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In situ synthesis and densification of submicrometer-grained B_4C–TiB_2 composites by pulsed electric current sintering

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Abstract

B_4C composites with 15 and 30 vol% TiB_2 were pulsed electric current sintered from B_4C–TiO_2–carbon black mixtures in vacuum at 2000 °C. Full densification could be realised when applying an optimized loading cycle in which the maximum load is applied after completion of the B_4C–TiB_2 powder synthesis, allowing degassing of volatile species. The influence of the sintering temperature on the phase constitution and microstructure during synthesis and densification was assessed from interrupted sintering cycles. The in situ conversion of TiO_2 to TiB_2 was a complex process in which TiO_2 is initially converted to TiB_2 with B_2O_3 as intermediate product at 1400–1700 °C. At 1900–2000 °C, B_2O_3 reacted with C forming B_4C and CO. The B_4C and TiB_2 grain size in the fully densified 30 vol% TiB_2 composite was 0.97 and 0.63 μm, combining a Vickers hardness of 39.3 GPa, an excellent flexural strength of 865 MPa, and modest fracture toughness of 3.0 MPa $m^{1/2}$.

Keywords: Pulsed electric current sintering; Borides; Powders-solid state reaction; Grain size; C. Mechanical properties

1. Introduction

As one of the hardest materials known, boron carbide ranks third behind diamond and cubic boron nitride. Being intrinsically brittle, B_4C often requires different additives to improve its sintering behaviour and mechanical properties. Numerous researchers have shown that the addition of TiB_2 to B_4C can decrease the porosity level and improve the fracture toughness as well as flexural strength.[1–6] Furthermore, dense B_4C–TiB_2 composites can be easily machined using electrical discharge machining (EDM) since TiB_2 has a good electrical conductivity.[7–10] Since both B_4C and TiB_2 are covalently bonded compounds, sintering temperatures above 2200 °C were required for pressureless sintering of B_4C–TiB_2 particulate composites.[1,3] However, rapid grain growth and concomitantly decreased strength were observed in pressureless liquid phase sintered B_4C–TiB_2 composites. A recent study showed that hot pressing and pulsed electric current sintering aided in increasing the density of TiB_2 while decreasing the sintering time.[11,12]

Another way to make B_4C–TiB_2 composites is via in situ reaction of TiO_2, carbon and B_4C[3–5] or from elemental powders.[13] A flexural strength of 866 MPa and fracture toughness of 3.2 MPa $m^{1/2}$ were reported for fully dense B_4C-20 mol% (15 vol%) TiB_2 composites made from B_4C, TiO_2 and carbon black mixtures prepared by reaction hot pressing for 1 h at 2000 °C under a pressure of 50 MPa.[5] In situ TiB_2 formation is reported when sintering B_4C with TiO_2 or Ti addition in the 1800–2190 °C range.[14] A mixture of fine-sized B_4C with 40 wt% TiO_2 was transformed into a 95% dense B_4C–TiB_2 composite when sintering for 1 h at 2160 °C.[14] More recently, pseudo-eutectic micrometer grained TiB_2–B_4C composites were synthesized by PECS of mechanically alloyed elemental powders at 1200–1700 °C.[13] Phase formation was completed well before full density was achieved and bulk composite materials of nearly full density were obtained when PECS at 1700 °C.[13]

In the present study, B_4C–TiB_2 composites with up to 30 vol% TiB_2 were made by in situ synthesis from B_4C, TiO_2 and carbon black powder mixtures during densification by pulsed electric current sintering (PECS). The effect of the processing temperature on the densification, phase constitution, as well as microstructure of the sintered compacts was assessed.

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2. Experimental procedure

2.1. Material preparation

B_4C–TiB_2 composites were made by in situ reaction of B_4C (Grade HD20, H.C. Starck, Germany, $d_{50} = 0.5\,\mu m$), TiO_2 (Grade A-HR, Huntsman Tioxide Europe Ltd., crystal size = 0.17 μm) and carbon black (Grade 4, Degussa; Germany) powders. Composites B15T and B30T with a desired TiB_2 content of 15 and 30 vol% respectively were prepared by low energy multidirectional mixing (Turbula T2A, WAB, Switzerland) in ethanol for 24 h using ZrO_2 milling balls ($\phi = 5$ mm, grade TZ-3Y, Tosoh, Japan). The solvent was removed in a rotating evaporator at 65 °C and the powder mixture was additionally dried for 24 h at 80 °C. The starting compositions were determined so as to form B_4C matrix composites with 15 or 30 vol% TiB_2, which have a theoretical density of 2.82 and 3.12 g/cm^3 respectively, according to the rule of mixtures based on a density of 2.52 and 4.52 g/cm^3 for B_4C and TiB_2. The formation of TiB_2 phase can be described according to[3,4]:

$$B_4C + 2TiO_2 + 3C \Leftrightarrow 2TiB_2 + 4CO \quad (1)$$

Under standard state conditions, the change in Gibbs free energy of this reaction can be expressed as: $\Delta G = 732.7–6.5\,T$ (kJ), which is thermodynamically favourable at temperatures above 1150 °C.[14] Reaction (1) proceeds more rapidly when the CO partial pressure is below the equilibrium pressure, i.e. in vacuum or Ar atmosphere. In the absence of free carbon, TiO_2 can be converted to TiB_2 using B_4C as carbon source.[14–17]

In the present study, in situ powder synthesis and sintering was performed during PECS (Type HP D 25/1, FCT Systeme, Rauenstein, Germany) in a vacuum of 4 mbar. A pulsed electric current was applied with a pulse duration of 10 ms and pause time of 5 ms throughout all the experiments. Powder mixtures were poured into a cylindrical graphite die with an inner and outer diameter of 30 and 56 mm. The B30T powder mixture was PECS at 1400, 1700, 1900 and 2000 °C for 5–13 min, including outgassing, pressure loading and dwell time at the sintering temperature, under a maximum pressure of 60 MPa, with a heating and initial cooling rate of 200 °C/min. A representative thermal cycle is given in Fig. 1 for the powder mixture heated for 9 min at 2000 °C. In all experiments, a minimum pressure of 8 MPa was applied to ensure constant contact of the electrodes with the die/punch/sample system. Two different loading cycles were investigated. In loading cycle C1, the pressure was gradually increased from 8 to 60 MPa within 1 min upon reaching 2000 °C. In the optimized cycle C2, the maximum pressure of 60 MPa was applied within 1 min, 4 min after reaching 2000 °C allowing degassing of volatile species. Graphite paper was used to separate the graphite die/punch set-up and powder mixture. A 10 mm thick porous carbon felt insulation was placed around the graphite die to obtain a homogeneous temperature distribution and concomitant sintering behaviour. The sintering temperature was measured by a two-colour pyrometer (400–2300 °C, Impac, Chesterfield, UK), focused at the bottom of a central borehole in the upper punch, 2 mm away from the top surface of the sample. The actual set-up and temperature monitoring procedure is described in detail elsewhere.[18]

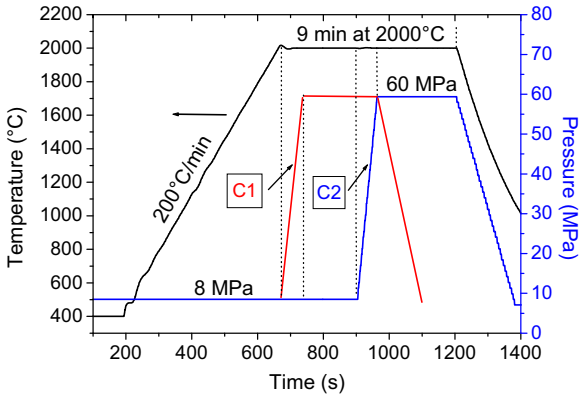

Fig. 1. Thermal and mechanical loading cycles during in situ synthesis and consolidation of B_4C–TiO_2–C starting powder mixtures without (C1) and with (C2) a degassing step upon reaching the targeted sintering temperature.

2.2. Characterization

After PECS and sand blasting, the sintered 4 mm thick discs were cross-sectioned and polished to a mirror finish. The bulk density of the sintered composites was measured in ethanol. The crystalline phases during the reaction were investigated by a θ–θ X-ray diffractometer (XRD, Seifert, Ahrensburg, Germany) using Cu-K_α radiation (40 kV, 40 mA). The microstructure and composition of the PECS materials were examined by scanning electron microscopy (SEM, XL30-FEG, FEI, Eindhoven, the Netherlands), equipped with an energy dispersive analysis system (EDS, EDAX, Tilburg, the Netherlands) for compositional analysis. The Vickers hardness, HV_1, was measured (Model FV-700, Future-Tech Corp., Tokyo, Japan) with an indentation load of 9.81 N. The fracture toughness, K_{IC}, was calculated from the length of the radial cracks of the indentations according to the formula of Anstis et al.[19] The elastic modulus, E, of the B_4C–TiB_2 composites was measured on rectangular bars by the resonance frequency method.[20] The resonance frequency was measured by the impulse excitation technique (Grindo-Sonic, Lemmens N.V., Leuven, Belgium). The flexural strength at room temperature was measured in a three-point bending test (Series IX Automated Materials Testing System 1.29, Instron Corporation) with a span width of 20 mm and a crosshead displacement of 0.1 mm/min on rectangular (25 mm × 3 mm × 2 mm) bars, which were cut from the PECS discs by electrical discharge machining. All surfaces were ground (grinding wheel type D46SW-50-X2, Technodiamant, The Netherlands) on a Jung grinding machine (JF415DS, Göppingen, Germany). The reported flexural strength values are the mean and standard deviation of five measurements.

3. Results and discussion

3.1. In situ synthesis of B_4C–TiB_2 powder

In the present study, a heating rate of 200 °C/min was applied to in situ synthesize TiB_2 and densify B_4C–TiB_2 composite