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Feature article

A comprehensive study on the influence of the polyorganosilazane chemistry and material shape on the high temperature behavior of titanium nitride/silicon nitride nanocomposites

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ABSTRACT

The high temperature crystallization behavior of polytitanosilazane-derived amorphous SiTiN ceramics was investigated in a nitrogen atmosphere using XRD, Raman spectroscopy, TEM, SEM and BET. At 1400 °C, TiN is the first phase to nucleate in SiTiN ceramics forming nanocomposites with a homogeneous distribution of TiN nanocrystals within an amorphous Si_3N_4 matrix. Above 1400 °C, XRD indicates that the temperature at which Si_3N_4 crystallizes depends on the volume fraction of TiN present in nanocomposites. This is closely related to the chemistry of the polyorganosilazanes used to synthesize polytitanosilazanes. The use of perhydridopolysilazane, the most reactive polyorganosilazane, allows preparing TiN/Si_3N_4 nanocomposites with a remarkable stability of the amorphous matrix up to 1800 °C as mesoporous materials and powders. Dense monoliths crystallize earlier than the powder analogs because of the use of an ammonia pre-treatment before polymer warm-pressing.

1. Introduction

Silicon carbide (SiC) and nitride (Si_3N_4) are engineering ceramics that have a number of favorable performance characteristics reliable at room and elevated temperatures which are appropriate for advanced component applications. Multinary ceramics offer substantial improvements with respect to specific properties over simple binary Si-C and Si-N materials prepared by conventional techniques [1–5]. Such materials are in general produced using ceramic (nano)powders. Coupled with pressure-assisted sintering techniques to consolidate (nano)powders, these processing routes lead to materials with good performances. However, the preparation of these nanocomposites and composites is a challenging task according to the fact that these processes unavoidably lead to size and structure in homogeneities of the different phases and presence of impurities (because of the use of sintering additives to consolidate the materials) which affect the properties. The performance of these nanocomposites could be significantly improved by controlling the distribution of the nanophase as well as the purity of the materials. We recently proposed alternative strategies using a "ceramic through chemistry" concept to prepare such materials [6–9].

Recently, we investigated the Polymer-Derived Ceramics (PDCs) route to design nanocomposites. Such a method uses inorganic (=preceramic) polymers as ceramic precursors which offer the advantages to tune the ceramic compositions and micro-/nanostructures of ceramics and to process materials at low processing temperatures in particular shapes and morphologies (dense or porous) that are difficult, or even impossible to obtain by conventional routes [10–20].

A first approach combines a preceramic polymer with an active (or a reactive) inorganic filler such as a pure, fine-grained metal to influence the chemical composition of the ceramic product [21,22]. We prepared TiC/SiC composites using titanium nanoparticles as active fillers and allylhydridopolycarbosilane as a SiC precursor [8]. The second approach involves the synthesis of *single source* molecular compounds that contain all the necessary elements of the desired nanocomposites [6,7,9]. The basis for this approach comes from the design of a suitable highly pure synthetic precursor in which uniform chemical composition is established at molecular scale. The synthesis of this precursor is directed to tailor the structure of the final materials: precursors are converted in a first pyrolysis step into single-phase amorphous ceramics. The later are subsequently annealed at higher temperature to initiate the

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crystallization and provide the material with tuned phase composition and nano-/microstructure organization. This is the strategy we applied to prepare titanium nitride/silicon nitride labeled *nc*-TiN/*a*-Si_3N_4 (*nc* for nanocrystalline, *a* for amorphous) [6,9]. In that case, ammonia is used as atmosphere during the first pyrolysis step and nitrogen is used during the second pyrolysis step. Interestingly, we could keep the matrix amorphous which allowed reaching high mechanical properties after pyrolysis at 1300–1400 °C. As an illustration, these nanocomposites prepared as dense monoliths are composed of TiN nanocrystals with an average diameter of 3.1 nm homogeneously distributed in an amorphous Si_3N_4 matrix. This allowed very high Vickers hardness (25.1 ± 4.0 GPa) and Young's modulus (171 ± 23 GPa) [6]. The mechanical performance is related to the homogeneous nanostructuration of TiN in the amorphous Si_3N_4 matrix which itself is correlated to the chemistry of the precursor.

By reporting the synthesis, processing and pyrolysis behavior of a series of *single-source* precursors, *i.e.*, polytitanosilazanes, we recently gained new insight into the reaction mechanisms of these materials and the understanding of the role of chemistry behind the processability and design of *nc*-TiN/*a*-Si_3N_4 nanocomposites [9].

A proper understanding of the high temperature behavior of such materials is important to optimize the stability of the amorphous matrix. Also, detailed investigations of the crystallization behavior according to the chemistry of polyorganosilazanes and the material shape and texture, *i.e.*, powders, monoliths (mesoporous and dense), on this behavior have not been examined so far. Within this context, the present work aims at the characterization of the high temperature behavior of *nc*-TiN/*a*-Si_3N_4 nanocomposites. We firstly prepared *nc*-TiN/*a*-Si_3N_4 nanocomposites by direct pyrolysis of titanium-modified polyorganosilazanes, i.e., polytitanosilazanes, with different molar Si:Ti ratios obtained from polymethylsilazane (PMSZ), perhydropolysilazane (PHPS) and a poly(vinylmethyl-co-methyl)silazane (HTT1800). Pyrolysis is performed under ammonia at 1000 °C and the subsequent annealing is achieved in flowing nitrogen. The materials have been characterized by XRD, Raman spectroscopy and HRTEM. We firstly discussed the influence of the chemistry and structure of the polymer on the structural properties of final materials. Then, we investigated the effect of the high temperature behavior of these materials as dense pieces and mesoporous monoliths. The schematic diagram of the general process for formation of TiN/Si_3N_4 nanocomposites from polytitanosilazanes with a particular focused on the high temperature behavior is given in Fig. 1.

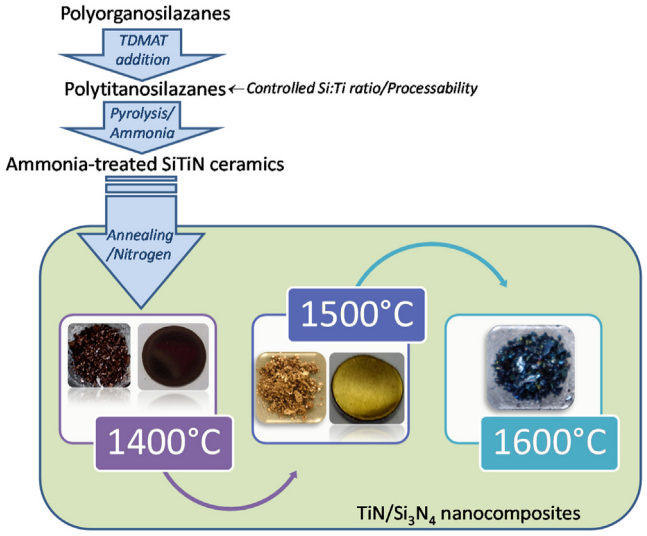

Fig. 1. Schematic diagram of the general process for formation of TiN/Si_3N_4 nanocomposites from polytitanosilazanes with a particular focused on the high temperature behavior.

2. Experimental

2.1. Sample preparation

The polytitanosilazane syntheses were carried out in a purified argon atmosphere (>99.999%) passing through successive columns of phosphorus pentoxide, siccapent™, and BTS catalysts by means of standard Schlenk manipulations and vacuum/argon-line techniques. Schlenk flasks were dried at 120 °C overnight before pumping under vacuum and filling them with argon for synthesis. Manipulation of the chemical products was made inside an argon-filled glove box (MBraun MB200B; O_2 and H_2O concentrations kept at <0.1 ppm). Tetrakis-(dimethylamino)titanium ($Ti[N(CH_3)_2]_4$, TDMAT, 99.99%, Acros Organics) was used as received. Toluene (99.85%, Extra Dry over Molecular Sieve, AcroSeal(R)) was obtained from Acros Organics. Perhydropolysilazane (PHPS, AQUAMICA NN-310) was provided by Mitsuya Boeki Ltd., Japan. ^{1}H NMR (300 MHz, C_6D_6, δ/ppm): 1.6–0.3 (br, N*H*), 5.8–4.3 (br, Si*H*); IR (CsI windows/cm^{-1}): ν(N—H) = 3374 (m), ν(Si—H) = 2125 (vs), δ (N—H): 1173 (m), δ (N—Si—N) = 1020–840 (vs). Polymethylsilazane (PMSZ) was synthesized by ammonolysis of dichloromethylsilane (DCMS, $HSiCH_3Cl_2$) in according to procedures described in the literature [23]. DCMS was obtained from Sigma-Aldrich and freshly distilled from magnesium at P_{atm} before use. ^{1}H NMR (300 MHz, C_6D_6, δ): 0.05–0.12 (vbr, SiCH_3), δ = 0.6 (br, N*H*); δ = 4.4–5.5 (br, Si*H*); IR (CsI windows/cm^{-1}): ν(N—H) = 3374 (m), ν(C—H) = 2954–2773 (s), ν(Si—H) = 2125 (s), δ_{asym} (CH_3) = 1463 (w), δ (Si—CH_3) = 1254 s; δ (N—H): 1173 (m), δ (N—Si—N) = 1020–840 (vs). HTT1800 was provided by Clariant compagny, Germany. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 0.4–0.1 (br, SiCH_3), 1.1–0.5 (br, NH), 4.9–4.4 (br, SiH), 6.3–5.7 (br, vinyl); FTIR (CsI windows/cm^{-1}): ν(N—H) = 3374 (m), ν (C—H) = 3024 (s), 2954 (s), 2898 (s), 2803 (m), ν(Si—H) = 2125 (vs), δ(vinyl) = 1601 (m), δ(CH_3) = 1375 (m), δ(Si—CH_3) = 1254 (s), δ (N—H): 1173 (m), δ (N—Si—N) = 1020–840 (vs).

Polytitanosilazanes have been prepared by reaction of polyorganosilazanes including PMSZ, PHPS and HTT1800 with different amounts of TDMAT leading to polymers labeled PMTiSZX, PHTiPSX and HTT1800TiX with controlled molar Si:Ti ratios (X being the Si:Ti ratio: $1 \leq X \leq 10$). The detail of the synthesis procedure has been published elsewhere [6,9].

Polytitanosilazanes were then placed in alumina boats to be transferred into a silica tube inserted in a horizontal furnace (Nabertherm type RS 80/500/11, Germany) under argon atmosphere (> 99.999%). The tube was pumped under vacuum and refilled with ammonia (> 99.995%). Subsequently, the samples were subjected to a cycle of ramping of 5 °C min^{-1} to 1000 °C, dwelling there for 2 h, and then cooling down to RT at 1 °C min^{-1} to produce the powders labeled **SiTiNX_10** ($1 \leq X \leq 10$). A constant flow (120 mL min^{-1}) of ammonia was passed through the tube. Then, ammonia-treated samples are introduced in a graphitic furnace (Gero Model HTK 8). The furnace was subsequently pumped then refilled with nitrogen to undergo an heating program through a cycle of ramping of 5 °C min^{-1} in the temperature range 1000–1800 °C, dwelling at each temperature in this temperature range for 2 h, and then cooling down to RT at 5 °C min^{-1} to generate the **SiTiNX_Y** ($1 \leq X \leq 10$, Y being the two first number of the temperature, *e.g.*, 12 for 1200 °C) samples. A constant flow (200 mL min^{-1}) of nitrogen was passed through the furnace.

To prepare mesoporous monoliths, monolithic activated carbon (Norit RX3® Extra, provided by Cabot Corporation with specific surface area of 953 m^2 g^{-1} and 2.1 nm of pore size) are infiltrated at reduced pressure by a solution of polytitanosilazane labeled

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