COMBUSTION SYNTHESIS OF CALCIUM PHOSPHATE POWDERS

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ABSTRACT

Calcium phosphate bioceramic powders closely resembling those found 'in vivo' in human body (hydroxyapatite and tri-calcium phosphate) have been synthesized by using synthetic body fluid solutions via the combustion synthesis (CS) method. Powder characterization was performed by XRD, ICP-AES, FTIR and SEM.

INTRODUCTION

Calcium hydroxyapatite (HA: $Ca_{10}(PO_4)_6(OH)_2$), the main inorganic matrix component of bones, is a member of "apatite" family. Biological apatites, which comprise the bioinert mineral phases of calcified tissues (enamel, dentin, and bone), differ from pure HA in stoichiometry, composition and crystallinity and in other physical and mechanical properties [1]. Minor elements, such as, Na^+, Mg^{2+}, K^+, acid phosphate $(HPO_4)^{2-}$, Cl^-, and F^-, and some trace elements (e.g., Sr^{2+}, Pb^{2+}, Ba^{2+}, Zn^{2+}, Fe^{2+}, etc.) are associated with biological apatites and may be seen as substituents in the apatite structure. On the other hand, the presence of resorbable calcium phosphate ceramics in human bones (such as, tricalcium phosphate, TCP: $Ca_3(PO_4)_2$) is mainly for the establishment of a mineralized framework for bone remodeling.

HA or TCP powders have generally been synthesized from aqueous solutions for use in bioceramic applications. It is known [2] that calcium hydroxyapatite is the least soluble and the most stable calcium phosphate phase in aqueous solutions at pH values higher than 4.2. However, HA has been preferred to be synthesized in neutral or highly alkaline media [3-10] to insure the thermal stability of the formed phase after high-temperature (1100°-1300°C) sintering. Synthesis of HA in neutral [5] or slightly acidic media [8] is known to be a more complicated and difficult task. The synthesis of bi-phasic mixtures of the phases of HA and TCP has also been studied by aqueous coprecipitation [11].

The synthetic body fluid (SBF) prepared in accord with the chemical analysis of human body fluids, having the ion concentrations nearly equal to the inorganic components of human blood plasma, was first used by Kokubo and his co-workers [12-14], to prove the similarity between *in vitro* and *in vivo* behaviors of certain glass-ceramic compositions. Combustion synthesis (CS) is not a new technique to be used in the field of materials synthesis. It has first been used by Kingsley and Patil [15] for the manufacture of high-purity α-alumina powders. The same researchers have also

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successfully used this method of materials synthesis in preparing several compositions in the ZrO_2-Al_2O_3 binary system [16]. The combustion being instantaneous and energy-saving have attracted much interest and been successfully utilized in the synthesis of $LaCrO_3$ [17], $Ba_2YCu_4O_8$ [18] and Y-Ba-Cu-O phases [19]. Recently, combustion methods using "glycine" as the fuel [20], and "urea" as the fuel [21, 22] have been reported for the preparation of Ca-doped $LaCrO_3$, pure $LaAlO_3$ and the binary phases of the CaO-Al_2O_3 system, respectively. A similar combustion technique was also demonstrated for the synthesis of YAG:Cr and Y_2O_3:Eu [23], and of YAG:Nd and YIG:Nd [24] powders using both of the above-mentioned fuels.

The purpose of this study was to prepare phase pure HA and bi-phasic HA-TCP bioceramic powders by using the technique of combustion synthesis in synthetic body fluid solutions containing dissolved calcium nitrate tetrahydrate and di-ammonium hydrogen phosphate salts, and to investigate their high temperature (600°-1150°C) calcination behavior in a stagnant air atmosphere.

EXPERIMENTAL PROCEDURE

The details of preparation of the synthetic body fluid (SBF) solutions used in this study were given in Table I.

Table I Preparation of Synthetic Body Fluids

Order	Reagent	Amount (gpl)	Ion	Concentration (mM)
1	NaCl	6.429	Na^+	142
2	$NaHCO_3$	2.520	Cl^-	125
3	KCl	0.373	HCO_3^-	30
4	$Na_2HPO_4.2H_2O$	0.178	K^+	5
5	$MgCl_2.6H_2O$	0.305	Mg^{2+}	1.5
6	$CaCl_2.2H_2O$	0.368	Ca^{2+}	2.5
7	$ZnCl_2$	0.136	HPO_4^{2-}	1
8	$CuSO_4.5H_2O$	0.125	Cu^{2+}	0.5
9	$FeC_6H_5O_7.3H_2O$	0.897	Fe^{2+}	3
10	$(CH_2OH)_3CNH_2$	6.057	Zn^{2+}	1
			SO_4^{2-}	0.5

The Merck-purity chemicals listed in the second column of this table were first added (by the amounts given in the third column) into 700 mL of boiled de-ionized water in the order given in the first column. The solution was heated to 37°C and then completed to 1 L by adding aliquots of a total of 25 mL of 1 M HCl (for pH adjustment to 7.4) together with the required amount of de-ionized water. After adjusting the volume to 1 L, the nominal ion concentrations in the prepared SBF solutions were as given in the fourth and fifth columns of Table I (with the only exception of Cl^-, which is going to be higher than the value given there due to the titration with HCl solution). Human plasma is known to contain small amounts of elements like Fe, Cu, and Zn [25].

The solutions used during the combustion synthesis were prepared as shown in Table II in seven groups of experiments (each repeated thrice for reproducibility). A 50 mL portion of the above SBF solution was placed in a clean Pyrex beaker of 250 mL capacity. $Ca(NO_3)_2.4H_2O$ and $(NH_4)_2HPO_4$ salts, of the amounts given in Table II, were respectively added into this solution.

Table II Experimental compositions studied by CS

Run	$Ca(NO_3)_2.4H_2O$ (gram)	$(NH_4)_2HPO_4$ (gram)	Ca / P (molar)
1	1.457	0.465	1.75
2	1.457	0.479	1.70
3	1.457	0.494	1.65
4	1.457	0.509	1.60
5	1.457	0.526	1.55
6	1.457	0.543	1.50
7	1.457	0.562	1.45

Thus formed opaque solution was then converted into a clear one, by adding 0.5 mL of concentrated nitric acid while stirring on a stir-plate at room temperature. 3 grams of urea was finally added into the clear solution, and following 2 minutes of stirring at room temperature, the Pyrex beaker was directly placed into an electrically-heated box furnace maintained at 505 ± 10°C. Initially the mixture boils and undergoes dehydration followed by decomposition, with swelling and frothing, resulting in a foam which ruptures with a flame and glows to incandescence [16]. The entire combustion process was complete in less than 15 minutes [22]. The product of combustion was a voluminuous, beige in color, foamy, crystalline and crisp calcium phosphate precursor. The precursors were lightly ground in an agate mortar into a fine powder and then calcined on α-alumina plates, in a stagnant air atmosphere, over the temperature range of 600° to 1150°C, for 17 hours.

Powder X-ray diffraction spectra were obtained from the as is and calcined samples for phase characterization purposes. A Rigaku (Tokyo, Japan) DMax/B powder diffractometer was used with CuK_{α_1} radiation at the step size of 0.02° and a preset time of 5 seconds. The FTIR spectra of the powder samples were collected by a Nicolet (USA) DX-510 spectrometer. Dried (at 90°C) powder samples were mixed in an agate mortar with 3 wt% KBr prior to pellet formation. Particle size and morphology of the powders were investigated from the photomicrographs taken with a JEOL (Tokyo, Japan)/JSM6400 scanning electron microscope. The samples were, first, sputter-coated with an approximately 25 nm-thick layer of Au-Pd alloy. Inductively-coupled plasma atomic emission spectroscopy (ICP-AES) (Perkin Elmer,

Model: Plasma-1000, UK) was used for the accurate chemical analysis of elements present in the produced calcium phosphate powders.

RESULTS AND DISCUSSION

Nitrate solutions usually decompose at temperatures <700°C with the evolution of the gases of nitrous oxides, such as NO_2, NO, and N_2O_5 [19]. Urea is also known [19, 22] to decompose into biuret (H_2N-CO-NH-CO-NH_2, i.e., $C_2H_5N_3O_2$), cyanuric acid (HCNO), ammonia (NH_3) when it is heated to about 200°C. Biuret itself then decomposes when heated at temperatures >300°C. Therefore, in an aqueous mixture of a metal nitrate and urea, the decomposition products are expected to consist of nitrous oxides, NH_3, and HCNO. This gaseous mixture will spontaneously ignite when the ambient temperature is about 500°C [22]. This ignition is believed to instantaneously increase the local temperature of the dried foam to about 1300°C [19], which, in a sense, is similar to the case of flash pyrolysis.

Figure 1 shows the XRD spectra of the combustion-synthesized calcium phosphate compositions listed in Table 2. The samples of this figure were all calcined in air at 1150°C for 17 h, following the CS. The variation in the nominal Ca/P (molar) ratio in the starting CS solutions was found to provide a powerful control in the final phase assemblage (in terms of HA and TCP distribution) of the 1150°C-calcined powders. Single-phase HA powders were only obtained for the Ca/P ratio (in the initial solutions) in excess of 1.70. Samples prepared from solutions with Ca/P < 1.70 all yielded bi-phasic mixtures of HA-TCP. In other words, the amount of TCP in the two phase mixtures increased with decreasing Ca/P ratio as follows; 5% TCP at 1.70, 10% TCP at 1.65, 15% TCP at 1.60, 35% TCP at 1.55, 80% TCP at 1.50, and 95% TCP at 1.45. Phase assemblage in these samples consisted of a mixture of both α- (high-T) and β- (low-T) polymorphs of tri-calcium phosphate. The powder synthesis method presented here is regarded as a quick way of producing the bi-phasic mixtures of HA-TCP, as well as for pure HA.

Figure 2 shows the XRD spectra of the combustion-synthesized powder samples by using an initial (solution) Ca/P ratio of 1.75, after being heated at different, consecutively increasing temperatures. The "as is" powders obtained immediately following the CS process were found to be crystalline, and they basically consisted of the phases of $Ca_8H_2(PO_4)_6.5H_2O$ (ICDD PDF 26-1056), $Ca(OH)_2$ (PDF 4-733) and CaO (PDF 4-777). After heating (15°C/min heating and 5°C/min cooling) these powders in a stagnant air atmosphere at 600°C for 17 h, the above phase assemblage was almost retained. Calcination of the same powders at 800° and 1000°C caused the initial formation of HA phase (ICDD PDF 9-432), and the powders heated at 1150°C were found to consist of single-phase calcium hydroxyapatite. The lattice parameters of the 1150°C-calcined HA samples were measured to be a = 9.431 and c = 6.884 Å. These values were in good agreement with those reported [26] for bone apatites.

The results of the ICP-AES analysis performed on the 1150°C-calcined, combustion-synthesized HA powder samples were given in Table III. The samples were first dissolved in HNO_3 and the ICP analysis were carried out on these solutions.

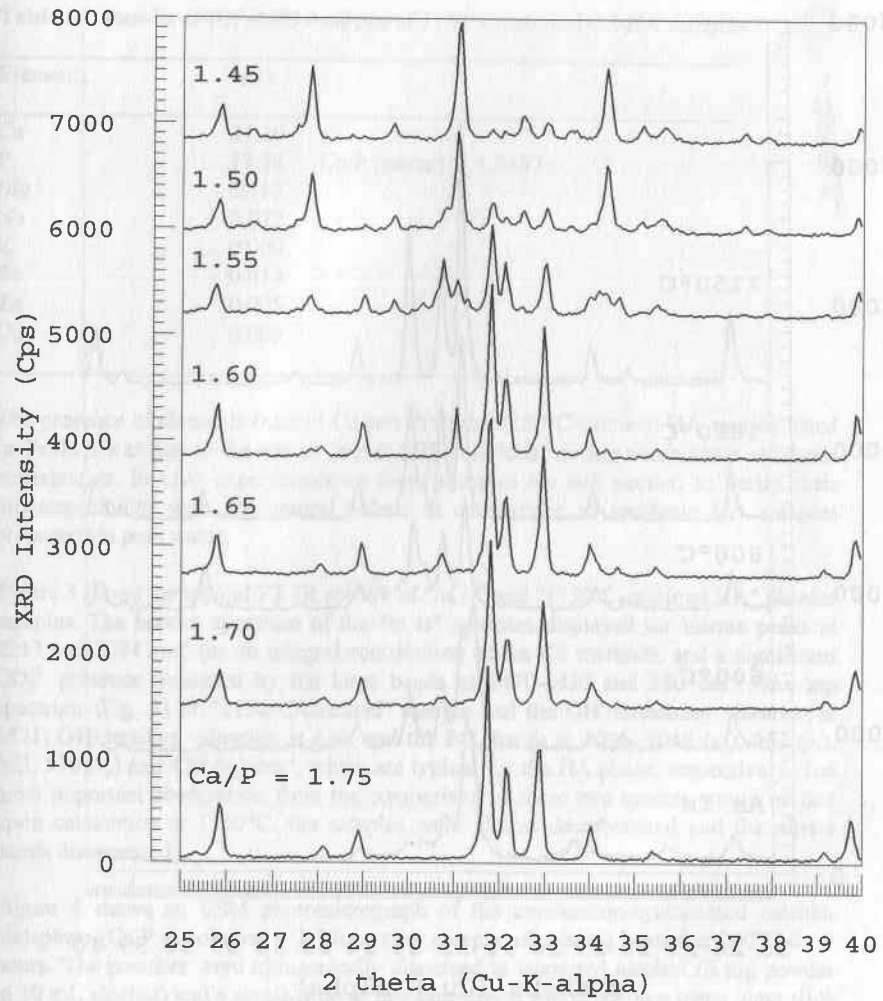

Fig. 1 XRD spectra of combustion-synthesized calcium phosphate compositions given in Table 2 (1150°C, air, 17 h)

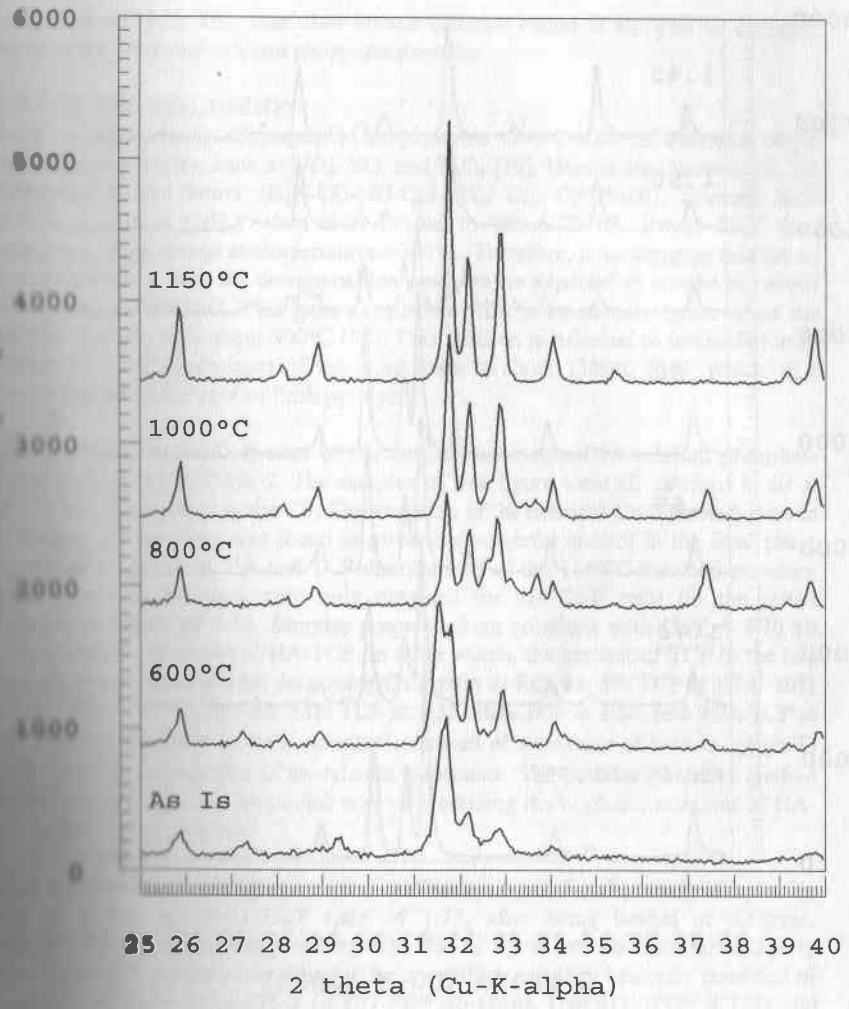

Fig. 2 XRD spectra showing the crystallization behavior of combustion-synthesized powder samples having the initial solution composition of (Ca/P =) 1.75 (Air, 17 h each heating)

Table III Results of ICP-AES Analysis of 1150°C-calcined CS-HA samples

Elements	wt%	
Ca	37.10	
P	17.38	Ca/P (molar): 1.6497
Mg	0.113	
Na	0.072	
K	0.009	
Fe	0.014	
Zn	0.005	
Cu	0.003	

The presence of elements (except Ca and P) in the 1150°C-calcined HA sample listed in Table 3 was due to the use of "novel SBF solutions" during combustion synthesis experiments. In vivo experiments on these samples are still needed to verify their biocompatibility with the natural bones, in comparison to synthetic HA samples prepared via pure water.

Figure 3 shows the typical FT-IR spectra of "as is" and "1150°C-calcined HA" powder samples. The bottom spectrum of the "as is" powders displayed the nitrate peaks at 2213 and 2034 cm^{-1} (as an integral contribution of the CS method), and a significant CO_3^{2-} presence indicated by the large bands at 1470-1420 and 880 cm^{-1}. The top spectrum (Fig. 3) of "1150°C-calcined" sample had the OH^- stretching vibration at 3571, OH^- bending vibration at 636, and the PO_4 bands at 1096, 1045 (ν_3), 962 (ν_1), 603, 570 (ν_4) and 470 (ν_2) cm^{-1}, which are typical for the HA phase, respectively. The most important observation from the comparison of these two spectra would be that upon calcination at 1150°C, the samples were almost decarbonated and the nitrate bands disappeared.

Figure 4 shows an SEM photomicrograph of the combustion-synthesized calcium phosphate (Ca/P in solution = 1.70) powder sample after being heated at 200°C for 6 hours. The powders were ultrasonically dispersed in isopropyl alcohol (5 mg powder in 10 mL alcohol) and a single drop of this suspension was dried on a clean glass slide prior to the SEM study. The particles are observed to be sub-micron and non-agglomerated.

CONCLUSIONS

Combustion synthesis was shown to be an alternative way of sub-micron powder synthesis for calcium phosphate bioceramics like calcium hydroxyapatite and tri-calcium phosphate. The use of a novel synthetic body fluid, instead of pure water, during synthesis, which included the small concentrations of transition elements, such as iron, copper and zinc was shown to facilitate the chemical incorporation of such trace elements into the powder body.

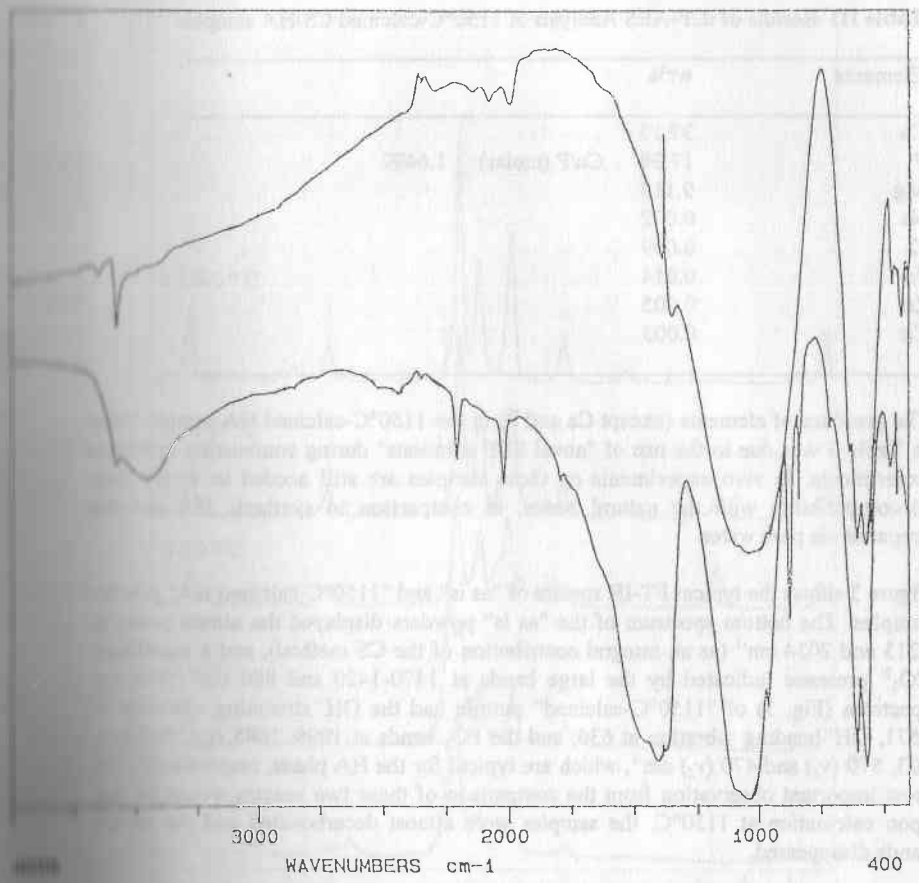

Fig. 3 FT-IR spectra of the combustion-synthesized powder samples having the initial solution composition of (Ca/P =) 1.75 (*Top*: 1150°C-calcined, *Bottom*: as is powders)

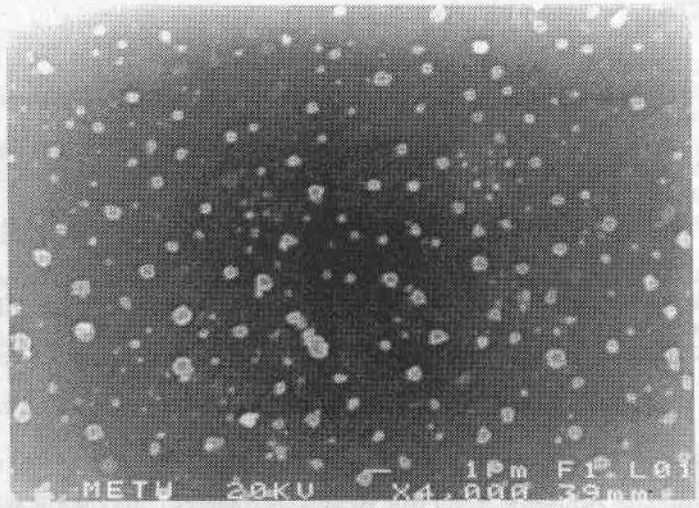

Fig. 4 A typical SEM micrograph of combustion-synthesized calcium phosphate powder samples having the initial solution composition of (Ca/P =) 1.70 (200°C, 6 h)

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COMBUSTION SYNTHESIS OF NANOSIZE SILICON CARBIDE AND ITS DENSIFICATION CHARACTERISTICS

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The synthesis of nanosize silicon carbide powders and whiskers from elemental silicon and carbon reactants by gas phase transport assisted combustion synthesis has been demonstrated. The effects of carbon powder sources, the initial concentration of reactive additives, such as $KClO_3$, NH_4ClO_4 and Teflon, and the gas atmosphere pressure, on the product morphology, the average particle size have been studied in detail. It has been found that combustion synthesis of silicon carbide can be accomplished both in nitrogen or argon atmosphere. It has been shown that there is a formation of silicon oxynitride during the synthesis in nitrogen atmosphere using carbon powder with very high specific surface area and relatively high oxygen content. Average particle size of silicon carbide synthesized from high purity silicon and carbon powders in a presence of reactive additives is approximately 200nm, and it is affected by the concentration of additives and gas pressure of atmosphere. In the presence of growth promoters such as Ni, Fe, and Co, SiC whiskers can be formed. Preliminary results of pressureless sintering are presented as well.

INTRODUCTION

A new class of processes, with an enormous technological flexibility and capability, so called combustion synthesis or self-propagating high-temperature synthesis (SHS) was developed and successfully applied in the last three decades. Over five hundred ceramic and composite powders have been synthesized using this technique [1-3]. However, this technique can be only applied to exothermic reacting systems which generate a sufficient amount energy to be self-sustaining (e.g., Ti + C, Al + Fe_2O_3, Ti-B, Si-N_2, Ni-Al, and many others).

The direct reaction between Si and C elemental powders is weakly exothermic (ΔH_{298}° = -69 kJ/mole) with the adiabatic reaction temperature being 1800 K [4]. Therefore, the direct combustion synthesis of SiC from Si and C is not self-