

The Effect of Gravity on the Combustion Synthesis of Porous Biomaterials

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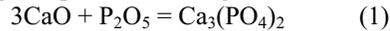
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Abstract

Production of highly porous composite materials by traditional materials processing is limited by difficult processing techniques. This work investigates the use of self propagating high temperature (combustion) synthesis (SHS) to create porous tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), TiB-Ti, and NiTi in low and microgravity. Combustion synthesis provides the ability to use set processing parameters to engineer the required porous structure suitable for bone repair or replacement. The processing parameters include green density, particle size, gasifying agents, composition, and gravity. Tricalcium phosphate produced through the reaction:



has the ability of being resorbed in-vivo. Currently titanium is used in a number of biomedical applications. The reactions incorporating Ti investigated here are:



The advantage of the TiB-Ti system is the high level of porosity achieved together with a modulus that can be controlled by both composition (TiB-Ti) and porosity. At the same time, NiTi exhibits shape memory properties. SHS of biomaterials allows the engineering of required porosity coupled with resorbtion properties and specific mechanical properties into the composite materials to allow for a better biomaterial.

Introduction

Currently a wide range of porous materials are being investigated for bone reconstruction purposes. In conjunction with this research, new processing methods of these materials (i.e. use of gravity) are also being studied. The advantage of porous over solid materials is their ability to provide a biologic interlock with the surrounding tissues by providing a scaffold for vascularization, soft and bone tissue infiltration, and allowing for the capacity to match the mechanical properties of the device to the surrounding tissue[1]. Bioresorbable materials have the added caveat that the material must be removed at the same rate as new tissue is generated[1, 2].

Materials & Methods

SHS reactions take advantage of the process exothermicity of various chemicals[3]. When certain chemical reactants are combined and excited to a high enough temperature, they will combust and produce enough heat to ignite the next layer of reactants. This process will continue or self propagate until the reactants have been exhausted. Temperature-enthalpy relations, as shown below in Figure 1, determine theoretically if SHS reactions are possible. An SHS reaction will take place when 1) the enthalpy of the products has a greater negative value than the reactant, 2) the adiabatic temperature (T_{ad}) is $\sim 1800^\circ\text{C}$, and 3) there is enough enthalpy to ignite the next layer considering heat loss through conduction and radiation. Figure 1 shows the theoretical temperature enthalpy diagram for the $3\text{CaO} + \text{P}_2\text{O}_5 = \text{Ca}_3(\text{PO}_4)_2$ reaction system in a 1 g environment. The adiabatic temperature (T_{ad}) is the theoretical temperature that corresponds to the maximum temperature achieved during reaction with no heat loss. If there is significant heat loss, then the reaction will not sustain itself. Considering this heat loss, the measured maximum temperature achieved during reaction is the combustion temperature (T_c). The diagram shows the start of the reaction at the initial temperature (T_0). For this system it is very difficult to measure the ignition temperature since the reaction occurs in propagating mode.

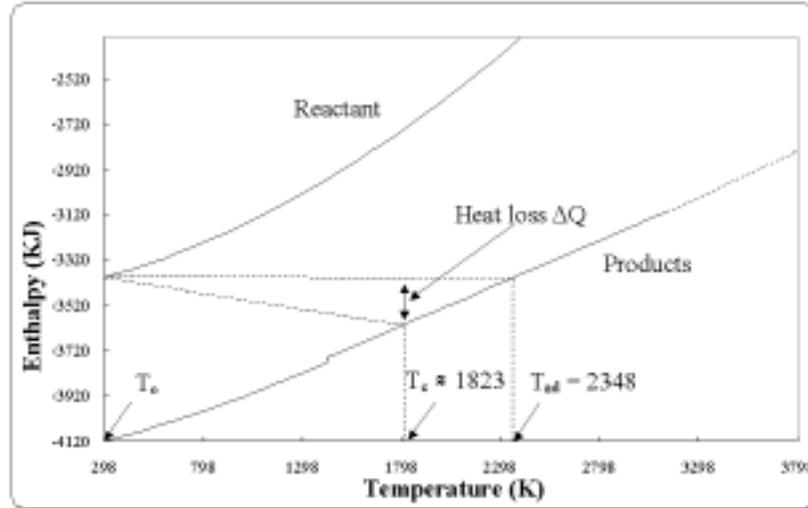


Figure 1. Theoretical temperature enthalpy diagram for the $3\text{CaO} + \text{P}_2\text{O}_5 = \text{Ca}_3(\text{PO}_4)_2$ system.

A typical SHS process includes 1) mixing of reactant powders, 2) forming of pellet by uniaxial or preferably isostatic pressing, 3) loading into the combustion chamber, and 4) ignition of the combustion reaction.

All samples were pressed into cylinders (dia =1.27cm., h=1.27-2.1cm) and ignited via a tungsten coil in an argon atmosphere. Reaction systems including the combination of CaO and P_2O_5 , require that all mixing, pressing, and test reactions occur in a high purity inert atmosphere (i.e. glovebox). This is due to the hygroscopic nature of the P_2O_5 . Physical data for the reactants are listed below in Table 1.

Table 1. Physical data for the reactant powders.

	CaO	P_2O_5	Ti	B	Ni
Particle Size (μm)	<45	<94	<45	<45	<45
Purity (%)	99.99	99.9	99.5	99	99.9
Melting Point ($^\circ\text{C}$)	2888		1660	2300	1453
Molecular Mass (g/mol)	56.07	141.92	47.87	10.81	58.69

SHS experiments were conducted in low gravity through the NASA KC-135A Reduced Gravity Research Program. Parabolic flight patterns are used to obtain ~20 seconds of low gravity and 40 parabolas per day are generally flown. A special rack is used to perform the SHS experiments aboard the plane. Temperature, video, and pressure data are obtained together with the production of samples.

Process parameters include green density, particle size, gasifying agents, composition, and gravity. All of the processing parameters affect the porosity, amount of interconnected pores, and pore shape. These properties allow the engineering of SHS produced materials with specific porosities as well as the construction of functionally graded porosities.

Scanning Electron Microscope (SEM) images were produced using a JEOL JXA-840 SEM. The SEM analysis was coupled with a Thermo NORAN Lithium drifted 10mm² Electron Dispersive X-ray (EDX). Samples were coated with Gold for SEM analysis. Xray Diffraction (XRD) analysis was performed with a Philips X'Pert MPD Pro Theta/Theta X-ray diffraction system. The microstructure of the TiB-Ti samples was studied with an Olympus SZX12 stereoscope.

Results

SEM micrographs shown below in Figure 2, show the difference in microstructure. Figure 2 (A) is a micrograph of a sample reacted in low gravity and partially cooled in a low gravity and ~2 g environment, due to the parabolic flight pattern of the KC-135. The grain exhibits the characteristics of particle ripening and six sided grain

growth features. Figure 2 (B), shows grains that have cooled in a 1g environment. The microstructure exhibits longitudinal grains with characteristic spots.

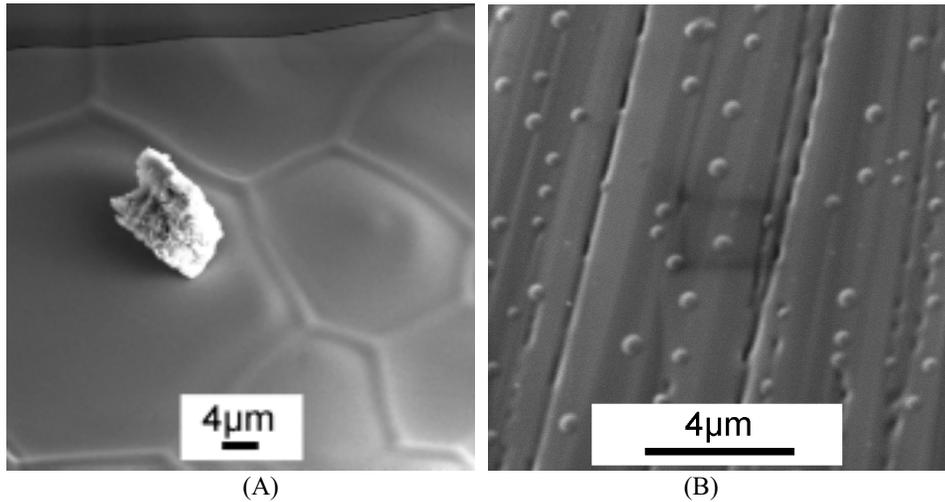


Figure 2. SEM images of $\text{Ca}_3(\text{PO}_4)_2$ produced in low gravity (A) and at 1 g (B).

EDX analysis (Figure 3) show spectra taken from the center of both grains from Figure 2. The low gravity sample shows almost the same calcium to phosphorus ratios while the 1 g sample exhibits a lower calcium to phosphorus ratio. The EDX/SEM samples were coated in gold, therefore deconvolution of the phosphorus and gold peak was performed.

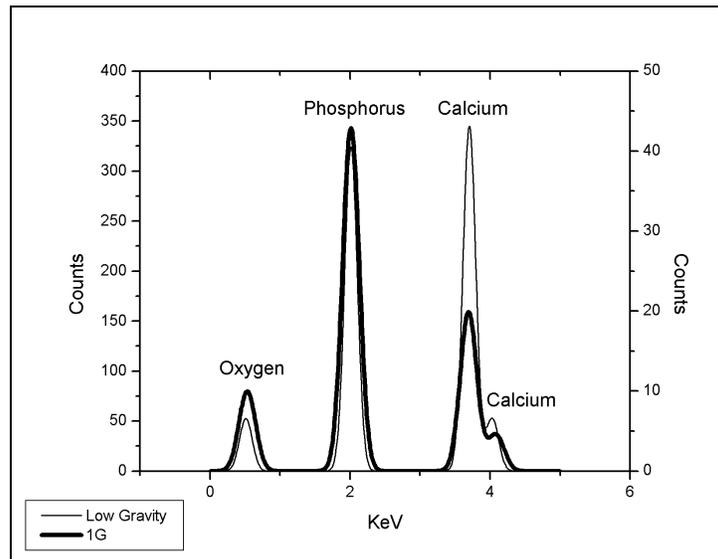


Figure 3. EDX spectra for $\text{Ca}_3(\text{PO}_4)_2$ produced in low gravity and at 1 g conditions.

XRD analysis of both the low-gravity and 1 g samples are shown below in Figure 4. Both spectra match the alpha phase for tricalcium phosphate (PDF 70-0364). Note that this is a bulk analysis and the above EDX analysis is a microanalysis.

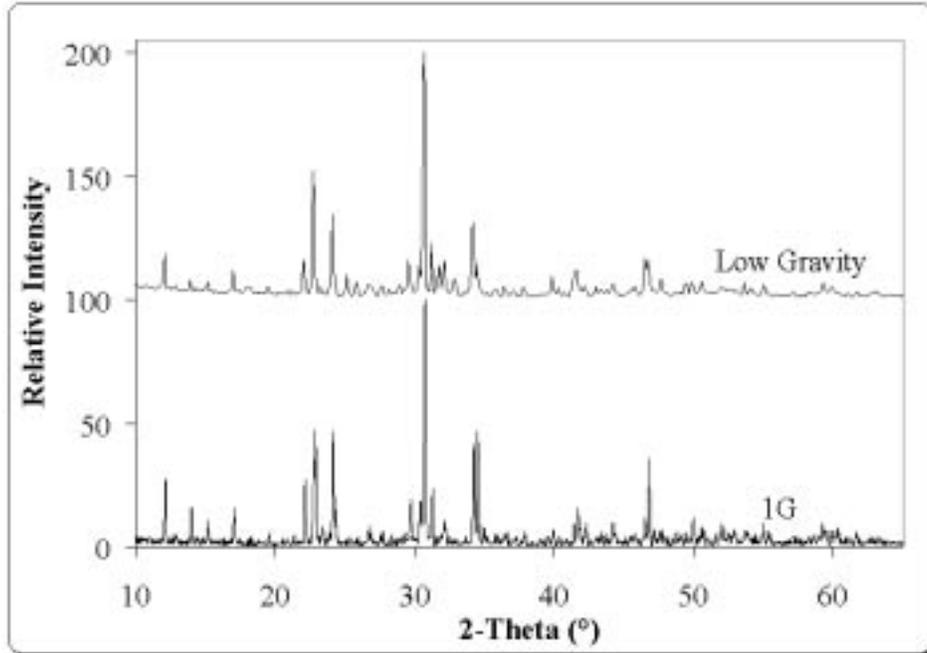


Figure 4. XRD spectra for $\text{Ca}_3(\text{PO}_4)_2$ produced in low gravity and 1 g conditions. Both spectra match PDF file 70-0364 alpha tricalcium phosphate (monoclinic).

The effect of gravity on the $(x+y)\text{Ti} + x\text{B} = y\text{Ti} + x\text{TiB}$ is shown below in Figure 5. The longitudinal or propagating direction is shown below with ignition from the lower side (bottom of sample). Sphere-like pores were produced in low gravity environments and radial pores were produced under terrestrial conditions.

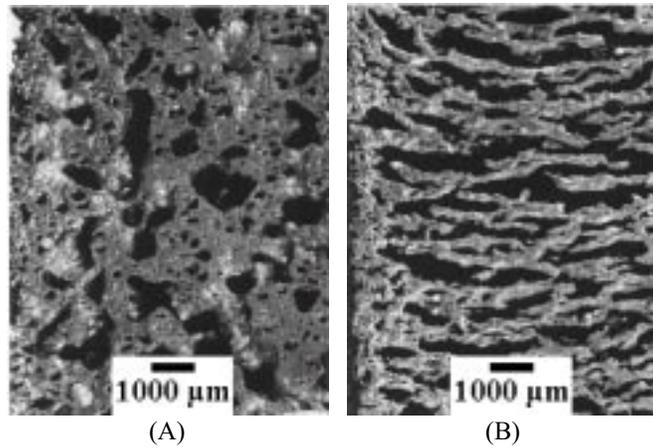


Figure 5. Effect of gravity on reaction system $(x+y)\text{Ti} + x\text{B} = y\text{Ti} + x\text{TiB}$. The as-produced materials are 92% TiB and 8%Ti. A was produced in low gravity and B was produced in terrestrial conditions aboard the KC-135.

SHS reactions were also investigated for the NiTi system. XRD analysis of NiTi produced via SHS is given in Figure 6. Ni₃Ti and NiTi₂ were formed with the NiTi in the combustion process (nonequilibrium).

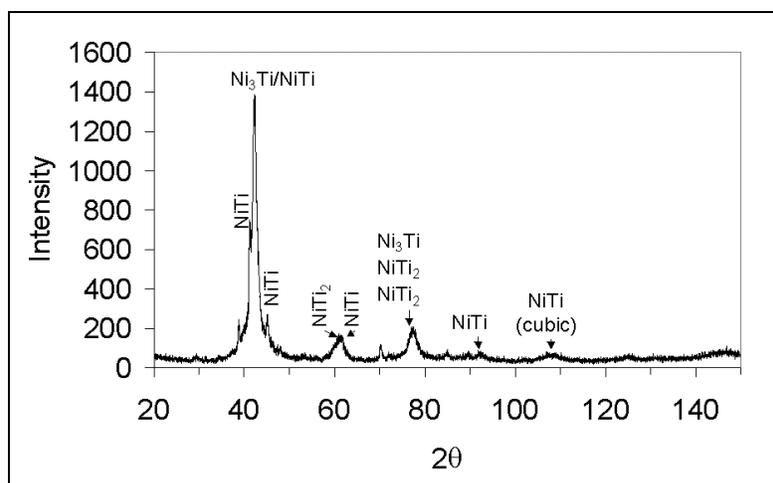


Figure 6. XRD of SHS produced NiTi under terrestrial conditions.

Discussion

Different gravity environments have a great effect on the Ca₃(PO₄)₂ microstructure produced by SHS. It is shown on the micrometer scale that the grain structure is significantly different according to Figure 2. Low gravity produces the classic Al₂O₃ type grain growth while the terrestrial environment yields long radial grains with characteristic spots. In Figure 3, EDX analysis shows that the calcium to phosphorus ratio is unity for grains manufactured on the KC-135 while the calcium to phosphorus ratio is lower for the sample produced under terrestrial conditions. The samples produced on the KC-135 were partially cooled in low gravity (~0 g) and high gravity (~2 g) conditions due to the parabolic flight path of the KC-135. Bulk analysis performed with XRD (Figure 4), showed that both Ca₃(PO₄)₂ samples produced in microgravity formed the alpha phase of tricalcium phosphate. The microstructure studied at the surface via EDX is in need of further investigation to explain the overall balance in the calcium to phosphorus atomic ratio. EDX will have to be carried out at the grain boundaries and throughout other features not shown in Figure 2. Longer low-gravity conditions (available on the International Space Station) may also prove to produce a more homogeneous sample. The processing conditions greatly affect the surface chemistry, which is directly related to the bioactivity of the sample in-vivo.

The TiB-Ti system produced in variable gravity is shown to have a great influence on the formation of pores. Spherical-like pores are produced in low gravity while longitudinal-radial pores are produced in terrestrial conditions. The pore structure is directly related to the strength of the material, in-vivo vascularization, and tissue ingrowth properties.

Ni₃Ti and NiTi₂ were formed together with the equiatomic NiTi during SHS according to the XRD results obtained in Figure 6. This is due to the non equilibrium conditions that are involved with SHS reactions. The formation of equiatomic NiTi only happens in a narrow almost equiatomic region (50-55 atomic %) in the phase diagram. The NiTi phase exhibits shape memory and superelasticity properties that are desirable for specific implant applications. The NiTi system is continually being investigated to produce a greater amounts of the equiatomic NiTi phase and ways to produce this material in variable gravity situations.

Acknowledgements

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