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ADDITIVE MANUFACTURING OF CARBIDES USING RENEWABLE RESOURCES

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ABSTRACT

Here we report initial results towards additive manufacturing of carbides. We shaped and heat treated biopolymers-metal oxide gel composites in order to obtain 3-D carbide structures. Renewable biopolymers such as iota-carrageenan, chitin and cellulose were used to form the gels. Heat treatment of the gel composites resulted in amorphous porous carbonaceous material with high surface area. The carbonaceous materials preserved the original 3D shape. The ongoing work is on optimization of the conditions for carbide synthesis. We are also studying the rheology of the gel composites to aid to the additive manufacturing.

INTRODUCTION

Carbides are one of the most important groups of material because of their high chemical stability, low thermal expansion, high thermal conductivity and high temperature resistance. Among the several synthesis methods of carbides, carbothermal reduction reaction is the most promising techniques as it allows to use a wide range of material as precursor [1]. Carbothermal reaction involves reduction of metal oxides in presence of carbon by heat treatment in an inert atmosphere [2].

Additive manufacturing (AM) is an emerging technology where objects are created from the bottom up using layer by layer deposition. The use of AM makes it possible to build 3D complex shapes that cannot be manufactured using traditional manufacturing techniques. Among the different materials that can be patterned using AM, gel materials are promising candidates. Gels that have been patterned include photocrosslinkable hydrogels [3], gelatin [4], collagen [5] and alginate hydrogel [6]. Applications of gel based AM are varied,

ranging from tissue engineering to additive manufacturing of food [7,8].

Here, we present initial results leading to novel additive manufacturing of carbides. To this end, we shape and heat treat a biopolymer-oxide composite featuring Bingham plastic behavior. Extrusion of such composite at room temperature allows for layer-by-layer fabrication; with the rheology of the composite dictating the scale of fabrication, *i.e.* thin gels for millimetric features, thicker gels for bigger structures. Upon heat treatment at 900 °C, the biopolymer carbonizes. As the temperature is increased to 1300 °C, the resultant carbon reacts with the oxide nanoparticles. We seek to form carbides through a carbothermal reduction reaction. Such manufacturing process could lead to a more energy-efficient route to complex carbides shapes. Renewable biopolymers replace petroleum-based ones as carbon source; and the temperature needed for carbide formation is drastically reduced due the colloidal proximity of the reactants. Additive manufacturing of a gel composite, that is precursor to carbides, could enable complex shapes, especially those currently challenging for powder pressing or machining of bulk carbides. In this work we focus on silicon carbide.

EXPERIMENTAL

Materials

Gels comprising a carrier and bio-filler are used as the carbon source. Iota-carrageenan (IC) is used as carrier while cellulose or chitin are used as bio-filler. They all were obtained from Sigma Aldrich, USA and used as provided. Amorphous silica nanoparticles were used as the oxide source and were purchased from US Research Nanomaterials, Inc. They featured an average diameter of 15-20 nm.

Methods

The complete experimental process is shown in Fig 1. Silica nanoparticles were dispersed in distilled water (Laura Lynn, USA) in a 5% weight ratio using sonication (35 W for 15 minutes, Qsonica Q700, Qsonica LLC, USA). In a parallel step, iota-carrageenan was manually mixed with cellulose or chitin in a weight ratio of 1:4. 5 g of the biopolymer powder mixture was then added to 15 ml of the silica nanoparticle dispersion and mixed together with a mixer in a try to achieve a homogeneous gel composite. Two different gels were then obtained. These gels were then manually aspirated into a 20 ml plastic syringe and finally manually extruded on an alumina substrate (96% alumina, Kyocera Ceramics, USA), as shown in step 2 of Figure 1.

The extruded spiral towers (8-10 mm) were heat treated in a furnace (TF1400, Across International, USA) under a constant nitrogen flow rate of 10 SCFH. The heating protocol was as follows: 1) room temperature to 300 °C with a heating ramp of 5 °C/min; 2) a dwell at 300 °C to eliminate any residual oxygen from the heating chamber; 3) from 300 °C to 1300 °C at 5 °C/min; 4) a 75 min dwell at 1300 °C to allow complete carbothermal reaction; and 5) natural cooling to room temperature by turning the furnace off, but keeping the nitrogen flow. The carbonaceous samples were then taken out from the furnace and prepared for characterization.

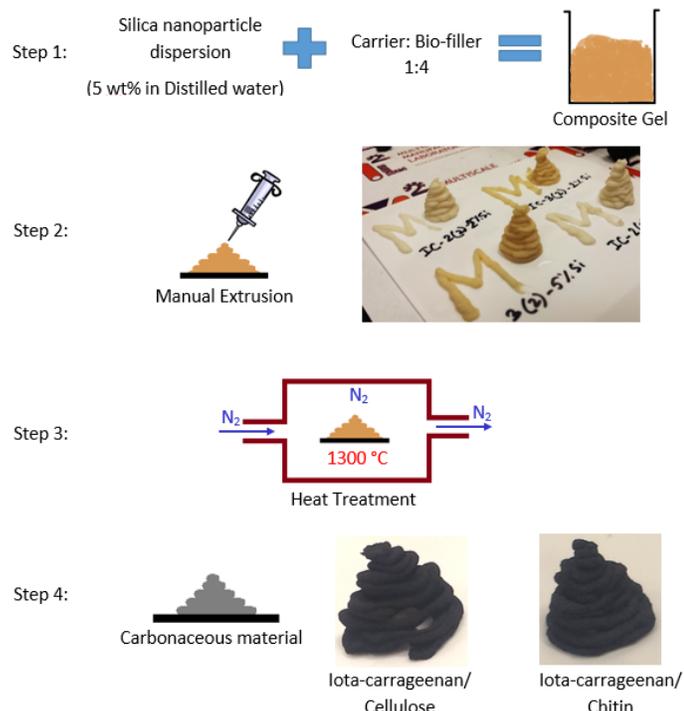


Figure 1: Schematic of complete synthesis process

Characterization

The morphology and composition of the carbonaceous samples was analyzed using Scanning Electron Microscopy SEM (Hitachi SU6600 SEM, Japan), Energy-dispersed X-ray spectroscopy EDX (Oxford Instruments, USA) mounted on the

SEM to obtain composition, X-ray diffractometer XRD (Scintag XDS 2000) to analyze crystallinity and composition, and Brunauer-Emmett-Teller (BET) analysis (Micromeritics ASAP 2020, USA) to determine surface area. Focused Ion Beam (Hitachi NB5000 FIB, Japan) was used to obtain cross-sections of selected samples.

RESULTS

Visual inspection of the carbonaceous samples evidence that the precursor shape is held during carbonization. The surface of the carbonaceous material from iota-carrageenan/cellulose precursor appears smoother than that from iota-carrageenan/chitin precursor.

XRD analysis leads to the results shown in Fig. 2. The only crystalline phase detected in both of the samples is of cristabolite SiO₂. Amorphous behavior dominates in the case of iota-carrageenan/chitin precursor. No crystalline phase of SiC is identified in the XRD results for any of the samples.

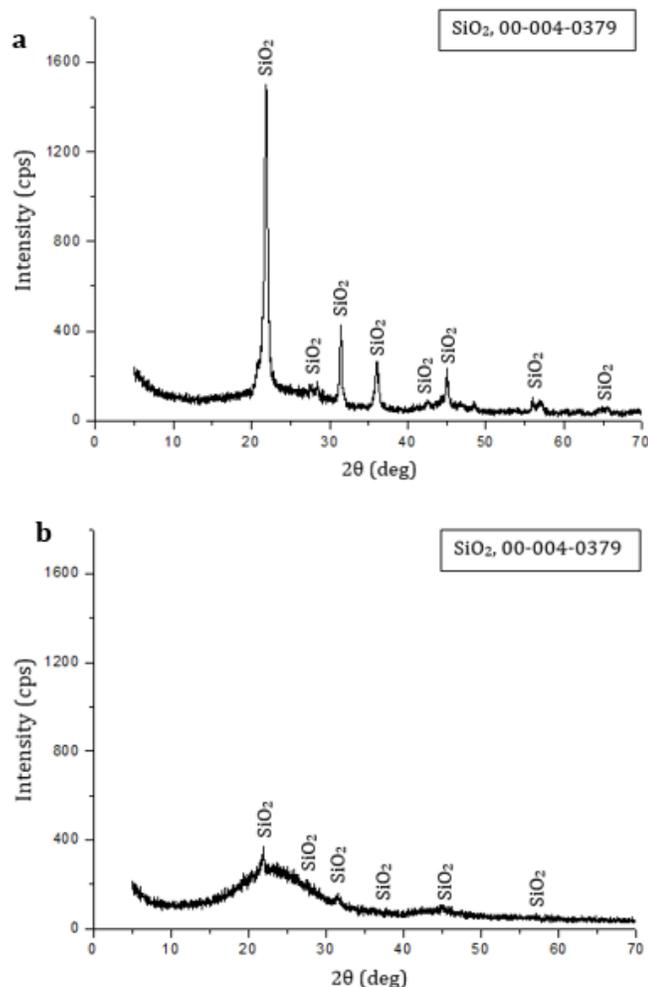


Figure 2: XRD patterns for synthesized material from precursor (a) Iota-carrageenan/cellulose and (b) Iota-carrageenan/chitin

The results from SEM analysis are shown in Fig. 3. A cross section of the sample is obtained with FIB as shown in Fig. 3a. When all the images of the FIB milled sections are stacked together, it is found that pores propagate throughout the whole sample volume. In Fig. 3b, the surface SEM of the sample from iota-carrageenan/chitin precursor shows the clustered morphology of the material.

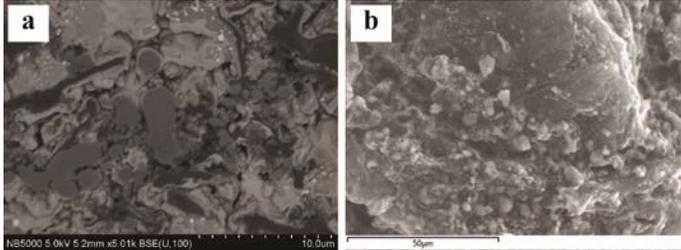


Figure 3: (a) SEM image of FIB milled cross-section of sample from iota-carrageenan/cellulose precursor; (b) SEM image of surface of the sample from iota-carrageenan/chitin precursor

The presence of silicon and carbon is confirmed from EDX analysis as shown in table 1. Along with silicon and carbon, several other elements were detected.

Table 1: EDX results showing elemental composition of different samples

Sample	Element							
	C	Si	O	K	Na	Ca	S	Mg
IC/Cellulose + 5 wt% SiO ₂	22.5	13.9	38.7	8.3	6.5	7.3	1.6	0.6
IC/Chitin + 5wt% SiO ₂	36.5	20.5	25.7	5.1	3.2	6.8	1.8	0.4

The surface area measured for the carbon samples from iota-carrageenan/cellulose and iota-carrageenan/chitin precursors is 399.6723 m²/g and 232.0953 m²/g, respectively.

DISCUSSION

Heat treatment of the composite gels results in porous carbonaceous material. No crystalline SiC is present in the material. If SiC is present in the samples, it is expected to be amorphous. Most of the amorphous silica has transformed into cristobolite form. This may be the result of reaction temperature used in this study. The reaction temperature is not sufficient for the silica particles to react with the carbon to form crystalline carbide. Low reaction temperatures also lead to the formation of the clustered morphology [9]. Moreover, the proportion of silica particles to the carbon reduced from the biopolymer

precursor may not be optimum to complete the carbothermal reaction for carbide synthesis.

EDX results show the presence of several contaminants such as potassium, sodium, calcium, sulfur and magnesium in the sample. Iota-carrageenan contains sulfur in its chemical structure. Sulfur contributes around 15% weight in the single unit of iota carrageenan, as calculated from the chemical structure of iota-carrageenan. The iota-carrageenan content in the gel composites is 18% of the total weight. Hence the amount of sulfur contributed by iota-carrageenan should be 2.5% of the total weight of the gel composite. This estimation is close to both of the EDX results. Other precursors i.e. cellulose and chitin do not contain any of the contaminant materials detected. The fact that both chitin and cellulose were purchased in purity above 95% and used as provided eliminate the possibility that the contaminants come from these reactants. Hence, we assume that the distilled water source used for making the silica nanoparticle dispersion is to blame for the contaminants.

Initial results show how the geometry of the precursor is preserved during carbonization. This is encouraging towards AM. The scale of the AM process could be determined by optimizing the rheology of the gel. Other important parameters to be studied include layer bonding and stability of overhangs. For example, thin gels allow molecular diffusion among layers, which increases the inter layer bonding. For overhang feature, the gels should be stiff and light enough so that it does not fall down.

Besides chitin and cellulose, coconut flour has been used as the bio-filler material. Konjac Glucomann has been used as an alternative to iota-carrageenan for a carrier. All these polysaccharides are renewable. For example, cellulose is one of the most abundant biopolymers on earth, synthesized by plants, algae, tunicate sea animals and some bacteria [10,11]. Chitin is also abundant as the primary structural element of the exoskeleton of shrimp, crab and lobsters [12]. Iota-carrageenan is a sulfated polysaccharide originally synthesized by red marine algae *Rhodophyceae* [13] and widely used in the food industry as thickener. Konjac glucomannan is extracted from the plant *Amorphophallus* and is also widely used as a food additive [14,15]. While cellulose, chitin and coconut flour mixed with water make thin solutions, the addition of iota-carrageenan or konjac powder has proven to be a viable way to tailor viscosity in a wide range.

CONCLUSION AND FUTURE WORKS

Initial results demonstrate manufacturing of carbonaceous 3D shapes from a biopolymer-oxide composite. Though silicon carbide synthesis is targeted through carbothermal reaction, porous carbonaceous material with high surface area are obtained at the present reaction temperature of 1300 °C. This temperature seems insufficient for carbide synthesis as previously reported [16]. The proportion of the silica nanoparticle and the bio-polymer mixture used here is in question for carbothermal reaction. Several contaminants are

detected in the material, most likely originating from the water used in these experiments.

Ongoing work is on increasing the temperature during carbonization as well as implementing a more reductive atmosphere and longer dwells at the target temperature. We are also optimizing the proportion of the silica nanoparticle and bio-polymer mixture to successfully implement the carbothermal reaction. To avoid the contamination, ultra-pure water is used instead of distilled water to make the silica nanoparticle dispersion.

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