Preparation of multi-phase composite of tungsten carbide, tungsten boride and carbon by arc plasma melting: characterization of melt-cast product

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Abstract

Arc plasma melting of $WC+B_4C$ followed by an *in situ* furnace cooling produced a multi-phase composite consisting of tungsten carbide, tungsten boride and carbon. The melt-cast product was prepared in six different compositions by varying the boron carbide content (within 1–15 wt%) at the charge stage. XRD, SAED and XPS characterizations of the product showed the major phases to constitute of W_2B, WB, W_2B_5 (WB_2), WC, W_2C and C. Carbon was found to exist in three different forms, such as graphite, diamond / DLC and nanocrystalline diamond (C–C sp^3 coordination). FESEM, TEM and BET studies revealed the surface morphology, microstructure and non-porous nature of the composites respectively. From micro Raman spectra it was evident that W_2C and all tungsten boride phases were non-Raman active with 514 nm radiation (Ar^+ laser). Preliminary mechanical characterization of the polished composite samples (in solid forms) showed the hardness to increase with increase in B_4C content (range: 1–10 wt%). An extraordinary hardness of 3835 ± 80 VHN with corresponding Young's modulus of 695 ± 33 GPa was observed for the typical composition of $WC+10$ wt% B_4C. However, the hardness showed decreased value for 15 wt% B_4C added sample.

1. Introduction

Tungsten carbide and boron carbide are two industrially important transition metal carbides that exhibit excellent ceramic properties and withstand very high temperature (~2700 °C and more). Tungsten carbide (WC) exhibits hardness in the range of 16–22 GPa, Young's modulus to the extent of 550–720 GPa and fracture toughness of the order of 28 MPa m$^{1/2}$ (when bonded with Co) [1–5]. It is characterized by high density (15.6×10^3 kg m^{-3}), high compressive strength (5 GPa at 20 °C), and high thermal conductivity (29–121 W/m K), in addition to high oxidation and corrosion resistance [1,5–7]. The wide application of this carbide in manufacturing cutting tools, wear resistance components, ballistics, hard facing coatings, ball point tips, guide sleeve in machines, etc. is well established. On the other hand, boron carbide (B_4C) is a hard refractory compound (harder than WC, hardness: ~38 GPa) characterized by low density [8,9]. It therefore finds application in manufacture of personal armours, bullet proof vests, etc. In such a background, it is thought that if a new composite can be prepared from WC and B_4C, the resulting product would show some novel and improved mechanical properties due to combined contribution of both the compounds. The preparation of the envisaged composite is not an easy job. In literature, tungsten carbide is known to be prepared by pyro-metallurgical process involving reaction of tungsten metal with carbon at 1400–2000 °C [10]. It is also prepared by fluidised bed reduction process involving tungsten metal or WO_3 with CO/CO_2 mixture and H_2 in the temperature range 900–1200 °C [11]. Other preparation methods in the literature include: heating WO_3 with graphite directly at 900 °C or in hydrogen at 670 °C followed by carburization in argon at 1000 °C [12] and chemical vapor deposition method (CVD) involving tungsten halides and carbonaceous gas in hydrogen medium at 350–670 °C [10]. Boron carbide, on the other hand,

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does not have many options in preparation. It is prepared by reduction of boron trioxide (B_2O_3) either with carbon or magnesium in presence of carbon in an electric arc furnace [13]. The carbon–boron trioxode reaction occurs at temperatures above the melting point of B_4C (~2763 °C) leading to formation of B_4C and accompanied CO liberation [14]. If Mg is used, the reaction is carried out in graphite furnace and Mg byproducts are removed by acid treatment [15]. It is therefore evident that various complications involved in the preparation of WC and B_4C have not made it possible so far to prepare their composites, particularly by melt route technique. Any melt route technique is generally preferable to produce porosity free cast products with improved toughness (for ceramic compounds). In case of WC (MP ~2870 °C) and B_4C (MP ~2763 °C), binder like Co is used to improve composite toughness and porosity (in product) if melt technique is not adopted. Addition of Co while improves mechanical property, it degrades neutron absorption/shielding property of WC+B_4C composite.

Owing to the unusually high melting points of WC and B_4C, conventional resistive heating furnaces cannot be used for melt-cast method of composite preparation of these compounds. Heating sources like induction furnace, arc furnace, graphite furnace, etc. are generally employed in industries to melt these carbides [16,17]. However, such heating processes are costly as well as energy intensive compared to arc plasma furnace and take few to many hours to reach required high temperature for melting. In contrast, arc plasma furnace (operating in transferred arc mode) is characterized with very high energy density (~10^6 W/cm^2) and high ion temperature. Arc plasma furnace / reactor (used in this work) is a fast melting device which takes not more than 30–40 min to completely melt kg scale of charge at around 3000 °C temperature [1,4,18,19]. Because of simple arc configuration adopted, the furnace is relatively cheaper from cost point of view and does not involve any sophistication. Hence, it was decided in this investigation to melt the WC+B_4C mixture of different compositions by two types of dc extended arc plasma reactors: (i) a 30 kW Linde type semi-open reactor (ii) a specially designed 50 kW closed reactor. Microstructural and mechanical properties of the melt-cast composites were evaluated using X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), field emission scanning electron microscopy (FESEM), energy dispersive spectra (EDS) of X-ray, X-ray photoelectron spectroscopy (XPS), micro Raman spectroscopy and nanoindention technique. Micro porosity in the produced composites was determined by BET (Brunauer-Emmett-Teller) method. The study reconfirms the non-Raman active nature of W_2C, reported earlier by the authors [1] and more importantly it establishes for the *first time* the non-Raman active nature of various tungsten boride phases produced in the melt-cast composites (using 514 nm Ar$^+$ laser as primary excitation). The most highlighting feature of this work is the production of a *zero porosity superhard composite* (from a starting composition of charge of WC+10 wt% B_4C) consisting of tungsten carbide, tungsten boride and carbon. The material properties of the arc plasma melted cast composite for the entire six different

compositions have been evaluated in detail and presented in this paper.

2. Materials and methods

WC and B_4C, taken in the form of powder, were mixed at six different ratios between 1 and 15 wt% of B_4C to prepare respective homogenous mixtures at 1 kg scale. The WC starting powder was procured from M/s Rapicut Carbides Ltd., India, and the B_4C powder was M/s Himedia Laboratories Pvt. Ltd. make.

Specifications of WC and B_4C at the charge stage were as follows:

Grain size of WC powder: 4–7 µm
C wt% in WC: 6.11–6.16 (bound C), 0.05 max (free C)
Grain size B_4C powder: 68 µm
Compacted pellets of WC+B_4C powder were prepared by varying the wt% of B_4C at 1, 2, 3, 5, 10 and 15 with respect to WC. One composition was prepared with 0% addition of B_4C i.e. from WC only. PVA (poly vinyl alcohol) solution (2% in water) was used as binder and a uniaxial compaction pressure of 156.06 MPa was applied on the die plunger for 30–60 s. Diameter of the compacted pellets varied in the range 2–4 cm. The green pellets were air-dried for 3–5 h to develop good handling strength. The air dried pellets were arc plasma melted at 1 kg scale in two types of reactors: (i) 30 kW (dc), (ii) 50 kW (dc). While melt-castings of the 5, 10 and 15 wt% B_4C added WC samples were carried out in the 30 kW reactor, the 0, 1, 2 and 3 wt% B_4C added WC samples were melted and cast in the 50 kW reactor. Both the reactors were operated in transferred arc mode using graphite crucible. The details of the melt-cast technique using a 30 kW reactor have been described in the earlier works of the authors [1,4,18–20]. The design of the 50 kW special reactor was done by the authors with a new concept to reduce energy consumption in melt-casting. Here, hot gas/flame emanating from the graphite crucible (during melting of charge) through its top open end was made to pass through the underlying zone lying between outer wall of crucible and insulating wall of furnace (hearth) in a down draft mode. Thus, the conduction heat loss through refractory lining of the furnace wall was compensated from the flue gas/flame and not from the graphite crucible. Thus 38–40% energy consumption for melting was found to reduce. To start melting, the crucible filled with the charge was initially connected to the positive polarity of a dc power supply via three graphite rods laterally positioned inside hearth of the reactor and mechanically fixed to the crucible. The charge and the crucible together worked as anode. Plasma forming gas, argon (Ar), was introduced into the reactor through the central axial hole provided in the top vertical graphite cathode. Transferred arc configuration was formed by bringing the top graphite cathode (vertically positioned from topside within the crucible) to the close proximaty of the charge (maintained with positive polarity) and melting was done by igniting the arc between the anode and the cathode. In a melting process, transferred arc delivers more energy (>95%) to charge than non-tranferred arc. The arc length between the anode and the cathode was