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From trimethylvinylsilane to ZrC–SiC hybrid materials

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Abstract

We describe a new route to synthesize hybrid ZrC–SiC materials in a one-pot procedure. Polycarbosilane was generated from trimethylvinylsilane in the presence of ZrC powder. A specific interaction between the polymer and the ceramic particles was evidenced. The conversion of precursor into composite was achieved by pyrolysis under argon up to 1100 °C. From thermogravimetric analyses, pyrolysis tests and SEM observations, it has been shown that these hybrid materials kept a stability above 850 °C, and their total mass loss remained lower than 20%.

Keywords: Composites; SiC; Polymer; Spectroscopy

1. Introduction

Zirconium and silicon carbides are known as high refractory ceramics with good thermomechanical properties. In ZrC–SiC_p composites, the combination of the passivating character of silicon carbide and the high melting temperature, hardness and thermal stability of zirconium carbide, should generate high-performance ceramics.[1] Such properties require a homogenous microstructure in terms of chemical composition and grain size distribution for these materials. However, in comparison with ZrB_2–SiC composites largely developed,[2] very few routes have been investigated for the elaboration of ZrC–SiC composites. Among them it can be mentioned notably the use of activation by microwave irradiation.[3] However, in such processes, it is difficult to overcome the structural and compositional heterogeneities.

To avoid chemical heterogeneities due to the mixing of the starting powders and, consequently, to obtain high-performance composites with a homogeneous microstructure, the precursor derived ceramics (PDC) method may be a promising alternative.[4] In such a method, a polymeric precursor of SiC (*e.g.* a polycarbosilane (PCS)) could cover ZrC particles. Then, the pyrolysis of this hybrid material could lead to a ZrC–SiC ceramic composite. The original way, which has been developed during the present study, rests on the use of a SiC polymeric precursor in a one-pot procedure, synthesized from a carbosilane monomer (i.e. the trimethylvinylsilane (TMVS)), and in the presence of ZrC.

2. Materials and methods

2.1. Material for polymer precursor synthesis and characterization

Experiments were carried out under flowing argon previously purified through $CaSO_4$ (drierite indicator), a fine quartzwool, and phosphoric anhydride (P_2O_5). All solvents and chemicals reactants were commercially available, and unless otherwise stated, were used as received. Trimethylvinylsilane was received from Acros Organics (97%). Indeed, this monomer has a low boiling point (55 °C) which would be appropriated to the present synthesis conditions, i.e. a thermal activation at 60 °C. Therefore, this molecular precursor should show specific reactivity *via* its double bond. It can be noticed that the monomer could lead to an appropriate Si/C ratio. Indeed a proportion too low produces gaseous monomers, difficult to handle. Furthermore the monomer stoichiometry could result in interesting Si/C ratios in the final ceramic. A large excess of carbon could also generate carbon in the final ceramic. To avoid the introduction of additional heteroelements such as oxygen, it has been chosen to implement a one-pot procedure using only TMVS and ZrC as raw materials and controlled atmosphere. The characterization of reaction products (PCS and ZrC–PCS) was performed by Fourier Transform IR (Spectrum One FT-IR, Perkin-Elmer). FT-IR analyses were carried out in absorbance mode (4000–400 cm^{-1}). All samples were prepared in a glove

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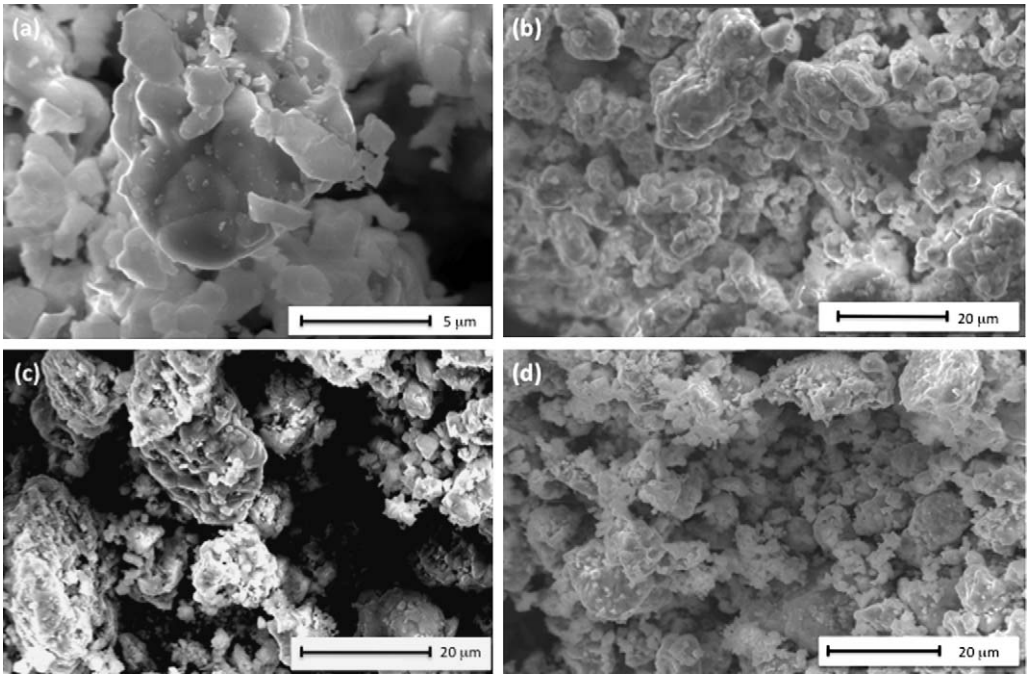

Fig. 1. SEM micrographs of (a) the starting ZrC powder, (b) powder coated with synthetic PCS (20 wt.%), (c) ZrC–PCS (20 wt.% of ZrC) pyrolysed at 850 °C and (d) TG residue of ZrC–PCS (20 wt.% of ZrC) at 1100 °C.

box. A drop of PCS was deposited between two KBr windows, and the cell was protected from ambient air pollution with a tight film. NMR spectra were recorded at 400.13 MHz with a Brüker DPX spectrometer.

2.2. Methods for characterization of starting ZrC and thermal conversion of ZrC–PCS hybrid material

The thermal analysis of the ZrC–PCS was carried out using thermogravimetric analysis (SETARAM thermobalance, type B60, Caluire, France). The heating was performed from 20 °C to 1100 °C with a heating rate of 5 °C min^{-1}. Thermal conversion of the ZrC–PCS mixtures into ceramic materials was achieved in a pyrolysis equipment. The thermal decomposition of the hybrid material was realized in tubular furnace containing an isothermal zone of 0.1 m in length. The heating program is composed of a first heating from 20 °C to 850 °C (heating rate of 5 °C min^{-1}) then a holding of 60 min at 850 °C and, finally, a cooling down to room temperature with a rate of 15 °C min^{-1}. The O content of the powders was determined by chemical analysis thanks to a specific apparatus (HORIBA, EMGA type). Field emission gun scanning electron microscope (FEG-SEM) observations (JEOL JSM-7400F, Tokyo, Japan), specific surface area (ASAP 2010, Micromeritics France SA, Verneuil Halatte, France) and helium pycnometry measurements (AccuPyc II 1340, Micromeritics France SA, Verneuil Halatte, France) were carried out to characterize the grain size, the morphology of the reaction products.

2.3. Starting ZrC powder

Starting ZrC powder was purchased from Alfa Aesar (99.5%). The specific area of 0.71 g m^{-2} was obtained by BET method which corresponds to an average diameter of 1.3 μm. This latter was computed from the following equation, i.e. considering all the elementary particles spherical and monodisperse in size:

$$\phi_m = \frac{6}{\rho S_{BET}} \quad (1)$$

where ρ represents the theoretical density of zirconium carbide,[5] S_{BET} the specific area and ϕ_m the average diameter of particles. A micrography of starting ZrC is shown in Fig. 1a. Density measurement for the zirconium carbide powder led to a value of 6.39. The oxygen content, which was given by elementary analysis, was equal to 0.32%.

3. Results and discussion

3.1. Polymerization

To elaborate ZrC–SiC composites, we have developed a new route for synthesizing polycarbosilane. This procedure firstly requires the coating of ZrC particles using the polymer elaborated *in situ* under argon, at 60 °C, without solvent or catalyst. Monitoring by FT-IR the reaction of TMVS (34 g, 339 mmol) only (Fig. 2), it can be clearly observed the existence of a polymerization because of the disappearance of the =C–H vibration at 3054 cm^{-1} after 53 h.[6] Furthermore, the bands at 2923 cm^{-1} (C–H stretching in Si–CH_2) and 1056 cm^{-1} (CH_2 bending in Si–$(CH_2)_x$–Si) indicated the presence of a Si–CH_2–Si chain in the backbone of the polymer.[7] These bands appear after 5 h of reaction. The absorption at 799 cm^{-1} (CH_3 rocking in –Si$(CH_3)_2$–) showed the evolution from –Si$(CH_3)_3$ (840 cm^{-1} for CH_3 rocking) to –Si$(CH_3)_2$–, suggesting that

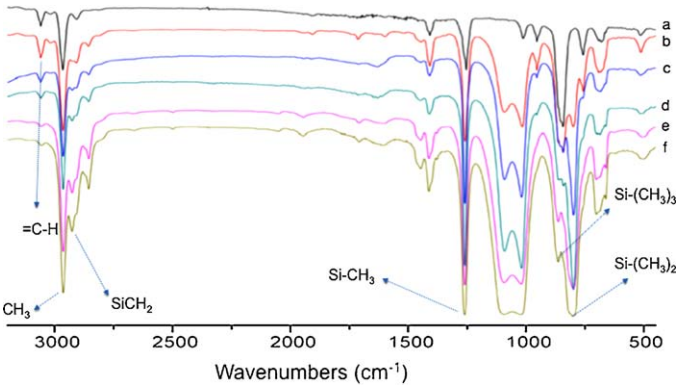

Fig. 2. FT-IR spectra of (a) TMVS and (b–f) polycarbosilane heat-treated: (b) 5 h; (c) 23 h; (d) 30 h; (e) 48 h; (f) 53 h.

the polycarbosilane backbone structure was modified during polymerization.[8]

The polymerization of TMVS in the presence of ZrC was undertaken under the same conditions. A solution of TMVS (34 g, 339 mmol) was added to ZrC (20 wt.%, 8.5 g, 82.3 mmol) then the mixture was heating during 53 h under flowing argon at 60 °C. The product so-obtained looked like viscous and black oil. It was used as such for the following steps of heating treatments and characterizations. The IR spectrum showed both a change in the relative intensity and a residual presence of the band situated at 3054 cm^{-1}. The presence of the alkene might indicate a specific interaction such as a hypothetical metal coordination by the metallic character of zirconium in ZrC, during the polymerization process. Such an interaction could lead to a chemical polymer grip on the zirconium carbide, giving a coating adapted to the subsequent pyrolysis of the hybrid material.

3.2. Thermal behaviour of ZrC–PCS

The TG curve of the ZrC–PCS (20 wt.% in ZrC) is reported in Fig. 3. The heating treatment was carried out under an inert atmosphere (*i.e.* flowing argon). As it can be seen on the TG curve, an overall mass loss of 17% is recorded from room temperature to 1100 °C. It corresponds to a mass loss of 21.3% for the PCS. From this thermogram, three domains are detected as a function of the temperature: (i) a first one without mass evolution was observed from 400 to 600 °C, (ii) a second one from 600 to 850 °C which is related to the most important mass loss and, (iii) finally, for temperatures higher than 850 °C, no mass variation was detected. The mass loss at low temperature ($T < 550$ °C) can be due to the volatilization of oligomers. In the temperature range between 600 and 850 °C, a three-dimensional network develops and leads to the loss of alkanes and dihydrogen species.[9] The pyrolysis conditions have then been established and lead us to an interesting mass yield, in agreement with previous works showing the link between the good ceramic yields and the presence of vinyl groups on the polymer.[10]

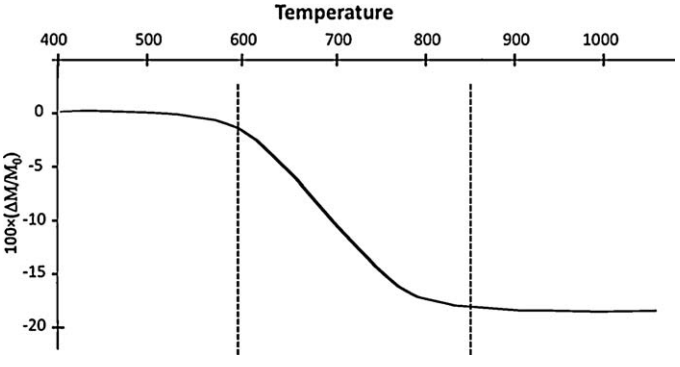

Fig. 3. Thermogravimetric curve (under argon) of the ZrC powder coated with PCS.

Comparing SEM micrographs of the starting ZrC powder to those of ZrC coated by PCS (Fig. 1), it can be noticed more rounded grains for the second one, that appear to be linked by an intergranular phase probably issued from PCS preceramic. This observation was confirmed by a density measurement carried out by helium pycnometry, which gave a value of 3.5 for ZrC–PCS against a value of 6.39 for the ZrC powder. The lower density could be explained by the presence of an organometallic amorphous phase in the ZrC powder. Concerning the residue after pyrolysis, SEM micrographs show, at 850 °C, ball-shaped entities within a secondary phase which seems to be characterized by crystallized particles formed after heating at 1100 °C. Nevertheless, at this range of temperature, the SiC coating phase, obtained from pyrolysed PCS, remains difficult to highlight.[4]

4. Conclusions

ZrC–SiC composites have been prepared using a novel route: the one-pot polymerization-coating process. A specific interaction between ZrC and PCS was demonstrated during the polymerization process. Further thermogravimetric analyses, pyrolysis treatments and SEM micrographs have been carried out and highlighted the thermal and morphological evolution of the hybrid material. Therefore, the as-treated materials appear homogeneous and should be composed of an amorphous SiC based phase and ZrC particles. This work is presently continuing towards fundamental and mechanistic aspects, and also towards the relationship between PCS structure and ceramic properties.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jeurceramsoc.2010.12.014.

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