



A simple route for organic covalent grafting onto zirconium carbide particles



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ABSTRACT

Starting from core-shell zirconium carbide powders, a covalent grafting was described, using a direct nucleophilic substitution in diethyl ether. Thus, two different organic molecules were attached onto the surface of the ceramic, through Si–O–Zr and C–O–Zr bonds. The materials were characterized by means of TEM and XPS characterizations. These new systems could represent an original route to elaborate zirconium carbide-based hybrid materials.

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1. Introduction

The core-shell systems are very important in a large domain of applications [1–4]. Particularly, the interface between organic and inorganic materials can be a key-step in the creation of new high-performance materials [5–7]. With this aim, numerous studies were previously undertaken notably on oxide systems such as silica [2,8]. However, the non-oxide systems are studied less despite their promising applications. Among them, zirconium and silicon carbides are well known as high refractory materials with interesting mechanical properties and passivation agents in oxidizing atmosphere, respectively [9–14]. Consequently, the elaboration of ZrC–SiC composites should generate promising high-performance materials, by combining the dual properties of these two carbides so that the passivating character of SiC could protect ZrC from an oxidative atmosphere [15–18]. In addition, high performance ceramics require homogenous microstructures in terms of chemical composition as well as grain size phase distribution. As a consequence, the fabrication of starting powders exhibiting a core-shell structure would then be well suited to generate a protective SiC layer onto ZrC particles. However, no previous study of the covalent grafting was carried out on the zirconium-carbide based ceramics.

To synthesize a core-shell structure, the route using the polymer-derived ceramics, seems to be promising [19]. Indeed, functionalizing and grafting organic polycarbosilanes onto ZrC particles should be an original synthesis way, in order to generate core-shell composites after an appropriate subsequent pyrolysis treatment. Nevertheless, before considering “grafting from” or “grafting to” approaches [20], the functionalization of ZrC surfaces should be examined. Even if covalent grafting of organic precursor has not been previously performed, some authors have studied the functionalization of ZrC particles [21–23]. The chemical modification already described in the literature is related to monolithic oxygen-modified ZrC surfaces, considering specific (1 0 0) or (1 1 1) orientations of ZrC. The (1 0 0) surface functionalization was then studied towards adsorption of oxygen-containing reactants like water or methanol.

Herein, a convenient approach for an efficient functionalization of micrometric ZrC powders is described. A combined TEM–XPS study is used in order to highlight the grafting of a carbosilane monolayer onto ZrC grains.

2. Experimental

2.1. Materials and measurements

Chlorotrimethylsilane (98%) and dibutylether (99%) were provided by Alfa Aesar. All the products were used as received. The ZrC powders were purchased from Aldrich (99.5%). To determine

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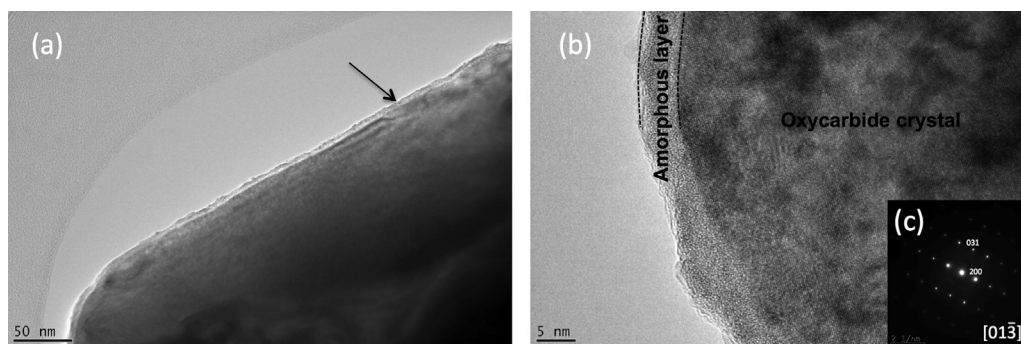


Fig. 1. (a) Low magnification TEM micrograph (b and c) Higher magnification TEM image of the initial ZrC_p, and its associated selected area electron diffraction pattern obtained on the carbide crystal (dark region).

the grain size distribution of the zirconium carbide powder, laser granulometry analyses were performed (AccuPyc II 1340, Micromeritics France S.A. Verneuil Halatte, France). The specific surface area (SSA) of powders was measured thanks to the gas adsorption method (ASAP 2010, Micromeritics France S.A., Verneuil Halatte, France). Samples (450 mg) were degassed at 250 °C for 12 h. Analysis was then carried out at 77 K under nitrogen (99.999%, Air liquide). The BET specific surface area was calculated from the nitrogen adsorption data in the relative pressure range from 0.05 to 0.30. The oxygen content was measured by elemental analysis (EMGA 620W, HORIBA Jobin Yvon S.A.S. Longjumeau, France). Oxygen of the sample reacts with the graphite crucible to form CO/CO₂ detected by infrared spectroscopy. Transmission electron microscopy (TEM) characterizations were carried out with a JEOL 2100 microscope coupled with an Energy Dispersive X-ray Spectroscopy (EDXS) device (JEOL, Tokyo, Japan) and operating at 200 kV. The samples were prepared by crushing the powders in an agate mortar. Then they were put in suspension in a drop of water that was deposited on a copper grid covered by a holey carbon film. Heating with light made the water evaporated and the powder stuck on the grid. The surface of functionalized and grafted ZrC was analyzed by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD spectrometer), using a monochromatic Al_{Kα} source (15 mA, 15 kV). All binding energy scales were charge referenced to the C_{1s} peak (285.0 eV) arising from surface contamination. The area analyzed was 300 μm × 700 μm. The pass energy was 20 eV for the high-resolution spectra and 160 eV for the surveys.

2.2. Synthesis: general procedure for covalent grafting onto the surface

In the first step of the covalent grafting of chlorotrimethylsilane onto the functionalized ZrC grain surface, ZrC (1 g) was treated with an excess of 0.2 mL chlorotrimethylsilane, *i.e.* 132 equiv., assuming a maximum of 10 OH per nm² onto the surface [24]. After 1 h of stirring the reaction at 40 °C in 5 mL of diethylether, the mixture was filtered on a 0.1 μm membrane, then washed with diethylether. The black residue was then dried, and retrieved for XPS and TEM analyses.

3. Results and discussion

In order to reach a core–shell structure with a core of ZrC surrounded by an organic monolayer, the chosen starting material was a micrometric and commercial ZrC powder. Laser granulometry measurements reveal an average grain size diameter of 8.6 μm while surface area characterization through BET provides a value of 0.72 m² g⁻¹. The oxygen and nitrogen contents of the raw powder,

Table 1

Elemental analysis (atomic percentage) performed by XPS on the particle surface.

Sample	C (%)	O (%)	Zr (%)	Si (%)
(1) ZrC	38.6	43.3	18.0	–
(2) ZrC–OSi(CH ₃) ₃	52.0	32.3	13.0	2.7
(3) ZrC–OCH ₂ C≡CH	55.2	31.6	13.2	–

given by elemental analysis, were respectively equal to 0.32% and 0.006%. TEM and XPS analyses were then carried out to identify the oxygen distribution in the starting ceramic powder.

Low magnification TEM images show that all carbide crystals display an external layer exhibiting bright contrast (Fig. 1a: see arrow). Higher magnification images obtained on these regions (Fig. 1b) attest that this external layer shows regular thickness of about 5 nm and a typical contrast (orange skin type contrast) characteristic of its amorphous character.

This native covering layer could be due to the oxidation phenomenon of the zirconium carbide particles during storage in wet air. However, the oxidation tendency of the outer part of crystals could not be confirmed by X-ray dispersive spectrometry analysis by TEM, because the electron beam systematically perforated the shell without giving suitable data. Then, to access the composition of the surface, an XPS experiment was preferred (Table 1). The atomic concentration of oxygen onto surface of ZrC grains **1** (43.3%) is far higher than that obtained thanks to global elemental analysis by infrared spectroscopy (0.32%). Furthermore, considering the XPS profile of the 3d state of zirconium (Fig. 2), and in addition to the ZrC signals, contributions related to Zr–O and Zr–OH bonds were highlighted at 182.7 eV and 184.2 eV, respectively [25]. These results

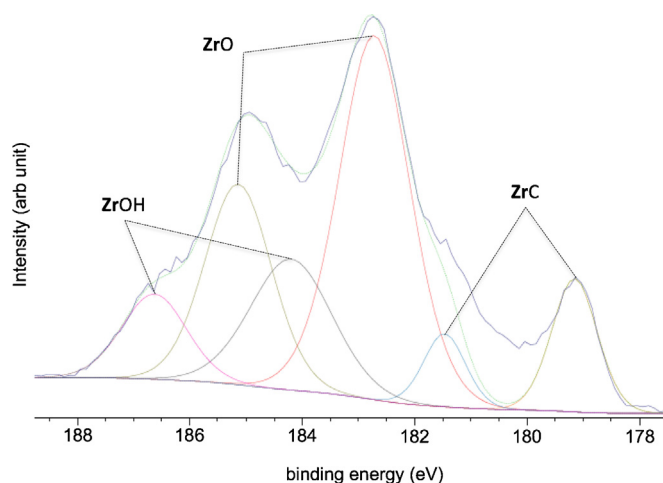


Fig. 2. XPS profile of the 3d state of zirconium for **1**.

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