



# Low-temperature synthesis of tantalum carbide by facile one-pot reaction

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## Abstract

Tantalum carbide (TaC) was synthesized by polycondensation and carbothermal reduction reactions from an inorganic hybrid. Tantalum pentachloride ( $\text{TaCl}_5$ ) and phenolic resin were used as the sources of tantalum and carbon, respectively. FTIR of as-synthesized dried complexes revealed formation of Ta-O. Pyrolysis of the complexes at  $800\text{ }^\circ\text{C}/1\text{ h}$  under argon resulted in tantalum oxide which after heat treatment at  $1000\text{--}1200\text{ }^\circ\text{C}$  transformed to tantalum carbide. The mean crystallite size of the precursor-derived TaC ceramics was less than 40 nm and Ta and C elements were homogeneously distributed in the ceramic samples. Mechanism for formation of TaC ceramic was analyzed.

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*Keywords:* Tantalum carbide; Sol-gel; Carbothermal reduction; Ceramics

## 1. Introduction

Comprising refractory borides, nitrides and carbides, ultra-high temperature ceramics (UHTCs) exhibit high melting point, high strength, thermal shock resistance and chemical stability, which are the most promising candidate materials for the use at ultra-high temperature [1–5]. In the family of UHTCs, tantalum carbide (TaC) is a candidate for high-temperature use, such as that required for high-performance cutting tools, rocket nozzles, and aerospace propulsion systems, due to its high melting point ( $> 3800\text{ }^\circ\text{C}$ ), high elastic modulus (537 GPa, a corrected value from the theoretical density), high hardness (15–19 GPa), and superior thermal and chemical stability [6].

TaC powders can be conventionally prepared by the carbothermal reduction of tantalum oxide [7] or the direct reaction of tantalum with carbon [8] at elevated temperatures. However, a high temperature and a long production period are usually required in the above methods, and the synthesized powders usually have relatively poor sinterability [9–11]. The sol-gel method is an effective way for low-temperature synthesis of ultra-fine powders for the intimate contact of the

reactants [12]. Interest in ultra-high temperature ceramics (UHTCs), especially introducing UHTCs into continuous fiber-reinforced ceramic matrix composites (CMCs) has increased significantly in the past few years. Yan [13] prepared C/C-TaC composites using inorganic precursors via sol-gel method. Lu [14] blended allyl-functional novolac resin with polytantaloxanesal, and synthesized TaC at a temperature of  $1400\text{ }^\circ\text{C}$ . However, sols or precursors prepared by above-mentioned methods are not very suitable for impregnation due to their poor processing property, high temperature, and complicated synthesis processes.

A new method of preparing tantalum carbide materials by facile one-pot reaction is reported herein. The phase compositions, the crystalline state, and the microstructures of products treated at different temperatures were characterized. Moreover, a hypothesized formation mechanism of TaC is also presented.

## 2. Material and methods

Tantalum pentachloride ( $\text{TaCl}_5$ ) and acetylacetone (Hacac), used to prepare tantalum precursors, were of analytical grade. Phenolic resin (THC-400; Shanxi Taihang Impedefire Polymer Limited Company, Shanxi, China) was used as the carbon source. The moles of C reported in this article just only

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correspond to the pyrolyzed char of phenolic resin whose char yield was about 60 wt%.

Stoichiometric amount of  $\text{TaCl}_5$  (36 g, about 0.1 mol) was dissolved in a mixture of 100 ml ethanol and 25 ml acetylacetone (about 0.25 mol). After concentration in an oil bath for 1–2 h, stoichiometric amount of phenolic resin was blended homogeneously to produce the liquid tantalum carbide polymer precursor. Three precursors with C/Ta molar ratios of 1, 2, and 4 were prepared. The liquid polymer precursors were solidified at 80 °C and then dried to remove some of the remaining water and ethanol at 200 °C for 2 h. The subsequent heat treatment was performed at a heating rate of 15 °C/min to the desired temperature of 400, 600, 800, 1000 and 1200 °C for 1 h.

The chemical composition of sample liquids was analyzed by Fourier transform infrared spectroscopy (FT-IR, Nicolet avatar 360 spectrometer). The thermal behavior of the precursor was investigated by thermal gravimetric analysis (TG) (STA49C, NETZSCH, Germany). The phases were determined by X-ray diffraction of polished cross-sections, with a Bruker D8 Advance using  $\text{Cu K}\alpha$  radiation. The microstructure of the resulting composites was evaluated using scanning electron microscopes (SEM, S4800), with accessorial energy-dispersive spectroscopy (EDS) and high-resolution transmission electron microscopy (HR-TEM, JEM-2100).

### 3. Results and discussions

To understand the chemical structure and transformation mechanism, FT-IR was performed on the TaC precursor polymer (Fig. 1). The respective assignments of the absorption peaks were 3200 ( $\nu(\text{O-H})$ ), 1628 ( $\nu(\text{C=O})$ ), 1604 ( $\delta_s(\text{H-O-H})$ ), 1547 ( $\nu(\text{C=C})$ ), 1401 ( $\nu(\text{C=O}) + \delta(\text{C-H})$ ), 1343 ( $\delta_s(\text{CH}_3)$ ), 1297 ( $\delta(\text{C-H}) + \nu(\text{C-CH}_3)$ ), 1238 ( $\nu(\text{C-O})$ ), 1163 ( $\nu(\text{Ta-O-C})$ ) [15], 1147 ( $\delta(\text{C-H}) + \nu(\text{C-O})$ ), 1105 ( $\rho(\text{CH}_3)$ ), 1014 ( $\delta(\text{C-H})$ ), 942 ( $\nu(\text{C-CH}_3) + \nu(\text{C=O})$ ), 854 ( $\nu(\text{Ta-O-Ta})$ ) [16], 775 ( $\nu(\text{C-H})$ ) [17], 668 (ring distortion +  $\nu(\text{Ta-O})$ ), 603 ( $\nu(\text{Ta-O})$ ), and 544 ( $\nu(\text{Ta-Cl})$ ) [18].

For the liquid precursor, as shown in Fig. 1a, a broad peak at 3600–2800  $\text{cm}^{-1}$  was a combination band involving O-H stretching vibration (3600–3320  $\text{cm}^{-1}$ ) and C-H stretching vibration of aliphatic hydrocarbons (2980–2880  $\text{cm}^{-1}$ ). The detected wavenumbers of O-H stretching vibration lowering than 3600  $\text{cm}^{-1}$  indicated the appearance of associated hydroxyl group [19] due to hydrolysis reaction of the tantalum ions. A weak peak at 544  $\text{cm}^{-1}$  was detected, which was attributed to the Ta-Cl stretching vibration. It showed the existence of -O-Ta-Cl functional group in the as-received TaC precursor [20].

With the increase of temperature, the characteristic peaks assigned to  $\nu(\text{C-O})$  of TaC precursor got broader and weaker because of dehydration, which did not complete even at 200 °C. The FT-IR spectra of precursor dried at 80 °C (Fig. 1b) revealed a similar spectrum to that of the liquid precursor. However, all the peaks (Fig. 1b) got broader and weaker in intensity indicating dehydration and carbonization of the precursor. The peaks centered at 1604  $\text{cm}^{-1}$ , 1343  $\text{cm}^{-1}$ , 1297  $\text{cm}^{-1}$ , 1147  $\text{cm}^{-1}$ , 1105  $\text{cm}^{-1}$ , 1014  $\text{cm}^{-1}$ , 942  $\text{cm}^{-1}$ , 775  $\text{cm}^{-1}$ ,

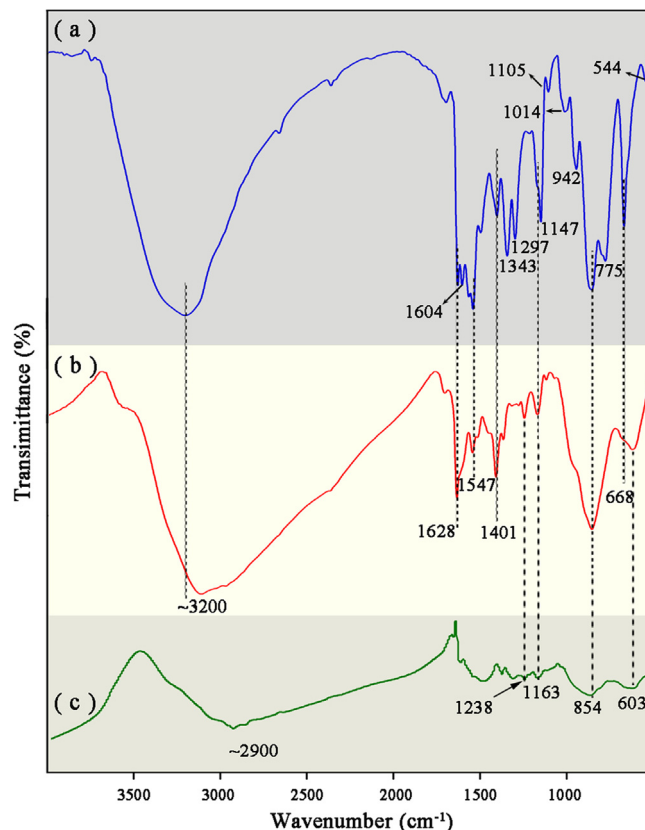


Fig. 1. FT-IR spectra of the TaC precursor: (a) as-received TaC precursor; (b) TaC precursor dried at 80 °C; (c) TaC precursor dried at 200 °C.

668  $\text{cm}^{-1}$ , and 544  $\text{cm}^{-1}$  disappeared, which indicated the decrease of organic components. Simultaneously, a new strong peak at 1163  $\text{cm}^{-1}$  attributed to Ta-O-C stretching vibration of the cyclic structure formed by ion chelation increased in intensity obviously. Besides, two strong bands occurred below 800  $\text{cm}^{-1}$  could be due to the formation of Ta-O-Ta (854  $\text{cm}^{-1}$ ) and Ta-O (603  $\text{cm}^{-1}$ ) chemical bonds via condensation reactions. When the temperature was elevated from 80 °C to 200 °C, all the peaks (Fig. 1c) got much weaker in intensity indicating further dehydration and carbonization of the precursor. The  $\nu(\text{C-O})$  and  $\nu(\text{C=C})$  peak disappeared, indicating that the cross-linking of phenolic resin completed.

TG-DTA analysis was conducted on the conversion process from the TaC precursor to ceramic. Fig. 2 presents the TG-DTA curves of the as-prepared TaC precursor between ambient and 1300 °C. The TG curve showed a total mass loss of 43 wt% at 1300 °C. There are four stages (A–D, in different color depth) of mass loss in TG curve. At A stage (below 190 °C, with approximate mass loss of 10 wt%), residual volatiles consisting predominantly of ethanol was removed, associated with a medium endothermic DTA peak measured at about 60 °C. The other exothermic peak at 96 °C might be caused by the pyrolysis of  $\text{TaOCl}$  [21]. At B stage (190–520 °C, with approximate mass loss of 20 wt%), another exothermic peak could be observed at around 436 °C in the DTA curve, probably due to the decomposition of phenolic resin. C stage between 520 °C and 920 °C was

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