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Spark plasma sintered tantalum carbide–carbon nanotube composite: Effect of pressure, carbon nanotube length and dispersion technique on microstructure and mechanical properties

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ABSTRACT

TaC–4 wt.% CNT composites were synthesized using spark plasma sintering. Two kinds of CNTs, having long (10–20 μm) and short (1–3 μm) length, were dispersed by wet chemistry and spray drying techniques respectively. Spark plasma sintering was carried out at 1850 °C at pressures of 100, 255 and 363 MPa. Addition of CNTs leads to an increase in the density of 100 MPa sample from 89% to 95%. Short CNTs are more effective in increasing the density of the composites whereas long CNTs are more effective grain growth inhibitors. The longer CNTs are more effective in increasing the fracture toughness and an increase up to 60% was observed for 363 MPa sample. Hardness and elastic modulus are found to increase by 22% and 18% respectively for 100 MPa samples by addition of long CNTs. Raman spectroscopy, SEM and TEM images indicated that the CNTs were getting transformed into flaky graphitic structures at pressure higher than 100 MPa.

1. Introduction

The borides and carbides of group IV–V metals such as zirconium, hafnium, and tantalum have high hardness, high melting points and good corrosion resistance. These compounds and their composites are particularly suitable for ultra-high temperature applications such as rocket nozzle throat liners, nose and edge components of re-entry vehicles, jet components and protection of carbon–carbon composites [1–6]. Properties such as high temperature stability, high temperature oxidation resistance, thermal shock resistance and high thermal conductivity are desirable for such applications. Pressure-less sintering [7–10], hot pressing [2,11–18], reactive hot pressing [19–21] and plasma spraying [22,23] have been utilized for the fabrication of monolithic or composite structures and coatings of these ultra high temperature ceramics (UHTCs). Spark plasma sintering is a relatively novel consolidation method that has the advantage of short sintering duration and has shown better densification and properties than hot pressing [24]. SPS has been extensively used for synthesis of UHTCs and their composites [11,14,17,25–29].

Tantalum carbide has high melting point of 3880 °C and is stable for a large range of C/Ta ratio of 0.76–1 [13]. The strong covalent–ionic bond results in high hardness of >20 GPa and elastic modulus of up to 550 GPa [30] which makes it extremely suitable for rocket components involving combustion temperatures up to 3500 K. TaC has been consolidated using techniques such as pressureless sintering [7,31], hot pressing [13,15,16,18,32], high frequency induction heating [33,34], vacuum plasma spraying [22] and spark plasma sintering [27,35,36]. Due to the low self diffusion coefficient, additives such as B_4C [15,18,36], carbon [15,31], TaB_2 [16,31] and $TaSi_2$ [34] have also been utilized to aid the sintering.

In the present study, we have synthesized TaC composites reinforced with carbon nanotubes (CNTs) using spark plasma sintering. CNTs have proved as effective reinforcement in increasing the fracture toughness of ceramic materials through mechanisms such as crack bridging and crack deflection [37–40]. Improvement in the CNT dispersion leads to significant improvement in fracture and wear properties of the composites and coatings [38,41,42]. Carbon fiber reinforced TaC composites have been prepared by infiltration of carbon fiber weave Ta and C containing solutions followed by vacuum sublimation treatments [43]. Recently, Khaleghi et al. have synthesized a TaC–0.77 wt.% CNT composite using spark plasma sintering. The relative density of the composite synthe-

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sized at 2300 °C and 30 MPa pressure increased from 92% to 96%, while the rupture strength increased from 336 to 550 MPa due to addition of CNTs. Carbon has also been reported to play an important role as a sintering aid [15,31] and grain growth inhibitor [15].

In the current study, the overall carbon concentration is 10.2 wt.% in Ta–C phase diagram near an eutectic of TaC and C. The addition of 4 wt.% carbon nanotubes is expected to have the following benefits:

(a) Improved fracture toughness of TaC.
(b) CNTs are expected to suppress grain growth and simultaneously aid densification [15,31,44].
(c) It is envisaged that CNTs would reduce the decomposition of TaC to Ta_2C by providing extra carbon. Although TaC is extremely stable, but under vacuum plasma spraying conditions it decomposes to Ta_2C [22].
(d) The oxidation resistance of TaC may be improved by suppressing formation of Ta_2O_5. Ta_2O_5 can be converted to TaC by the following reaction:

$$Ta_2O_5 + 7C = 2TaC + 5CO$$

($\Delta G = 1142.3–0.823 \times T$ kJ [45], −ve for $T > 1388$ K).

Multi-walled CNTs of two different lengths have been employed to evaluate the "*length effect*" on the densification, grain-growth and reinforcement efficiency. The effect of powder preparation technique leading to differences in CNT dispersion is elucidated. Spark plasma sintering was carried at 1850 °C for three pressures of 100, 255 and 363 MPa. The effect of the pressure on the grain size and densification behavior is also studied. This is a first study on TaC–CNT composites at such extreme pressures and temperatures in SPS environment, which also examines the structural stability of CNTs under the severe conditions.

2. Experimental

2.1. Powder preparation

Fine tantalum carbide powder (average particle size = 0.36 ± 0.13 μm) was obtained from Inframat Advanced Materials LLC, CT, USA. The composition of the powder by weight was a purity of 99.7% with total carbon ≥6.2%, free carbon ≤0.15%, Nb <0.3%, and O between 0.15 and 0.3%. Two kinds of multi-walled carbon nanotubes (CNTs) were employed in the study, long and short CNTs. The long –COOH group functionalized CNTs were obtained from Nanostructured and Amorphous Materials Inc., TX, USA, and were more than 95% pure and had a diameter of 30–50 nm and length between 10 and 20 μm. The shorter CNTs were obtained from Inframat Advanced Materials (Willington, CT, USA), and had a purity of more than 95%, diameter of 40–70 nm and length 1–3 μm. SEM images of TaC powder, long and short CNTs are shown in Fig. 1.

It is critical that CNTs are uniformly distributed in the matrix. Two different approaches were carried out for dispersing 4 wt.% CNTs in TaC powder. In the first approach using wet chemistry technique, 1 g of long CNTs were added to 100 ml of acetone in a beaker and ultrasonicated for 90 min. Subsequently, 24 g of TaC powder was added and the mixture was ultrasonicated again for 90 min. The mixture was allowed to dry for 12 h and then crushed to obtain the TaC–4 wt.% long CNT powder, which has been referred to as TaC–LC powder. The second approach included spray drying [46–48]. In this method, TaC powder and 4 wt.% short CNTs were added to prepare a water based slurry using a small amount of water soluble polymeric binder. The slurry is then atomized in a column where hot air is passed from the bottom. The droplet of the slurry dry up as they descent through the column and result in agglomerates. The binder helps in providing strength to the agglomerates. By this method, good dispersion of CNTs within micro- and nano-

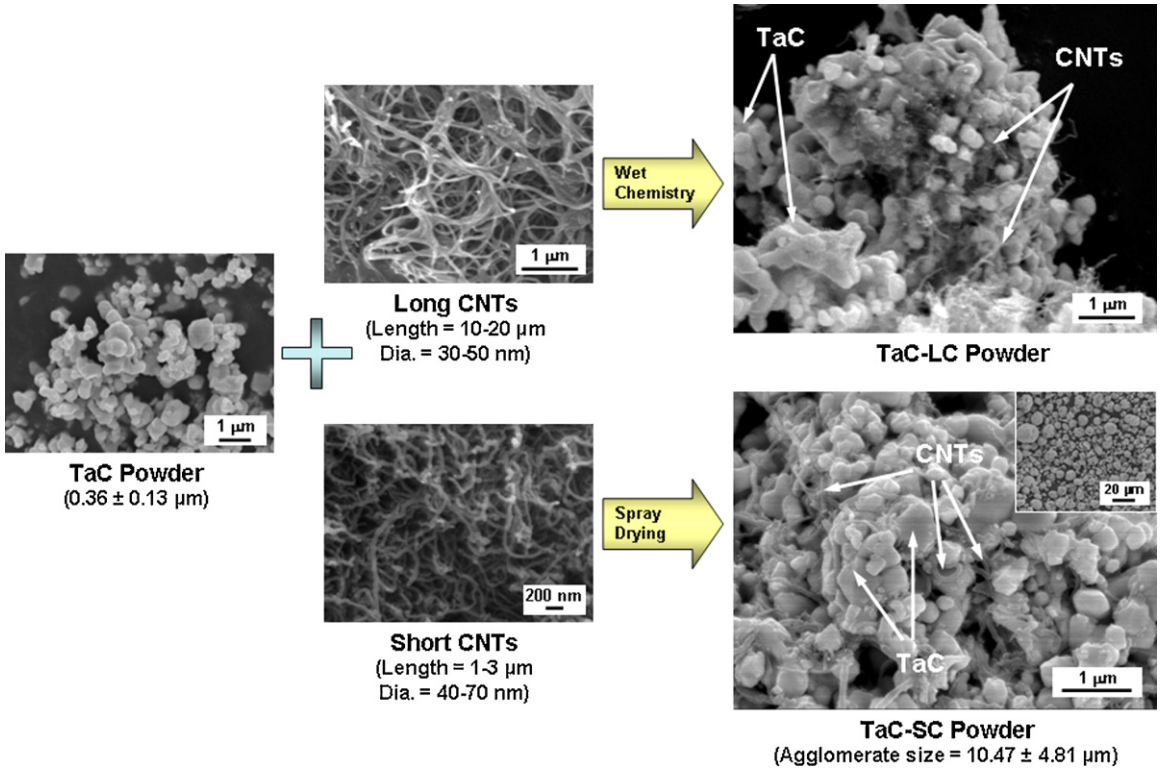

Fig. 1. SEM images showing starting TaC powder, the two kinds of CNTs used in the study and the composite powder mixtures prepared using wet chemistry and spray drying routes.