Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 42 (2016) 122–131

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Graphene/titanium carbide composites prepared by sol–gel infiltration and spark plasma sintering

Xiaojing Wang[a], Mingyuan Lu[b], Ling Qiu[a], Han Huang[b], Dan Li[a], Huanting Wang[c], Yi-Bing Cheng[a,*]

[a]Department of Materials Science and Engineering, Monash University, Vic. 3800, Australia
[b]School of Mechanical and Mining Engineering, The University of Queensland, Qld. 4072, Australia
[c]Department of Chemical Engineering, Monash University, Vic. 3800, Australia

Received 4 June 2015; received in revised form 4 August 2015; accepted 4 August 2015
Available online 12 August 2015

Abstract

Graphene/titanium carbide composites were synthesized by means of sol–gel infiltration and spark plasma sintering (SPS). The graphene used in this research was casted into a sponge-like shape, composed of a three-dimensional (3D) network of graphene sheets. The sol–gel infiltration synthesis method allowed the formation of nanostructured ceramics inside the porous structure of graphene networks, thus forming composites. The compositions and microstructures of the Ti–O–C composites changed with the amount of the polymerizable carbon source (i.e. furfuryl alcohol (FA)) in the solution. A high carbon ratio was required to maintain the structure of the graphene network, as the graphene sheets could become a carbon source to react with TiO_2 resulting in a lamellar-shaped grain morphology. Samples after SPS showed some toughening effects, such as de-bonding, bridging and formation of microcracks. Vickers hardness, electrical resistivity and thermal conductivity were examined for the composites.

Keywords: B. Nanocomposites; Ceramic matrix composites; Sol–gel; Spark plasma sintering; Titanium carbide

1. Introduction

Titanium carbide (TiC) is an ultra-high temperature ceramic (UHTC), with a low density (4.93 g/cm^3), high melting point (3067 °C), high Vickers hardness (28–35 GPa), high Young's modulus (410–450 GPa), low thermal expansion and high electrical and thermal conductivity [1,2]. Attributed to these characteristics, TiC has been extensively investigated for many applications, including cutting tools, refractory components, electronic elements, aerospace engineering and so on [2,3]. In the last few years, ceramic/carbon composites have attracted tremendous attention from researchers due to their excellent mechanical and functional properties compared with the monolithic counterparts [4–7].

Carbon nanotubes (CNTs) and carbon fibers are often used in the manufacturing of ceramic composites [5–7]. Recently, the interest in the application of another form of carbon, graphene, is increasing due to its extraordinary mechanical, electrical and thermal properties [8]. The addition of graphene in different ceramics has been investigated [9–12]. Dusza et al. reported a Si_3N_4–grpaphene platelet (GPL) composite with improved fracture toughness; the presence of GPLs played an important role in the toughness enhancement by introducing crack deflection, branching and bridging [9]. Ramirez et al. reported GPL/Si_3N_4 composites had improved electrical conductivity [10]. Similar studies have been done for other graphene reinforced composites, such as GPL/Al_2O_3 [11,12]. However, to the best of our knowledge, there are few studies so far investigating the formation and properties of carbide/graphene composites.

Furthermore, the carbon material used in this work is a three-dimensional (3D) graphene network, like a sponge,

*Corresponding author.
E-mail address: yibing.cheng@monash.edu (Y.-B. Cheng).

http://dx.doi.org/10.1016/j.ceramint.2015.08.017
0272-8842/

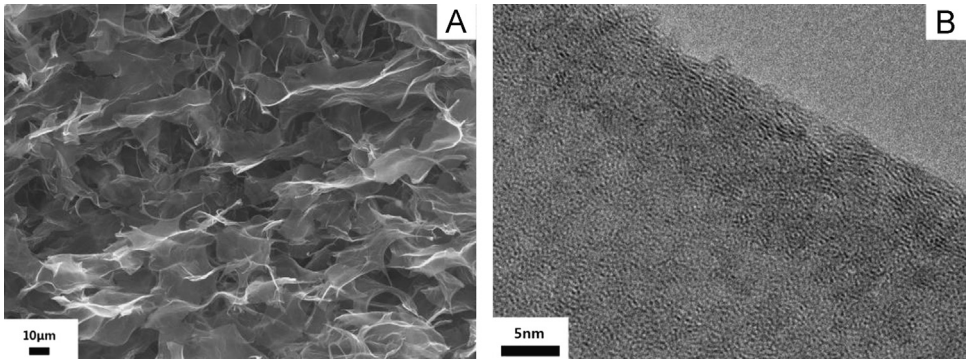

Fig. 1. (a) SEM and (b) TEM micrographs of the 3D graphene network.

instead of the traditional two-dimensional (2D) graphene nanosheets. This continuous 3D network is composed of multi-layer graphene sheets and has a cork-like hierarchical structure (Fig. 1). This material is fabricated through thermal reduction of freeze casted graphene oxide (GO) and exhibits low density, high porosity, and good electrical conductivity and energy absorption efficiency [13–16]. These extraordinary properties promise a wide range of applications of the material, such as electrodes and sensors [16,17]. But in this paper we report its application in the fabrication of ultra high temperature ceramic (UHTC) composites.

In order to fabricate ceramic composites using this 3D graphene network, traditional powder metallurgy approach is not practical, because powders have difficulty to gain full access to the micro-sized pores of the graphene network. Therefore, a sol–gel technique was applied in this study. TiC was synthesized by direct carbothermal reduction of titanium–oxygen–carbon (Ti–O–C) precursors. The Ti–O–C precursor is a sol–gel mixture of titanium alkoxide and furfuryl alcohol (FA), which is as the carbon source [18–20].

In the present work, novel graphene/TiC composites featuring uniformly distributed graphene sheets and fine TiC grains (the grain size was less than 100 nm) were synthesized. This composite material showed improved toughness and generous energy absorption upon (low-velocity) impact.

2. Experimental procedure

2.1. Chemicals and synthesis

To synthesis the Ti–O–C precursor, the sol–gel process started with the poly(ethylene oxide)-b-poly(propylene oxide)-b-poly (ethylene oxide) copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, $M_n \sim 5800$; Sigma-Aldrich). P123 (4.64 g) was dissolved into absolute ethanol (C_2H_5OH, 99.7%) (6.9 g) to form a solution under continuous stirring, to which titanium tetraisopropoxide (TTIP, $Ti(OCH(CH_3)_2)_4$, 97%; Sigma-Aldrich) (11.368 g) was added as the titania source. Meanwhile, another solution was prepared by mixing with hydrochloric acid (HCl, 10 M) (2.0 g) and absolute ethanol (2.3 g). The acid solution was then added dropwise into the first solution containing TTIP under vigorous magnetic stirring. After half hour, furfuryl alcohol (FA, $C_5H_6O_2$, 98%; Sigma-Aldrich) was added into the mixed solution as a carbon source under stirring. Different amounts of FA were added to control the molar ratio of C/Ti in the solutions from 0 to 9. The C/Ti ratio in each composition was calculated based on the amount of FA without consideration of graphene. The solutions were aged for 3 days at the ambient temperature around 25 °C. During the whole process, the continuous stirring was necessary and all the bottles were sealed immediately after mixing. The color of the solution changed from transparent to brown after mixing with FA and then turned to dark brown after 6 h ageing, indicating the polymerization of FA.

To synthesis the composite precursor, the prepared solution above was then infiltrated into graphene network cells (~5 mg/ml) until all the cells were saturated. After that, the solution infiltrated graphene were dried in an oven at 80 °C until the solution becoming a gel. The dried gel was heated to 550 °C at 5 °C/min for 5 h under nitrogen in order to achieve a mesoporous Ti, O, C matrix with graphene sheets surrounded through pyrolysis of organic components, and then the precursor was infiltrated with the prepared solution again followed by the next steps, and three cycles were applied. Then the samples were further heated to 1450 °C at 2 °C/min for 5 h under argon for carbothermal reduction to form TiC based graphene composites. The synthesized composites are denoted as G-*x*C, and referenced TiC are denoted as *x*C where *x* indicated the C/Ti ratio in the sol–gel. For example, G-3.8C means sol–gel with C/Ti ratio of 3.8 infiltrated graphene composites, while 3.8C means TiC synthesized from sol–gel with C/Ti ratio of 3.8C. After calcinations, all the samples were crashed and sintered at 1800 °C for 5 min using SPS, at a maximum heating rate of 200 °C/min under vacuum and a pressure of 40 MPa.

2.2. Characterization

Several characterization methods were used to examine the samples. X-ray diffraction (XRD) patterns were recorded from 10° to 80° of the 2θ values, using a step size of 0.02° and a scan rate of 2°/min, through a Philips PW1140/90 diffractometer operated with CuKα radiation at 40 kV and 25 mA. The thermogravimetric analyzer (Perkin-Elmer, Pyris 1) was conducted in air to 800 °C at a heating rate of 5 °C/min to obtain the thermogravimetric analyses (TGA) graphs. Raman spectra were recorded on a Renishaw inVia Raman Microscope with a 514 nm argon ion laser at room temperature. A JEOL 7001F