing composites with more extensive sintering of the Co-Cr-Mo particles. Thus, this heat treatment is recommended for fabricating the Co-Cr-Mo/HA composite from a Ca+β-Ca₂P₂O₇+Co-Cr-Mo precursor.

3. The precursors with (Ca + β-Ca₂P₂O₇) + Co-Cr-Mo alloy could be converted into composites of HA + Co-Cr-Mo with ≥ 74% relative density and a volume change as small as 1%.
APPENDICES
Appendix A

BACKGROUND OF HA, TCP, AND Ca₂P₂O₇

STRUCTURES AND POLYMORPHS

i HA

As stated by Elliot [3], apatite refers to a type of chemical compound: M₁₀(XO₄)Z₂, where M can be Ca²⁺, Pb²⁺, Cd²⁺, or Zr⁴⁺. XO₄ can be PO₄³⁻ or MnO₄³⁻. Z can be OH⁻, F⁻, Cl⁻, or CO₃²⁻. The cation and anion Z positions might be partially filled with vacancies in order to preserve the electroneutrality of the crystal.

HA is one of the most important apatites, where M is Ca, XO₄ is PO₄³⁻ and Z is OH⁻. HA possesses a pseudo-hexagonal structure with a P₆₃/m space group and cell dimensions a = b = 9.42Å and c = 6.88Å. It is reported that the OH group inside crystallized HA is ordered as ..OH OH OH within each column located at z = ¼ (see Fig. A1.). The presence of an F⁻ ion impurity provided a point for column reversal. .. OH OH F HO HO.. which is desirable in dental application as it can prevent a cavity from growing inside the teeth. Since vacancies often exists along these columns, the conductivity of HA results from OH⁻ ion diffusion along this Z column [3]. However, the highly crystallized HA mentioned above is produced via high temperature sintering. In natural bone, HA is composed of small crystals of 100 nm or less. Thus, such HA exhibits broad peaks in the XRD pattern and low conductivity.

ii TCP

There are three polymorphs of TCP. [3]. β-TCP is stable from room temperature to 1120°C. α-TCP is stable from 1120°C to 1470°C. while γ-TCP is stable from 1470°C to its melting point, 1756°C.
γ-type Ca₂P₂O₇ can be produced by thermal decomposition of dicalcium phosphate (CaHPO₄) between 320 to 340°C [4]. Further heating of the γ-Ca₂P₂O₇ at a temperature above 700°C will allow γ-Ca₂P₂O₇ to transform into β-Ca₂P₂O₇, which is stable up to 1200°C. α-Ca₂P₂O₇ becomes the stable phase at a temperature between 1200 and 1400°C.
Appendix B

CALIBRATION OF THE CAHN 171 TGA

Pure metal wires of Sn, Al, and Au (> 99.9% purity) were used as temperature standards. A metal wire of approximately 0.5 mm diameter was used to support a light weight (inert ceramic piece ~.2g). The experiment was conducted with the thermal couple located immediately below the sample basket where we want the T/C to be in the real run.

The furnace was programmed to heat to a temperature 50°C higher than the melting point of the standard metal. A heating rate of 1°C/min was used. The reaction tube was purged with Ar for 1 hour prior to heating (PO₂ is 30 to 50 ppm). The temperature where a dramatic drop in weight was recorded by the balance was compared to the melting point of the standard metal.

After the furnace was cooled down to room temperature, the remaining metal wire was examined for the location of melting, so as to determine the hottest spot in the furnace. The data are summarized below:

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<th>Al</th>
<th>Au</th>
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<tr>
<td>m.p</td>
<td>231°C</td>
<td>666°C</td>
<td>1060°C</td>
</tr>
<tr>
<td>Detected in TGA</td>
<td>207°C</td>
<td>660°C</td>
<td>1040°C</td>
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</tbody>
</table>

Table B.1. Calibration for the temperature in TGA.

The result indicated that the TGA temperature reading was 6 to 24°C below the m.p of the standard metals. This discrepancy could be due to the location of the thermocouple, which was not located exactly at the position of the TGA control thermocouple.
## APPENDIX C. THE DIMENSIONAL DATA FOR THE DISK-SHAPED MONOLITHIC SPECIMENS AFTER VARIOUS HEAT TREATMENTS (TABLE C.1)

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**After 850°C, 4 h in air**

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<td>2.30</td>
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<td>1.13</td>
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**After 850°C, 4 h in air**

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</tr>
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<td>2.31</td>
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<td>Std.</td>
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<td>0.04</td>
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<td>0.03</td>
</tr>
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</table>

**After 1150°C, 1 h in H2O/O2**

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<th></th>
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</thead>
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<tr>
<td>Avg.</td>
<td>349</td>
<td>13.44</td>
<td>1.11</td>
<td>157.5</td>
<td>2.22</td>
</tr>
<tr>
<td>Std.</td>
<td>75</td>
<td>0.03</td>
<td>0.25</td>
<td>34.0</td>
<td>0.02</td>
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<tr>
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<td>336</td>
<td>13.08</td>
<td>1.09</td>
<td>146.5</td>
<td>2.29</td>
</tr>
<tr>
<td>1312</td>
<td>346</td>
<td>13.11</td>
<td>1.12</td>
<td>152.2</td>
<td>2.29</td>
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<tr>
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<td>1.17</td>
<td>157.2</td>
<td>2.33</td>
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<tr>
<td>Avg.</td>
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<td>1.13</td>
<td>151.6</td>
<td>2.31</td>
</tr>
<tr>
<td>Std.</td>
<td>16</td>
<td>0.02</td>
<td>0.04</td>
<td>5.39</td>
<td>0.03</td>
</tr>
</tbody>
</table>

**Note:** Wt., Dia., Thk., Vol., Den., and Por., are abbreviations of weight (mg), diameter (mm), thickness (mm), volume (mm^3), density (g/cm^3), and porosity (volume %), respectively.

* & †: The porosity was calculated by comparing the densities to the theoretical densities for Precursor (2.64 g/cc), completely oxidized sample (3.168 g/cc), and HA (3.156 g/cc); respectively.

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APPENDIX D. THE DIMENSIONAL DATA FOR THE BAR-SHAPED COMPOSITE SPECIMENS AFTER VARIOUS HEAT TREATMENTS (TABLE D.1)

<table>
<thead>
<tr>
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<th>Precursor</th>
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<th>After 850°C, 4 h in air</th>
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<tr>
<td>Avg</td>
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- Wt., Dia., Thk., Vol., Den., and Por., are abbreviations of weight (mg), diameter (mm), thickness (mm), volume (mm³), density (g/cm³), and porosity (volume); respectively.

* and +: The porosity was calculated by comparing the densities to the theoretical densities for Precursor (6.941 g/cc), completely oxidized sample (7.186 g/cc), and HA converted sample (7.156 g/cc); respectively.
Appendix E

JCPD CARDS FOR THE COMPOUNDS THAT HAVE BEEN EXAMINED IN THIS STUDY

<table>
<thead>
<tr>
<th>JCPD card</th>
<th>Compound</th>
<th>JCPD card</th>
<th>Compound</th>
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<tr>
<td>37-1229</td>
<td>(Cr0.77Co0.15Mo0.08)23C6</td>
<td>9-432</td>
<td>Ca5(PO4)3(OH)</td>
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<td>41-489</td>
<td>Ca2P2O7</td>
<td>45-345</td>
<td>Ca9Cr(P04)7</td>
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<td>CaCO3</td>
</tr>
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<td>a-Ca3(PO4)2</td>
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<td>CaO</td>
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<td>b-Ca3(PO4)2</td>
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Table E.1: The JCPD cards that have been checked against the phases existed in the specimens.
APPENDIX F. THE DIMENSIONAL DATA FOR THE BAR-SHAPED COMPOSITE SPECIMENS AFTER VARIOUS HEAT TREATMENTS (TABLE F.1)

<table>
<thead>
<tr>
<th>Precursor</th>
<th>After 850°C, 4 h in H₂O/O₂</th>
<th>After 1150°C, 4 h in Ar</th>
<th>After 1050°C, 4 h in Ar</th>
<th>After 850°C, 4 h in H₂O/O₂</th>
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<th>After 1150°C, 4 h in Ar</th>
<th>After 1050°C, 4 h in Ar</th>
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APPENDIX F (CONTINUED).

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Note: Wt., Dia., Thk., Vol., Den., and Por., are abbreviations of weight (mg), diameter (mm), thickness (mm), volume (mm³), density (g/cm³), and porosity (volume %); respectively.

* , #, and +: The porosity was calculated by comparing the densities to the theoretical densities for Precursor (6.941 g/cc), completely oxidized sample (7.186 g/cc), and HA converted sample (7.156 g/cc); respectively.
REFERENCES


34. Sandhage, K.H., Processes for Fabricating Structural Ceramic Bodies and Structural Ceramic-Bearing Composite Bodies. in U.S. Patent #3. 1995.


50. JCPDS Cards: #23-430 for Ca, #9-346 for Ca₂P₂O₇. #9-169 for Ca₃P₂O₉. #9-342 for Ca₁₀(PO₄)₆(OH)₁₂.


31. JCPDS_Cards: #05-"27", #15-806, #6-694, #42-1120, #9-52, #29-489, #26-425, #37-1229, #35-"83, #36-1482, #11-550, #3-935, #42-890.


36. Macgregor, D.C., The porous surface electrode A new concept in pacemaker lead design.


23. JCPDS Cards: #23-430 for Ca, #9-346 for Ca$_3$P$_2$O$_7$, #9-169 for Ca$_3$P$_2$O$_8$, #9-342 for Ca$_{10}$(PO$_4$)$_2$(OH)$_2$.
