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Reaction-formed W_2B_5/C composites with high performance

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Abstract

Highly densified W_2B_5/C composites with W_2B_5 content from 30 to 70 vol% were fabricated by reaction hot pressing of the powder mixture of B_4C, WC and carbon black. The reaction products were identified by XRD analysis to consist of only W_2B_5 and carbon, regardless of carbon content. The reaction formed composites have excellent mechanical properties (the maximum flexural strength and fracture toughness of 786 MPa and 8.9 MPa $m^{1/2}$ respectively), electrical conductivity (the highest electrical conductivity of $1.64 \times 10^6\ \Omega^{-1}\ m^{-1}$), and resistance to both wear and oxidation because of the presence of the plate-like W_2B_5 grains. In this paper, the preparation, microstructure and properties of this new composite are investigated, and the strengthening, toughening, conduction mechanisms are discussed.

Keywords: Carbon composites; Microstructure; Mechanical properties; Electrical conductivity

1. Introduction

Carbon materials are widely applied in some fields, such as machine, aerospace and metallurgy industries because of their merits of very high thermal stability, self-lubrication and thermal-shock resistance and so on. But low strength and poor oxidation tolerance of carbon materials are required to be solved for many applications. An introduction of hard ceramics into carbon to form carbon/ceramic composites is a promising method to raise the strength and oxidation resistance of carbon materials. For this purpose, C/B_4C, C/SiC, C/B_4C/SiC and C/B_4C/TiC composites have been extensively studied [1–5], and much improvement has been achieved in strengthening carbon materials.

However, for increasing the strength of carbon/ceramic composites to a high value, high content of ceramic phases must be added, which would, on the contrary, reduce the electrical conductivity of carbon materials because most of the applied ceramic phases, such as B_4C and SiC, have poor electrical conductivity. Therefore it is disadvantageous for the composites to be used in the fields requiring both high strength and high electrical conductivity, for example, as high performance electrodes. Moreover, the preparation of carbon/ceramic composites by traditional methods, as studied in the past [1–4], would result in the high sintering temperature and bad boundary bonding due to the sintering inertness of both carbon and ceramics, which makes the improvement of mechanical properties for carbon/ceramic composites limited.

In present study, a kind of refractory metal borides, W_2B_5, is introduced into carbon materials owing to its superior properties, i.e. high melting point, high hardness and abrasion resistance, especially the excellent electrical conductivity. So combining W_2B_5 with carbon, we would formulate a novel kind of carbon/boride composites which would have not only improved strength, fracture toughness, resistance to both oxidation and wear, but also increased electrical conductivity. Furthermore, a relatively new method, so-called in situ reaction sintering was employed for fabricating W_2B_5/C composites. In general, the composites made by this method demonstrate some

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special microstructural features, superior mechanical properties or wear resistance [6–9]. In our previous studies, the TiB_2–TiC composites were prepared by reaction sintering of B_4C and Ti powders, and a fracture toughness of 12.2 MPa $m^{1/2}$ was reached by virtue of the formation of the platelet TiB_2 grains [10].

In present study, the reaction between B_4C and WC was attempted to form W_2B_5/C composites according to the following reaction [11]:

$$5B_4C + 8WC = 4W_2B_5 + 13C \quad (1)$$

Based on this formula, if the reaction is complete, the volume percentage of carbon in the W_2B_5/C composites is about 30%, where the theoretical densities of W_2B_5 and carbon were used as 11.18 and 2.22 g/cm^3 respectively. In order to get a better wear performance and higher thermal shock resistance and machinability, high level of carbon content of W_2B_5/C composites were also considered to prepare by adding carbon black into the starting materials. In present work, a series of the W_2B_5/C composites have been prepared by this reaction, with the W_2B_5 contents of 30–70 vol% with a composition interval of 10 vol%. Here xW_2B_5/C is used to refer to the W_2B_5/C composite containing x vol% W_2B_5. The preparation, microstructure, mechanical properties, electrical conductivity, oxidation and friction and wear behavior of this kind of composites are reported here.

2. Experimental procedures

Commercially available B_4C, WC and carbon black powders were used as starting materials. The mean particle size of B_4C powder was 1.5 μm ($d_{10} = 0.89$ μm, $d_{50} = 1.41$ μm and $d_{90} = 1.82$ μm) with 2.42% free carbon, 0.64% free boron and 0.42% B_2O_3 as the main impurities (from MuDanJiang Diamond Boron carbide Co., Ltd., China). The average particle size of WC powder was 2.2 μm ($d_{10} = 1.26$ μm, $d_{50} = 2.01$ μm and $d_{90} = 2.70$ μm) with impurity $\leqslant$0.073% (from Zhuzhou Lizhou Cemented Carbide Co., Ltd., China). The carbon black was from Qichang chemical Co., Ltd., HeNan, China. It was in the form of porous agglomerates of carbon particles of average size 30 nm, a nitrogen specific surface area of 120 m^2/g, a volatile content of 1.5%, a maximum ash content of 0.5% and a density of ~1.9 g/cm^3. The starting compositions are summarized in Table 1. After uniformly mixed, the powder mixtures were hot-pressed at 2000 °C and 25 MPa, for holding time of 1 h.

Table 1
Starting and final composition of the materials

Materials	Starting composition (wt%)			Final composition (vol%)	
	B_4C	WC	Carbon black	W_2B_5	Carbon
30W_2B_5/C	10.9	61.9	27.2	30	70
40W_2B_5/C	12.5	71.3	16.2	40	60
50W_2B_5/C	13.7	77.3	9	50	50
60W_2B_5/C	14.5	81.8	3.7	60	40
70W_2B_5/C	15.1	84.9	–	70	30

Bulk densities of the composites were measured by using Archimedes' principle. X-ray diffraction was used to identify the reaction products. TEM was used for detailed microstructural analysis. Both polished and fractured surfaces were examined by SEM. The dimensions of samples used to measure flexural strength and fracture toughness were $36 \times 4 \times 3$ mm^3 and $36 \times 2 \times 4$ mm^3 respectively. Flexural strength was measured on a three-point bending fixture with a 30 mm span at a crosshead speed of 0.5 mm/min. The K_{IC} values were determined by the SENB method with a crosshead speed of 0.05 mm/min. Each mechanical property data point presents an average of 5–6 measured values. The electrical conductivity was measured by four-terminal electrode of direct current.

Dry sliding wear tests were conducted using a block-on-ring type machine. The samples were machined into rectangular blocks of $4 \times 6 \times 20$ mm^3, and the faces of 6×20 mm^2 were put in contact with the slider rings. The slider ring (out diameter 40 mm) was made of GCr15 type bearing steel with a hardness of HRC63 ± 1. All the tests were carried out at room temperature with a relative humidity of ~30%. The normal load F_N of 15N and a constant line speed of 0.4 m/s were used. The sliding time for each test was normally 40 min. Wear tests were also performed on graphite at the same condition for reference. The friction torsion M was recorded every 30 s during each test, and the friction coefficient was calculated by the formula $\mu = M/R/F_N$, where R is the radius of the sliding ring. The width of the wear track was measured, and then converted into the volume loss. After the wear test, the worn surfaces were examined using a scanning electron microscope (SEM) coupled with EDAX.

Isothermal oxidation tests were carried out at the temperature of 800 °C for 20 h. The specimens were cut into dimensions of $10 \times 4 \times 3$ mm^3 and were suspended under a balance with Pt wires in a heated air–atmosphere tube furnace.

3. Results and discussion

3.1. Reaction products

The reaction products of the sintered samples were first subject to XRD analysis. The results are shown in Fig. 1. Only the diffraction peaks of W_2B_5 and carbon were detected in all the five specimens confirming that the reaction between B_4C and WC was almost complete according to the reaction (1). The diffraction intensity of carbon was much weaker than that of W_2B_5 in each sample, the reason might be that the mass ratio of carbon to W_2B_5 in the composite was very small. The values of d_{002} of carbon measured by XRD were listed in Table 2 (the diffraction peak of carbon in 70W_2B_5/C was too weak to be detected). It can be seen that the interlayer spacing (d_{002}) of carbon decreased largely compared to that of carbon black, which indicated that the reaction formed carbon and the added