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Successful Synthesis of Tungsten Carbide Based Composite by Arc Plasma Melting

Among the transition metal carbides, tungsten carbide (WC) has received considerable attention as an advanced material in the world of materials, especially in cutting tools, ballistics, hard face coatings, etc. because of its ultra-hardness, high melting point, low friction coefficient, improved oxidation resistance, etc. Fused tungsten carbide, i.e., WC-W_2C (tungsten semi-carbide) composites synthesized from WC by thermal arc plasma technique within 4 min. of plasma treatment. W_2C phase was found to be more intense with the increasing duration of plasma treatment. X-ray diffraction (XRD) study confirms fused tungsten carbide formation (WC-W_2C). Field-emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and Brunauer–Emmett–Teller (BET) analyses infer about the high density with negligible porous nature of composites. Composite samples show a density of more than 15.72 g/cm^3. The total pore volume measured in the composites in the range of 0.07-0.09 cm^3/g. Compared to pure WC, we found the composites with improved microhardness. In this work, a 4 min. plasma-treated WC sample shows a relatively higher microhardness of 2190±21 VHN.

Keywords: Tungsten carbide; Thermal arc plasma; Composites; Microhardness
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1. Introduction

There are two phases of tungsten carbide; tungsten mono carbide (WC) and tungsten semi-carbide (W_2C) [1]. The recent literature reports higher hardness for W_2C [2] compared to WC. WC shows an extraordinarily high melting point (~2700 °C) and high microhardness (~23 GPa) [1-6]. It is one of the major ceramics used for making drill bits for ruck cutting, compaction dies, balls for grinding and milling, cutting tools, abrasive components, etc. However, the brittleness of tungsten carbide limits its applications. Tungsten carbide in the form of cemented carbides called cermet shows excellent properties. Generally, WC shows outstanding applications when reinforced by some metallic phases like Co, Fi, Ni, etc. [7-14]. These metallic phases lower the processing temperature required for developing components from tungsten carbide. However, the addition of metallic phases improves the ductility of WC at the expense of loss of hardness. So it is very important if tungsten carbide composite components can be developed with good properties without the addition of metallic binder phases. Generally, refractory carbides such as WC based composites process by powder metallurgy or melt-cast techniques. The conventional powder metallurgy route for processing tungsten carbide components involves steps like homogenous mixture, compaction (hot and cold), and sintering. The process is not economical and not effective in developing composites with less porosity and defects. On the other hand, plasma technology with high energy density and high reaction kinetics can provide suitable processing techniques to process products from WC-based materials. Plasma treatment of composite can be carried out under the desired environment during plasma treatment. Thermal arc plasma method is considered as the unique method for reducing time and energy consumption. It also has better control over the kinematics of phase transformation under control environment. The typical information about thermal arc plasma is reported in literature [15-17]. When a single phase tungsten carbide is melted and cast, it converts its composite form of WC-W_2C by eutectoid transformation at a temperature of around 2380 °C (Fig. 1) [18,19]. This composite shows better microhardness property compared to pure WC [20-22]. The paper reports on the successful synthesis of composites of WC-W_2C by thermal arc plasma technique with improved microhardness.

2. Methodology

WC powder material was procured from M/s Rapicut Carbides Ltd., India. At first, the WC powder was added with polyvinyl alcohol (3% concentration) as a binder. Then the samples were compacted under the application of 200 MPa load for 1 min. to develop samples of 25 mm diameter and 5 mm thickness. Then the samples were air dried for 3-4 hours. The air-dried samples as charged were put in the graphite crucible and kept in a plasma reactor. The plasma reactor was operated under voltage of 50 V and current of 200 A. For stable plasma generation and to prevent oxidation in composites, argon (Ar) gas has been introduced at a rate of 2 litre/min in the plasma reactor through a graphite cathode. The plasma treatment of WC samples was carried out in two batches for 2 and 4 minutes of treatment. After melting of samples, the samples are in situ cooled (underflow of argon) inside the reactor till room temperature is achieved. In the

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plasma reaction, around 12 kWh/0.1 kg energy was consumed for the preparation of composites. After plasma melt-cast completed in the plasma furnace, they were taken to evaluate their properties. Crystallographic behavior was determined by XRD analysis (PANalytical X'Pert Pro diffractometer (CuKα, λ=0.15406nm). Chemical bonding of the plasma-treated WC sample was studied by Fourier-transform infrared (FTIR) spectroscopy (Thermo Nicolet iS50). The total pore volume was determined by the Brunauer–Emmett–Teller (BET) method (Quantachrome autosorb IQ). An FEI TECNAI G2 TEM has been used to study and observe the nano-level morphology of the composite. FE-SEM (model ZEISS SUPRA 55) was employed to explore microstructure at micron level. Density of sample was measured by Archimedes principle. The Microhardness of samples was determined by a LECO tester with a Berkovich-type diamond indenter at a load of 0.5.

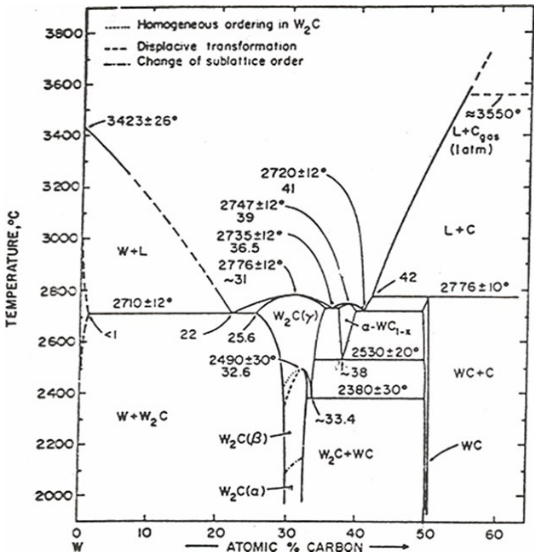
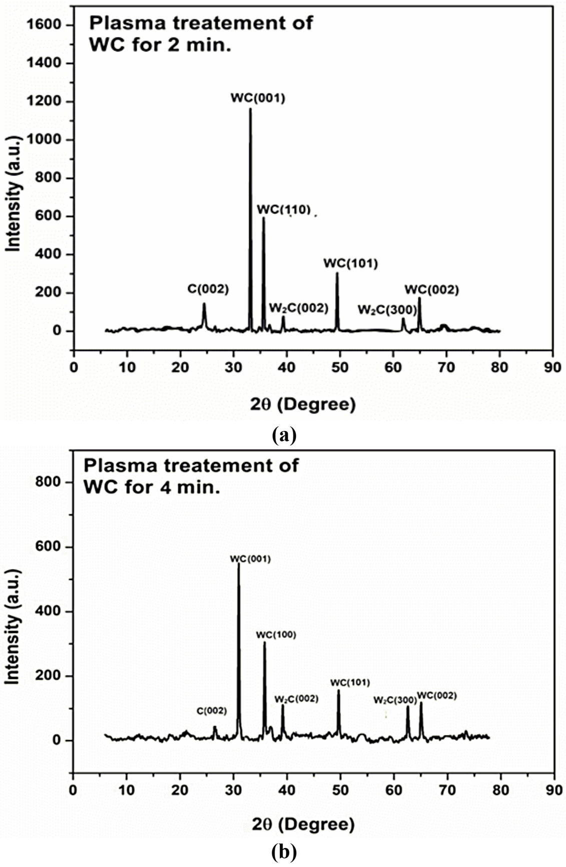


Fig. (1) W-C thermodynamic phase transition system [10,11]

3. Results and Discussion

Thermal arc plasma melting of WC samples was carried out only for 2 min and 4 min. The composite ingots were produced with more than 85% of yield. 100 g sample per batch was taken for plasma treatment. The WC-W_2C composite formation was confirmed from the XRD analysis for 2 min and 4 minutes plasma treated WC samples and shown in figures (2a) and (2b), respectively. Standard JCPDS 1999 data files used for identifying various phases present in the arc plasma melt-cast samples. The following JCPDS files were used: WC (hexagonal): 73-0471, W_2C (hexagonal): 79-0743, C(graphite) (hexagonal-2H polytype): 41-1487. XRD results (figures 2a and 2b) show the presence of phases like WC, W_2C, and C(graphite). The major phase of WC is observed at around 2θ of 31°C. W_2C major phase appeared at around 2θ of 39°C. The peak intensity of W_2C increases with increasing time duration of plasma treatment. On the other hand, WC peak intensity becomes less intense as the time duration of plasma treatment increases. The results indicate that more amount of WC dissociates to W_2C and C with increasing time duration of plasma treatment. There are no unwanted phases identified in the composite. The peak intensity and full-width at half maximum (FWHM) infer the crystalline nature of the composite. Unit cell volume for WC, W_2C and C (graphite) phases were determined from XRD results. The 2 minutes-plasma treated WC sample shows unit cell volume for WC, W_2C and C (graphite) phases as 0.02088, 0.1208 and 0.04562 nm^3. However, 4 min. plasma treated WC sample shows unit cell volume for WC, W_2C and C (graphite) phases as 0.02178, 0.1345 and 0.0564 nm^3. The increase of unit cell volume of different phases can be attributed to the relatively increasing the time duration of plasma treatment from 2 to 4 minutes of WC sample. Lattice constants expands on increasing duration of plasma treatment which help to lead the expansion of unit cell volume and enhances kinetics of phase transformation.



(b)

Fig. (2) XRD patterns of melt-cast WC samples for treatment of (a) 2 min, and (b) 4 min

FTIR analysis (Fig. 3) of a typical 4 minutes plasma-treated WC sample shows three wavenumbers at 1059 cm^{-1} (W-C), 1630 cm^{-1} (C=C) and 3470 cm^{-1} (O-H). Plasma-treated WC samples show a density of more than 15.72 g/cm^3. Such high density helps to improve microstructure and microhardness. The total pore volume present in the plasma-treated composites was measured by the BET method in the range of 0.07-0.09 cm^3/g. The above result indicates that samples have almost negligible porosity.

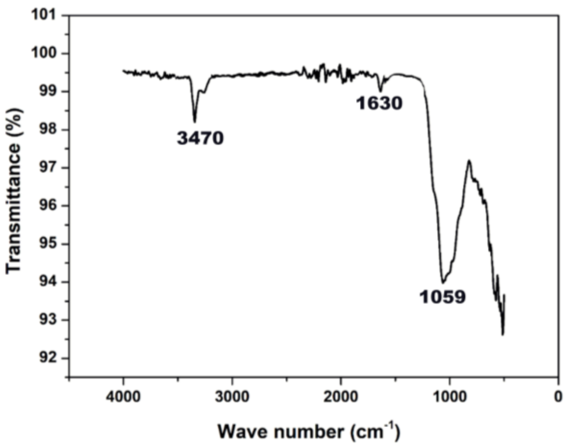


Fig. (3) FTIR spectrum of 4 min. plasma treated WC sample

FE-SEM microstructure obtained for the typical WC sample treated for 4 min. by thermal arc plasma is presented in Fig. (4). It shows multiphasic and polycrystalline morphologies. Microstructure of granular type is found in the FE-SEM image. Three types of phases such as grey, white and dark were seen in the FE-SEM structure. These phases were identified by EDS analysis. The EDS spectra taken on grey, white and dark phases of FE-SEM image (Fig. 4) are presented in Fig. (5) and their relative quantitative results is presented in table (1). Grey phase displays C and W at atomic % of 56.34 and 45.66, respectively. This result indicates the WC phase. White phase displays C and W at atomic % of 32.58 and 67.42, respectively. This result infers to the W_2C phase. On the other hand, dark phase shows C and W at atomic % of 98.12 and 1.88, respectively. This result infers to the C phase. FE-SEM with EDS results can be corroborated to XRD result about very less amount of presence of C (graphite) in the composite of WC-W_2C formed after arc plasma treatment of WC sample. Morphological analysis by both FE-SEM (Fig. 4) and TEM of typical 4 min. plasma treated WC (Fig. 6) show a very highly dense microstructure. Unlike FE-SEM result, it shows three types of phase contrasts (white, grey and dark) in the composite.

The microhardness of plasma-treated WC sample was determined on the mirror-polished surface of the samples. The microhardness value was evaluated at an applied load of 0.5 kg. The 2 min and 4 min. plasma treated WC samples show microhardness of 1910 ± 15 VHN and 2190 ± 21 VHN respectively. 4 min. plasma treated WC shows relatively higher hardness than 2 min. plasma-treated WC sample possibly due to having high intensity peak of W_2C. The above microhardness values are compared to the microhardness value of pure WC which shows a hardness of 1670-1708 VHN [12]. The above-increased microhardness of composites is attributed to their superior microstructure with less pore volume. In this work, successful composite of WC/W_2C has been prepared from starting WC material with employing only a maximum of 4 min. of thermal plasma operation.

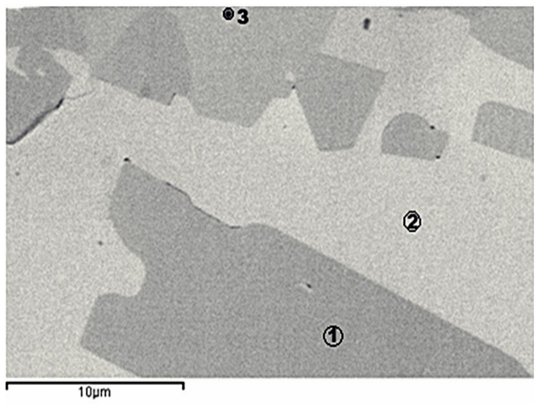


Fig. (4) FE-SEM image of typical 4 min plasma treated WC sample

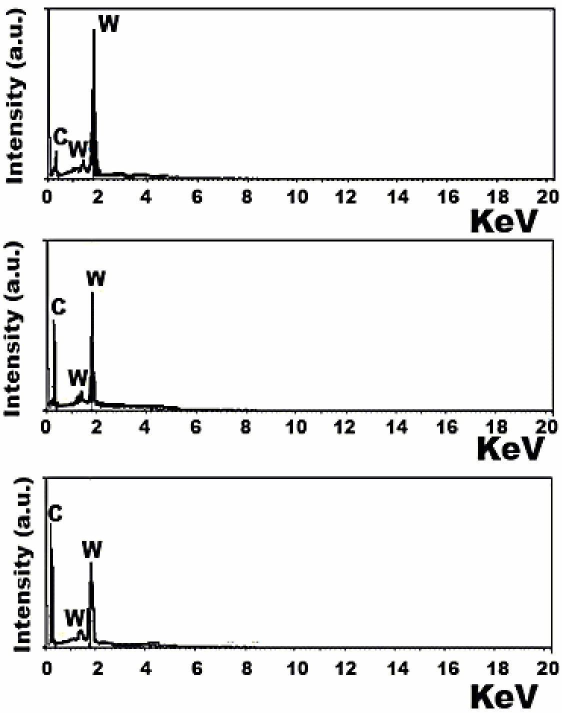


Fig. (5) EDS results on the phases marked by 1 (upper) grey phase, 2 (middle) white phase, and 3 (lower) dark phase, respectively on the FE-SEM microstructure (Fig. 4)

The main objective of the paper was to develop a novel ceramic hard composite with minimum time

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(plasma treatment adopted here) of synthesis procedure which can be adopted in industry for the production of tungsten carbide-based composites for various applications instead of following the conventional powder metallurgy route which involves complex steps and time-consuming methods. We report that the objective is achieved in this work.

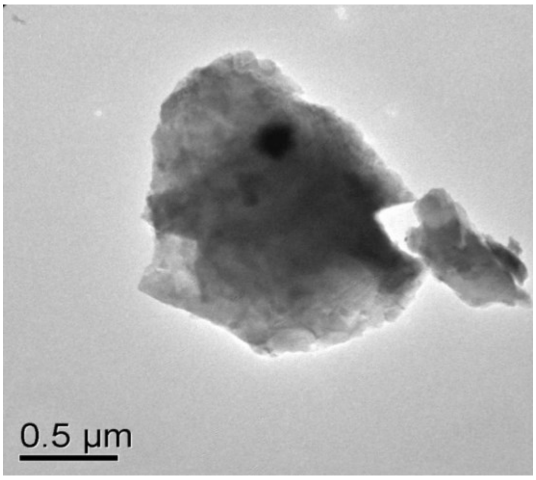

Fig. (6) TEM analysis of 4 min. plasma treated WC sample

4. Conclusions

We report the successful synthesis of a hard composite of WC-W_2C from pure single phase WC only within 4 min. of thermal plasma operation instead of using a complex and time-consuming powder metallurgy route. It has been observed that after plasma treatment of WC, it dissociates to W_2C and C(graphite). The intensity of the W_2C peak increases with increasing duration of plasma treatment. The total pore volume measured by the BET method of composites lies in the range of 0.07-0.09 cm^3/g. The value indicates that samples have almost negligible porosity. Very highly dense microstructure of a typical 4 min. plasma-treated composite was confirmed. The WC-W_2C composite formation with very trace amount of C(graphite) was also revealed. The composite samples show a density of more than 15.72 g/cm^3. 2 min and 4 min. plasma treated WC samples show microhardness of 1910 ± 15 VHN and 2190 ± 21 VHN respectively. 4 min. plasma treated WC shows relatively higher hardness value compared to 2 min. plasma-treated WC and pure WC.

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Table (1) EDS analysis results recorded on the FESEM analysis of typical 4 min plasma treated WC sample

Grey Phase			White Phase			Dark Phase		
Element	Wt.%	At.%	Element	Wt.%	At.%	Element	Wt.%	At.%
CK	9.88	56.34	CK	2.98	32.58	CK	83.86	98.12
WM	90.12	45.66	WM	97.02	67.42	WM	16.14	1.88

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