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Effect of C/Ti ratio on densification, microstructure and mechanical properties of TiC_x prepared by reactive spark plasma sintering

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ABSTRACT

Titanium carbide (TiC) has been widely used as reinforcement in metal matrix composites and is known to exist over a wide range of stoichiometry. In this study, the effect of C/Ti ratio on the densification kinetics, grain size, lattice parameter, hardness and elastic modulus of TiC_x prepared by reactive spark plasma sintering (RSPS) is presented. Commercial purity titanium was ball milled with 5, 7.5, 10, 12.5, 15 and 17.5 wt% carbon black powder for 5 h and subjected to RSPS to prepare TiC_x samples with different C/Ti ratio. Dense TiC_x samples with 'x' ranging from 0.34 to 0.78 could be prepared by RSPS at 1400 °C. Increasing C/Ti ratio was found to increase the activation energy thereby reducing the rate of sintering and also resulted in finer grain size. The lattice parameter and the ratio of intensities of (200) to (111) peaks were correlated with the C/Ti ratio. The hardness and elastic modulus were shown to increase significantly with increase in C/Ti ratio.

1. Introduction

Several carbides of technological importance such as TiC, VC, NbC etc. having rock-salt structure are known to be stable over a wide range of stoichiometry i.e. carbon to metal ratio [1,2]. It is known that their properties are significantly dependent on the carbon to metal ratio. Some examples include hydrogen storage in non-stoichiometric TiC [3,4], better irradiation resistance of sub-stoichiometric ZrC_x [5], improvement in hardness of non-stoichiometric NbC_x with increase in C/Nb ratio [6]. It is known that TiC exists as a single phase for a range of C/Ti ratio from 0.48 to 1. It is very difficult to synthesize stoichiometric TiC (C/Ti = 1) as vacancies always exist during high temperature synthesis. It was reported in literature that the melting point of TiC_x and its various properties vary with stoichiometry [7,8].

The effect of TiC_x stoichiometry on its densification behaviour, grain size [9], morphology [10,11], bulk modulus [8], Vicker's hardness [12] was reported. By controlling or altering the stoichiometry, it is possible to achieve desirable properties. TiC_x is reported to be useful in hydrogen storage [4] by inserting hydrogen in non-stoichiometric TiC [13]. TiC is commonly used as wear resistant coating on most of the metals and alloys [14–16] and the significance of its stoichiometry on substrates was reported by S. Ramalingam [7]. TiC has been used as reinforcement in Al [17], Mg [18], Cu [19], W [20], high strength steel [21], Ti [22] and other metallic matrices [23–25] to increase its hardness, wear resistance, yield strength and tensile strength. Since the reinforcement plays a major role in strengthening and performance improvement of composites, it is essential to study the effect of stoichiometry on its properties. It was found that increasing C/Ti ratio increases the TiC_x lattice parameter and the same has been correlated by Holt et al. [26] and was found to be around 0.4330 nm for stoichiometric TiC [10,27].

TiC_x has been synthesized using many techniques such as combustion synthesis, explosive synthesis, reactive milling, spark erosion, ion-beam synthesis [28], laser cladding [29], and atomic layer deposition [30]. Sintered TiC compacts can be used as wear resistant inserts or as targets for thin film deposition. Since it has very high melting point (> 3000 °C) it is difficult to sinter stoichiometric TiC below 1800 °C through most of the sintering techniques [31–33]. Researchers have used sintering additives such as WC [34] and chemical modification of TiC powders [35] to improve its densification at lower temperatures. In recent years increasing attention has been paid to rapid synthesis of carbides [36,37] and borides [38] using reactive spark plasma sintering at relatively low temperatures compared to conventional techniques.

In this study, efforts have been made to synthesize TiC_x of various stoichiometries using ball milling of Ti-C mixtures followed by reactive spark plasma sintering (RSPS) at relatively low temperatures. The effect of C/Ti ratio on the sintering behaviour, lattice parameter, microstructure and mechanical properties of TiC_x is presented.

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Table 1
Sample nomenclature and composition details.

Sample name	CB added (wt%)	wt% C in SPS compacts (CHN analysis)	C/Ti atom ratio of TiC_x	Measured lattice parameter, (Å)
Ti-5CB	5	7.79	0.34	4.2688
Ti-7.5CB	7.5	9.91	0.44	4.2969
Ti-10CB	10	12.07	0.55	4.3149
Ti-12.5CB	12.5	14.41	0.67	4.3240
Ti-15CB	15	16.23	0.78	4.3276
Ti-17.5CB	17.5	18.32	0.90	4.3283
TiC As-received	–	–	–	4.3307

2. Experimental procedures

2.1. Materials and TiC_x synthesis

Titanium powder (99.9% pure, −325 mesh particle size, Alfa Aeser) and acetylene carbon black (Alfa Aeser) were used as starting materials for preparing TiC_x. Stoichiometric TiC was prepared from 99.5% pure Titanium carbide powder (2 μm size, Alfa Aeser). Ti powders were mixed with 5 wt%, 7.5 wt%, 10 wt%, 12.5 wt%, 15 wt% and 17.5 wt% carbon black and wet milled in toluene for 5 h in a Fritsch Pulverisette 5 ball mill. Carbon black was used due to its high surface area and reactivity so as to avoid presence of any un-reacted carbon in the final compact. The nomenclature used for the samples and other details are presented in Table 1. Milling was carried out in tungsten carbide lined vials with tungsten carbide balls with a ball to powder weight ratio of 10:1. The compositions were chosen to synthesize TiC_x (C/Ti from 0.3 to 1) with the consideration of carbon pick up from toluene which was observed earlier in our studies [39]. The milling process was interrupted after every hour for 30 min to avoid overheating. Powders after every one hour were collected for studying phase evolution. The 5 h ball milled powder mixtures were dried in a fume hood at room temperature. The powders were compacted using spark plasma sintering (Dr Sinter, Model SPS-625, SPS Syntex Inc.,) at 1400 °C with a heating rate of 100 °C/min and an applied load of 50 MPa and hold time of 10 min at the maximum temperature. A cylindrical graphite die of 20 mm inner diameter was used. A hole was drilled half-way along the length of the die reaching to about 1 mm from the inner surface of the die. An optical pyrometer (CHINO, Model IR-AH, Japan) was focussed on the hole to measure the temperature. It was noted that the temperature measured was called as SPS temperature, which was very close to the surface of the sample and was reported in all literature involving SPS. Given the high thermal conductivity of graphite and TiC_x and the fact that the heating takes place within the powders as well due to joule heating, the sample temperature was expected to be very close to the measured temperature.

2.2. Characterization and mechanical testing

The SPS compacts were cut using a wire electrical discharge (wire EDM) machining equipment to study the microstructure, phases present and hardness in the cross sectional region. The heat affected zone due to wire EDM was removed by grinding with SiC papers and polishing with diamond paste. Scanning electron microscopy (FEI INSPECT F, USA) was used to study the morphology of milled powders and the microstructure of sintered compacts. A PANalytical XPert Pro XRD instrument was used to analyse the phase evolution of powders after milling and compacts after sintering. The density of sintered compacts was measured by water immersion method based on Archimedes' principle. A CHNS/O analyser (2400 Series II-Perkin Elmer) was used to measure the carbon content of the sintered compacts. A micro Raman spectrometer (LabRAM HR, Horiba Scientific) employing a 488 nm light was used to study the phases present in the compacts. Raman peaks were studied in the Raman shift range of 100–2000 cm^{-1}. A Vicker's microhardness tester (Wolpert Wilson 432SVA) was used to measure the hardness of the polished cross section of the sintered specimens at a load of 1 kg and dwell time of 10 s. An average of 20 indents was reported. The nanohardness and elastic modulus were measured on the polished cross-sections of the compacts using a nanoindenter (Hysitron Triboindenter TI950). The loading pattern consisted of increasing the load to 8000 μN in 10 s followed by holding for 5 s and finally unloading to zero load in 10 s. An average of 20 indents was reported.

3. Results and discussion

3.1. Effect of ball milling on dispersion and phase evolution

The SEM micrographs of 5 h ball milled Ti-CB powder mixtures are shown in Fig. 1(a-f). Ti powders having a flaky morphology with CB

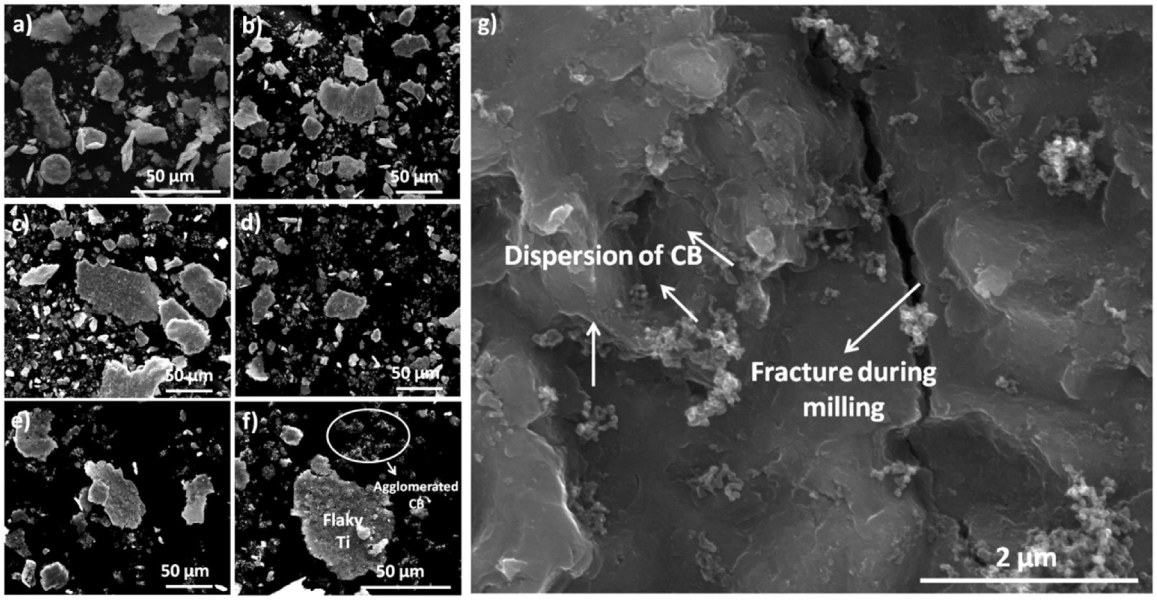

Fig. 1. SEM micrographs of 5 h milled powder of a) Ti- 5CB, b) Ti – 7.5CB, c) Ti-10CB, d) Ti-12.5CB, e) Ti-15CB, and f) Ti-17.5CB. A high magnification SEM image of Ti-10CB powder is shown in 1(g).