



Polymer-derived Si-C-Ti systems: From titanium nanoparticle-filled polycarbosilanes to dense monolithic multi-phase components with high hardness

Vanessa Proust^a, Mirna Chaker Bechelany^a, Rudy Ghisleni^b, Marie-France Beaufort^c,
Philippe Miele^a, Samuel Bernard^{a,*}

^a IEM (Institut Européen des Membranes), UMR 5635 (CNRS-ENSCM-UM), Université Montpellier, Place E. Bataillon, F- 34095, Montpellier, France

^b Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Mechanics of Materials and Nanostructures, Feuerwerkerstrasse 39, Thun CH-3602, Switzerland

^c Institut Pprime, CNRS – Université de Poitiers – ENSMA – UPR 3346, Département Physique et Mécanique des Matériaux, Bd Marie et Pierre Curie, BP 30179, 86962 Futuroscope Chasseneuil Cedex, France

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ABSTRACT

This paper describes the fabrication of Si-C-Ti ceramics from titanium nanoparticle filled allylhydridopolycarbosilanes (Ti NP-filled AHPCS) using a casting/curing technique followed by pyrolysis at 1000 °C under argon. TGA and XRD have been applied to investigate the mass loss behaviour during ceramization and to gain structural information on the decomposition process of Ti NP-filled AHPCS. TiC is the first phase to nucleate in an amorphous SiC matrix around 800 °C, whereas titanium silicide and MAX phases grow between 800 and 1000 °C. Densities measurements have been done and structural characterization of the final specimens is carried out using XRD and Raman spectroscopy. The process leads to (nano)composites with a density increasing from 2.45 to 2.90 g/cm³ and a Vickers hardness ranging from 17 to 20.9 GPa according to the AHPCS:Ti ratio fixed in the early stage of the process. The titanium silicide and MAX phases are decomposed during a further heat-treatment between 1000 and 1400 °C to generate TiC/SiC (nano)composites.

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1. Introduction

Silicon carbide (SiC) attracts much attention as key engineering components in many future advanced technology programs, primarily due to its good mechanical and chemical properties, and also its reliability at room and elevated temperatures. The manufacturing process of SiC was initiated by Acheson in 1892 [1,2] and is still applied today to produce the commercially available SiC (α -SiC). SiC powders are fabricated into articles *via* classical high-temperature metallurgical techniques. Whereas the stringent processing schemes often involve many steps, the quantitative properties of a finished product often do not match those of the pure starting material. These shortcomings as well as the need to fabricate complex architectures and/or SiC-based (nano)composites have stimulated searches for alternative “ceramic through chemistry” concept.

Yajima et al. reported in 1975 the preparation of β -SiC through pyrolysis of methyl-substituted polysilanes, namely polycarbosilanes (PCS) [3–5]. PCS, a solid, fusible and soluble preceramic polymer, has been investigated as a precursor for SiC fibers for over 30 years. This discovery touched off a rapid development of preceramic polymers for the preparation of simple carbides, carbonitrides and nitrides of various main groups and transition elements [6–8] as well as homogeneous mixtures or solid solutions of pseudo-binary combinations of ceramics and (nano)composites [9–11]. The implementation of the PDCs route is firstly motivated by the possibility to generate complex ceramic compositions and micro-/nanostructures (amorphous, crystalline or (nano)composite). Secondly, it proposes the advantage to process materials in particular shapes such as powders, fibers, coatings/membranes, and 3D structures as well as morphologies (dense or porous) that are difficult, or even impossible to obtain by conventional routes [12–26].

One area that benefits greatly from the development of preceramic polymers is (nano)composites [9–11,27–30]. Although most pure ceramics have a number of favorable performance character-

* Corresponding author.

E-mail address: Samuel.Bernard@umontpellier.fr (S. Bernard).

istics which are appropriate for advanced component applications, ceramic (nano)composites and solid solutions of two or more pure phases often exhibit dramatically enhanced properties. For example, we recently demonstrated that TiN/Si₃N₄ (nano)composites display a significant improved hardness in comparison to Si₃N₄ [9,30]. In some cases, these materials also display unique electrical, magnetic and/or optical properties [29].

Three general approaches based on preceramic polymers may be applied to generate these (nano)composites. A first approach consists to blend two precursors of the desired composition or copolymerize two precursors [31]. The second approach involves the synthesis of *single source* molecular compounds that contain all the necessary elements of the desired (nano)composites [30]. In the third method which is in fact the simplest, a preceramic polymer is combined with an active (or a reactive) inorganic filler such as a pure, fine-grained metal. The use of active fillers in preceramic polymers has been investigated by Greil [32,33]. The main focus of these works was to study the formation of new phases during the polymer-to-ceramic conversion and the possibility to influence the chemical composition of the ceramic product. Furthermore, it has been suggested that the addition of active fillers might alleviate the limitations in the use of preceramic polymers for the formation of dense articles, *i.e.*, the degree of shrinkage and porosity that develops upon pyrolysis of a polymeric green body. Greil and Seiboldz [34] have produced a model to predict critical volume fractions for potential fillers. In particular, thermodynamical calculations have been performed leading to phase stability diagrams of metallic titanium and chromium in the presence of silicon oxycarbide matrix in inert as well as in reactive atmospheres. The structural changes occurring during the polymer-to-ceramic conversion have been investigated by Erny [35].

Obvious benefits of this approach are that ceramic yields are improved and off-gas evolution is reduced because of the reaction of fillers with the gaseous by-products. Seyferth et al. [36] investigated this approach to prepare Si-C-W systems using polysilazanes and W powders. In the same study [36], Ti and Zr were combined with the polysilazane and pyrolyzed under Ar at 1500 °C to form mixtures of TiN, ZrN and SiC. Pyrolyses of a polycarbosilane (Nicalon PCS) with Al, Ti, V, Zr, Nb, Ta, and W in a M-Si ratio of 1:1 under Ar at 1500 °C gave primarily mixtures of the respective metal carbides and SiC [36]. The polymer/metal filler mixtures were successfully used to fashion near net shape articles. Riedel et al. mixed titanium powders with polysiloxane to form after pyrolysis to 1100 °C mixtures of titanium carbide and metal silicide [37]. More recently, a series of studies has been reported on the dispersion of titanium powders in polycarbosilanes with the objective to form the well known MAX phase Ti₃SiC₂ [38–42]. All these works illustrate the simplicity of this polymer approach. However, additional studies in this area are warranted, and the results will likely be practical and useful. As an illustration, the use of nanoparticles (diameter ≤ 100 nm) as active nanofillers in organosilicon polymers to prepare monolithic Si-C-Ti components is not reported whereas nanostructured materials are known to propose improved or new properties compared to their microstructured counterparts.

Within this context, we report a detailed investigation of the dispersion of titanium nanoparticles (Ti NPs) in an organosilicon polymer (allylhydridopolycarbosilane (AHPCS), SiC precursor [6,43,44]) followed by casting, curing and pyrolysis processes to generate monolithic multi-phase ceramic components. Our objective was to characterize the microstructural evolution of the (nano)composites, the processibility of green bodies into useful compacts as well as the benefits that accrue in increased ceramic yields and reduced shrinkage and porosity. The structural, textural and thermal evolution of the materials has been followed during pyrolysis by XRD coupled to TG experiments. The materials in form of monoliths prepared at 1000 °C under argon are characterized by

XRD, Raman spectroscopy, He pycnometry and micro-indentation according to the AHPCS:Ti ratio fixed in the early stage of the process. Multi-phase components composed of titanium carbide (TiC), titanium silicide (Ti₅Si₃, TiSi₂) and MAX (Ti₃SiC₂) phases are produced at 1000 °C. Upon further pyrolysis to 1400 °C under argon, TiC/SiC (nano)composites are generated. The overall flow chart of the process is shown in Fig. 1.

2. Experimental

2.1. Materials

Allylhydridopolycarbosilane (AHPCS labeled SMP-10, Starfire Systems® Incorporation, New York, USA) with a density of 0.998 g/cm³ is used as-received. SMP-10 is a clear, amber-colored, viscous liquid. Titanium nanoparticles (<100 nm particle size) are available in mineral oil (98.5% trace metals basis, Sigma-Aldrich). They are used after thoroughly washed with hexane then toluene (twice for each solvent) to remove the mineral oil. Then, they have been re-dispersed in toluene to form a homogeneous solution. Argon (>99.995%) is purified by passing through successive columns of phosphorous pentoxide, siccantTM and BTS catalysts. The handling of the chemical products is made inside a MBraun glove box (< 0.1 ppm H₂O and O₂, Germany) under argon atmosphere. Toluene (99.8%) extra-dry and hexane extra dry (<50 ppm) over molecular sieves and stabilized Acroseal are purchased from Acros Organics.

2.2. Sample preparation

Ti NP-filled AHPCS mixture preparations are carried out in a purified argon atmosphere by means of standard Schlenk manipulations and vacuum/argon-line techniques. In our process, a solution of AHPCS in toluene is added to Ti NP suspension in toluene according to different molar AHPCS:Ti ratios from 10 to 1 in an ultrasonic bath. Toluene is then removed by vacuum distillation (3×10^{-2} mbar/60 °C) via an ether bridge to deliver black solutions labeled **Ti-AHPCS.X** (X being the AHPCS:Ti ratio, X = 1 → 10) whose viscosity inherently increases with Ti content.

Samples **Ti-AHPCS.X** (X = 1 → 10) are directly converted into the corresponding (nano)composites labeled **Si-C-Ti1000.X** (X being the AHPCS:Ti ratio, X = 1 → 10) by pyrolysis into an alumina tube inserted in a horizontal tube furnace (Carbolite BGHA12/450B; Bibby Scientific France SAS). The tube is pumped under vacuum and refilled with argon (120 mL/min) to be subjected to a cycle of ramping of 5 °C/min to 1000 °C, dwelling there for 2 h, and then cooling down to RT at 5 °C/min. The sample **SiC1000** is obtained from AHPCS following the same procedure. It serves as a reference.

To prepare pieces, AHPCS and the samples **Ti-AHPCS.X** (X = 1 → 10) are cast into a PTFE mould (11 mm of diameter and 2 mm of thickness), hermetically sealed in a steel die and thermally cross-linked at 230 °C into an alumina tube inserted in a horizontal tube furnace (Carbolite BGHA12/450B; Bibby Scientific France SAS) to form fully dense, black infusible green bodies. The tube is pumped under vacuum and refilled with argon (120 mL/min) to be subjected to a cycle of ramping of 1 °C/min to 230 °C, dwelling there for 12 h, and then cooling down to RT at 5 °C/min. The cross-linked green bodies are unmolded in an argon-filled glove-box to form disc shaped. As-obtained monoliths are transferred into the same tube to be pumped under vacuum and refilled with argon. Subsequently, the samples are subjected to cycles of ramping of 1 °C/min to 1000 °C under argon, dwelling there for 2 h, and then cooling down to room temperature (RT) at 2 °C/min to deliver the final materials labeled **MSiC1000** (from AHPCS) and **MSi-C-Ti1000.X** (X = 1 → 10) with diameter and thickness depending on

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