Development of Robust Harder Composites from Tungsten Carbide and Titanium Carbide by Arc Plasma Melt-Cast Method

Ranjan K. Moharana [1]
Tapan Dash [1,2]
Tapan K. Rout [3]
Surendra K. Biswal [2]

[1] *Centurion University of Technology and Management, Odisha, INDIA*
[2] *International PranaGraf Mintech Research Centre (IGMRC), Bhubaneswar, Odisha, INDIA*
[3] *Research & Development Department, Tata Steel Ltd, Jamshedpur, INDIA*

This work develops robust composites from the mixture of tungsten carbide (WC) and titanium carbide (TiC) (0.5-4 wt.%) with enhanced hardness for various hard-facing industrial applications by thermal arc plasma method. Constituents of composites such as WC, W_2C, $TiWC_2$ (solid solution phase between WC and TiC), and C (graphite) were observed in XRD results. Melt-cast pure WC and 0.5 wt.% TiC reinforced WC composite shows an acicular type of morphology. Whereas in the case of 2 and 4 wt.% addition of TiC in WC, the morphology is found to be dendritic. No impurities are present in the post-processing of composites, confirmed by XRD and EDS studies. BET surface area and total pore volume of melt-cast WC and WC-TiC (0.5-4 wt.%) composites were found to be 0.14-0.22 m^2/g and 0.0003-0.0031 g/cm^3 respectively. The typical WC reinforced with 4 wt.% TiC composite shows an improved microhardness value of 3422±10 VHN, which is more than 70% of the microhardness value of plasma-treated WC (2010±06 VHN). The WC-TiC composites are characterized by high Young's modulus in the 675-710 GPa range.

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1. Introduction

Transition metal carbides have many potential industrial applications because of their outstanding behavior including its melting point, low friction coefficient, high hardness, and improved oxidation resistance. Among them, due to outstanding properties, tungsten carbide (WC) finds various applications in cutting tools, ballistics, hard face coatings, ballpoint tips, etc. [1-4]. WC-based cemented carbides are generally developed by making a composite between WC and binder phase (metallic phases, Ni, Fe-Ni, and Fe-Ni-Co are used) [5-8]. Due to having excellent mechanical properties, WC/Co is widely used as a cutting tool. Metallic binder phases enhance the toughness of the composite, resulting in a reduction of the brittleness of WC-based composites. On the other hand, adding metallic phases degrades properties such as anti-corrosion and hardness. Titanium carbide (TiC) shows better hardness in compared to WC. TiC with WC composite can be added for various hard-facing applications. It was observed that hardness of WC/Co composite increases by increasing TiC amount from 5 to 20 wt.% [9]. It has been reported that WC-TiC composites show improvement of microhardness values with increasing TiC content from 5 to 15 wt.% [10]. However, TiC addition decreased Young's modulus of composites up to 540 GPa compared to pure WC, which has Young's modulus value of 732 GPa. Energy consumption during the synthesis of WC/TiC composites was also found to be enhanced up to 28.56 kWh/kg with increasing reinforcement of wt.% of TiC in WC. The above result was caused due to TiC, which has relatively high melting point (~3160°C) compared to that of WC (2870°C). Hence, it has been decided that further optimization is required for WC/TiC composites. So, a suitable minimum amount of TiC as reinforcement in WC must be chosen without compromising the properties of WC/TiC, and the composites should be developed by consuming the possible minimum energy. The processing route for developing new composite from WC and TiC should be properly chosen. The conventional powder metallurgy route involves many steps, and the products show significant defects and lack improvement in significant mechanical properties. Hence, considering the above points, the present work uses the arc plasma melt cast technique to develop composites of WC/TiC. More about the arc plasma melt-cast technique is described elsewhere [11,12]. Arc plasma with high energy density, high enthalpy (10^5-10^6 W/cm^2), and large hot zone was generated by argon (Ar) gas for 10 min. to prepare a new composite from WC and TiC with significant improvement of microhardness and high Young's modulus.

2. Experimental Part

WC and TiC samples were taken from M/s Rapicut Carbides Ltd., India, and M/s Himedia Laboratories Pvt. Ltd., India. Pure WC and WC-TiC (0.5, 0.2, and 4 wt.%) mixture were chosen as the starting materials. With polyvinyl alcohol as a binder, the powder samples were compacted at 100 MPa for 5 min. The compacted pellets are produced with a 2 cm diameter. Then, the pellets were dried under sunlight for 3-4 hours. Then, the dried pellets

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were kept in the arc plasma reactor in a graphite crucible with a diameter of 4.5 cm. The plasma reactor was operated under voltage (V) of 45 V and current (I) of 200 A for 10 min. To maintain stable plasma energy and prevent oxidation in composites, argon (Ar) gas has been introduced at a rate of 1 ltr/min. in the plasma reactor through a graphite cathode. In the plasma reaction, 11.8-14.3 kWh/kg energy was consumed to prepare composites. Arc plasma was initiated by bringing the graphite cathode and anode (graphite crucible) very close to each other. Argon was introduced to the plasma reactor through the top graphite electrode. After melting, the *in-situ* casting was carried out in the same plasma reactor under an argon environment until the product reached room temperature. Phase presents in the arc plasma melt-cast pure WC, and WC-TiC composites were analyzed by X-ray diffraction (XRD) using PANalyticalX'Pert Pro diffractometer (CuKα, λ=0.15406nm). A ZEISS SUPRA 55 field-emission scanning electron microscope (FE-SEM) with attached energy-dispersive x-ray spectroscopy (EDS), was used for morphological and elemental analysis of samples. Brunauer-Emmett-Teller (BET) (auto sort automated gas sorption analyzer, Quantachrome instruments) was used to determine the surface area and pore volume of samples. A UMIS system (Fisher-Cripps, Australia) was employed to measure microhardness and Young's modulus at an applied load of 50 mN maximum.

3. Results and Discussion

The arc plasma melt-cast method was employed for 10 min. to prepare composites from the WC/TiC mixture, which is presented in table (1). The composite product recovery was found in the range of 98.3-99.4 wt.%. The arc plasma melt-cast gives high-yield products with more consistency. WC-reinforced TiC (0.5-4 wt.%) composites require relatively more energy (due to the high melting point of TiC) to prepare composites in comparison to pure WC. However, the overall energy consumption and time required for preparing composites can be considered more environmentally friendly than the conventional powder metallurgy route.

The XRD characterization of arc plasma melt-cast pure WC and WC-TiC (0.5-4 wt.%) composites have been carried out and presented in Fig. (1) and Fig. (2), respectively. XRD result of melt cast sample of pure WC (Fig. 1) shows significant phases of WC and W_2C. WC crystallographic planes such as (001), (100), and (101) are found to be more intense. Carbon (graphite) is a minor phase that appears as C(002) in the pattern. XRD results of WC-TiC (0.5-4 wt.%) melt cast composites are shown in Fig. (2). They show the peaks due to WC, W_2C, $TiWC_2$, and C (graphite). The solid solution phase $TiWC_2$ is grown in the composite due to the lattice interaction between WC and TiC. The following reaction takes place in plasma treatment to prepare the solid solution phase as TiC + WC → $TiWC_2$ (solid solution) [13,14]. Peak intensity of $TiWC_2$ and W_2C increases with increasing wt.% of TiC in WC. When WC dissociates after plasma treatment, it forms W_2C and C (graphite). There is no peak of TiC marked in the composite after plasma treatment. It indicates that the TiC compound appropriately interacts with the lattice of WC under optimized conditions. No other impurity is marked in the composite.

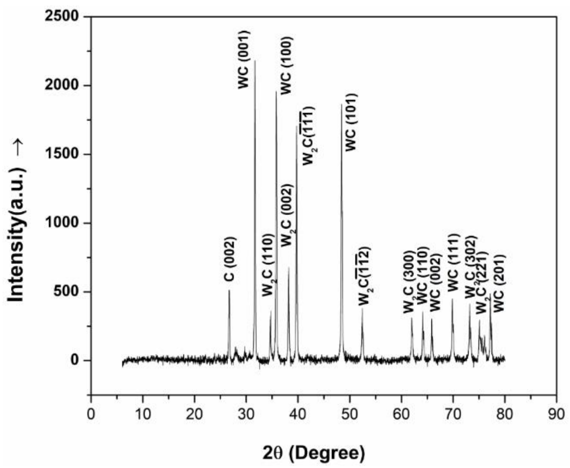

Fig. (1) XRD analysis result of melt-cast pure WC

The surface morphology of as-prepared melt-cast pure WC and WC-TiC (0.5-4 wt.%) composites evaluated by FESEM is shown in Fig. (3). Melt-cast pure WC (Fig. 3a) and TiC (0.5 wt.%) reinforced WC composite (Fig. 3b) show acicular type of morphology. On the other hand, it has been observed that when we reinforced 2 and 4 wt.% TiC in WC, the morphology changed from acicular to dendritic (Fig. 3c and Fig. 3d). The acicular microstructure is produced due to macroscopic slip in lattice planes [15]. The possible cause of the growth of dendrite structure is not well established, but it generally grows during the processing of materials having different thermal kinetic behavior with varying points of melting (WC ~2870°C, TiC ~3160°C) under thermal plasma treatment and it also follows undercooling of liquid metals. Such a dendritic structure could possibly be developed because of the increase in TiC content above 0.5 wt.% in WC. Such a microstructure is reported in the literature because of the solid solution $TiWC_2$ phase grown when the Ni-Cu alloy composite is reinforced by (Ti,W)C and coated over the Cu substrate [13]. In the literature [16], it has also been observed that a solid solution ($TiWC_2$) between TiC and WC is formed at 1400°C, and TiC dissolved ~73 mass% in WC, which increased further approximately to 95.5% at 2400°C. Hence, we got exciting collaboration between XRD and FE-SEM analysis results that XRD shows increasing peak intensity of $TiWC_2$ with increasing TiC content in WC, which results in the formation of dendritic type of structure in the composites formed by reinforcing 2 and 4 wt.% TiC in WC.

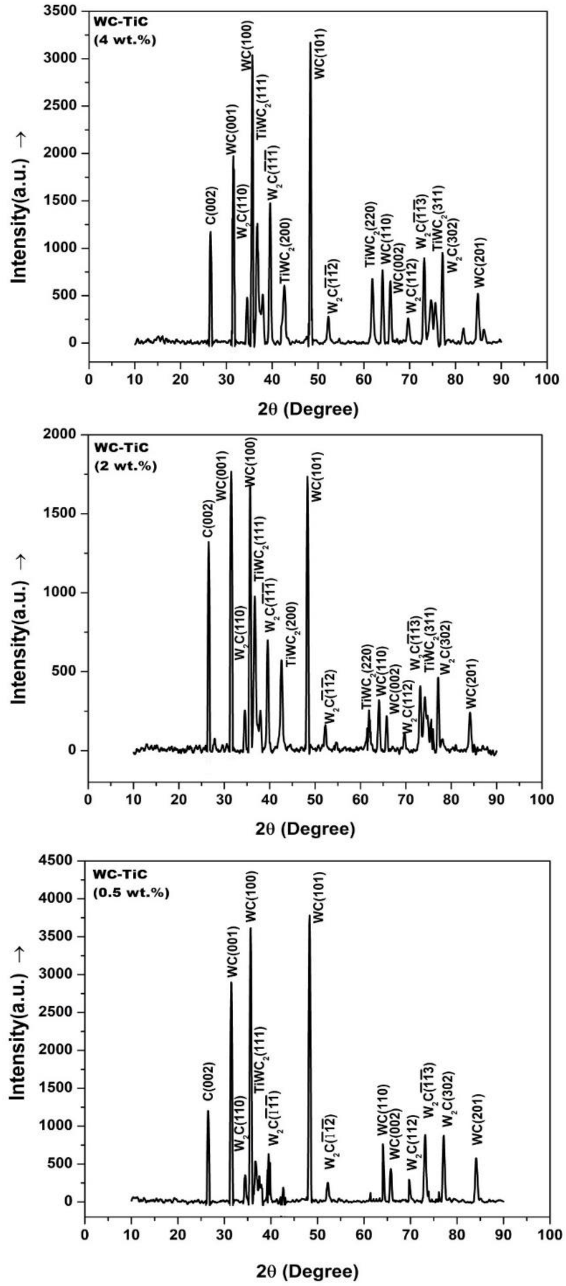

Fig. (2) XRD analysis results of melt-cast WC-TiC (0.5-4 wt.%) composites

The EDS analysis was carried out to determine the composition of the different grains, such as dark, grey, and white. EDS analysis of the typical WC-TiC (4 wt.%) composite (Fig. 3d) on selected grains was carried out. From the study, it was observed that white grain (Fig. 3d), marked box (1) contains intense high peaks of Ti and W with the presence of a relatively low intense peak of C (shown in Fig. 4a).

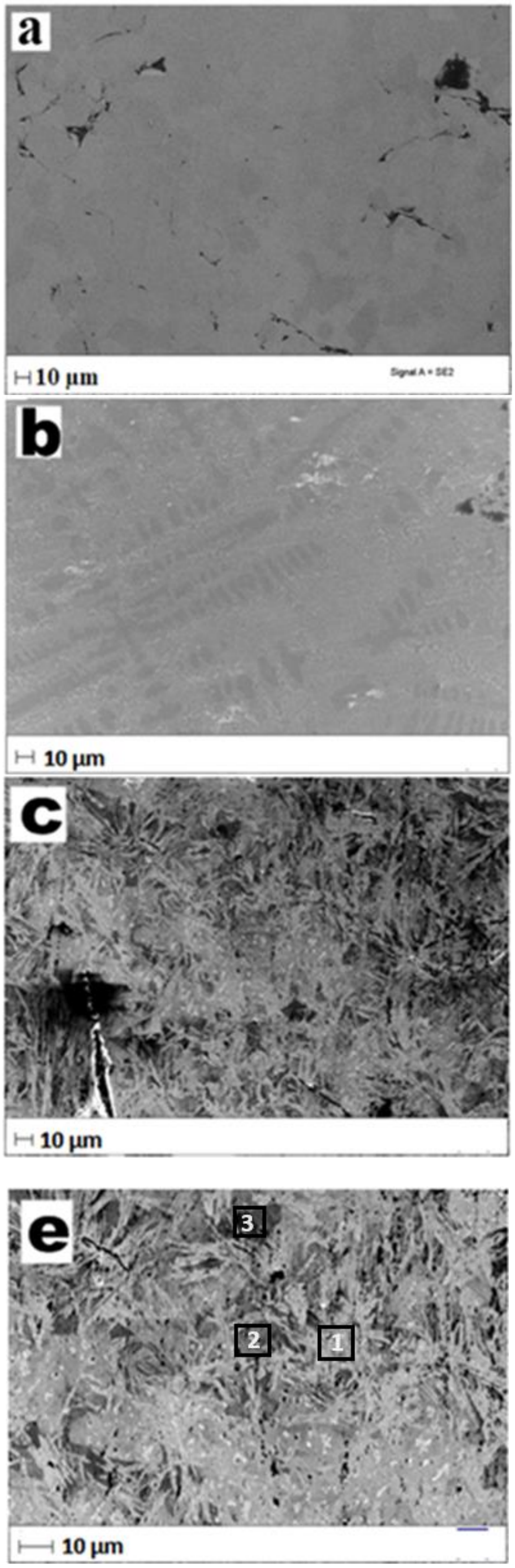

Fig. (3) Surface morphology by FE-SEM of melt-cast samples: (a) pure WC, (b) WC-TiC 0.5 wt. %, (c) WC-TiC 2 wt. %, (d) WC-TiC 4 wt.%

Constituents of grey grain (Fig. 3d), marked box (2) are W (high intense), Ti (Reduced intense), and C (shown in Fig. 4b). Figure (4c) shows C in a more intense peak along with reduced peak intensity of Ti and W in the case of dark grain (Fig. 3d), marked box (3).

The specific surface area determined by BET and Langmuir methods with a total pore volume of pure WC and four WC-TiC (0.5-4 wt.%) composites is shown in table (2). BET and Langmuir surface area of arc plasma melt-cast samples were observed in the range of 0.14 - 0.26 m^2/g and 0.61-0.88 m^2/g, respectively. Specific surface area values are found to be negligible. It has been found that the total pore volume of composites is in the range of 0.0003-0.0031 g/cm^3. The relatively lower values were observed in the case of the melt-cast 2 wt.% added TiC in WC composites. From BET studies, composite samples have a negligible porous nature, and this quality of materials can be attributed to the high enthalpy involved in the thermal plasma processing for preparing the materials.

Table (2) Specific surface area and total pore volume of plasma melt-cast pure WC and WC-TiC (0.5-4 wt.%) composites

Sample ID	BET Surface Area (m^2/g)	Langmuir Surface Area (m^2/g)	Total Pore Volume of Pores (cm^3/g)
Pure WC	0.26	0.82	0.0006
WC-TiC (0.5 wt.%)	0.18	0.88	0.0004
WC-TiC (2 wt.%)	0.22	0.79	0.0031
WC-TiC (4 wt.%)	0.14	0.61	0.0003

The microhardness of arc plasma treated WC and WC-TiC (0.5-4 wt.%) composites have been measured by taking the average value of five measurements and presented in table (3). Plasma-treated WC shows a microhardness of 2010±06 VHN. It has been observed that with increasing TiC wt.% in WC, the microhardness value of WC-TiC (0.5-4 wt.%) composites increases. The typical 4 wt.% added TiC in WC composite showed a significantly improved microhardness value of 3422±10 VHN, which is more than 70% of the microhardness value of plasma-treated WC. The improved microhardness value of this composite can be attributed to the relatively more intense peaks of $TiWC_2$ and W_2C compared to other WC-TiC composites. It was observed that $TiWC_2$ is a very hard phase compared to WC and TiC [10]. It has been reported that W_2C is the semi/sub carbide of tungsten, which has higher hardness than WC [17-19]. A similar range of microhardness value was achieved in the literature by reinforcing 20 wt.% TiC in WC [20,21]. However, a relatively greater amount of addition of TiC in WC generally develops brittleness in composites, which limits the application of tungsten carbide-based composites. However, in the present case, WC-TiC composites show high Young's modulus values in the 675-710 GPa range. No significant decrease in Young's modulus value was noticed after the addition of TiC in WC. Hence, we successfully prepared WC-TiC composites with high hardness and almost maintained Young's modulus of the WC matrix after only 10 minutes of plasma treatment.

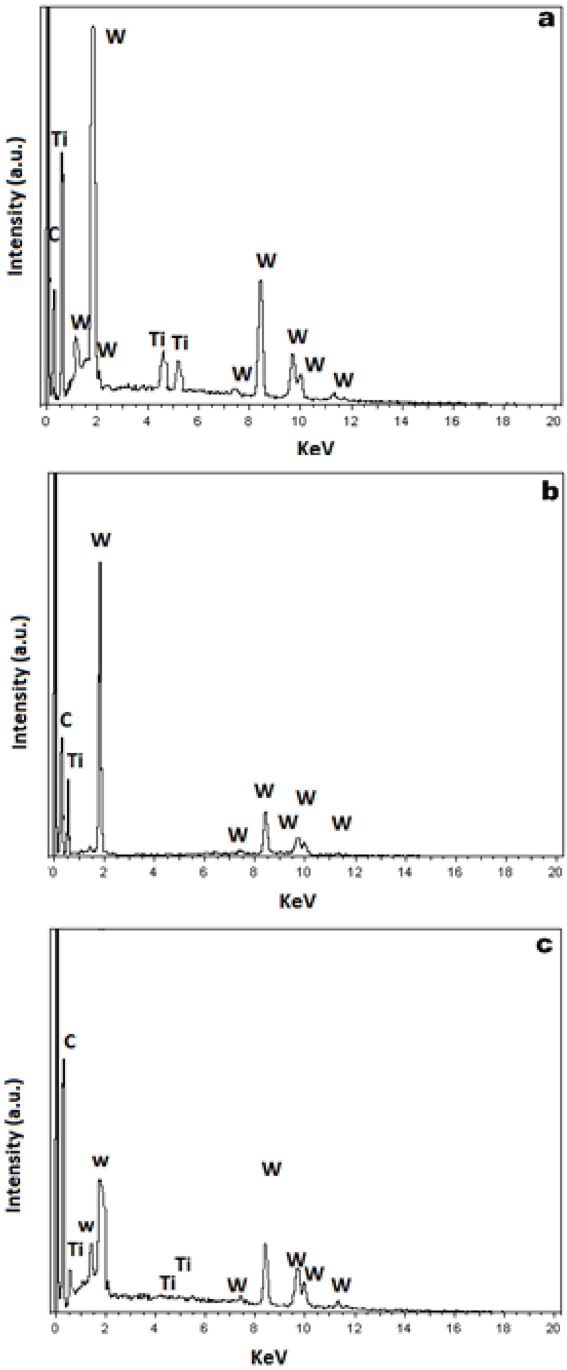

Fig. (4) EDS analysis of the typical composite sample WC-TiC (4 wt.%) observed on three grains/phases in FESEM (Fig. 3d): (a) taken on white grain marked as box 1, (b) taken on grey grain marked as box 2, (c) taken on dark grain marked as box 3

Table (3) Microhardness and Young's modulus values determined for melt-cast pure WC and WC-TiC (0.5-4 wt.%) composites

Sample ID	Microhardness (VHN)	Young's modulus (GPa)
Pure WC	2010 ± 06	740 ± 06
WC-TiC(0.5 wt.%)	2312 ± 12	710 ± 06
WC-TiC(2 wt.%)	2922 ± 14	690± 06
WC-TiC(4 wt.%)	3422 ± 10	675± 08

4. Conclusions

This work reports on the arc plasma melt-cast pure WC and composites prepared from WC and TiC mixture. TiC varies as 0.5-4 wt.% in WC at the charge stage. It has been observed from XRD that increasing TiC wt.% in WC from 0.5 to 4 wt.% increases the intensity of solid solution phase $TiWC_2$. Specific surface area and total pore volume values of arc plasma melt-cast WC and WC-TiC (0.5-4 wt.% composites) are found to be negligible. The typical WC-TiC (4 wt.%) composite showed BET surface area, Langmuir surface area, and total pore volume of 0.14 m^2/g, 0.61 m^2/g, and 0.0003 g/cm^3, respectively. The typical 4 wt.% added TiC in WC composite showed the maximum microhardness value of 3422 ± 10 VHN in the TiC addition range of 0.5-4 wt.% in WC, which is more than 70% of the microhardness value of plasma-treated pure WC. The improved microhardness value of this composite can be attributed to the presence of the relatively more intense peaks of $TiWC_2$ and W_2C in the composite with negligible pore volume. While pure WC showed Young's modulus value of 740 GPa, WC-TiC (0.5-4 wt.%) composites have high Young's modulus values in the 675-710 GPa range. The newly developed composites with improved hardness and high Young's modulus values can be recommended for various hard-facing applications.

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Table (1) Experimental sample preparation details of WC/TiC composites

Sample ID	Wt.% taken in charge stage		Used electrical energy (kWh /kg)	Composite product recovery (wt.%)	Dia. of circular cast disc produced (cm)
	TiC	WC			
Pure WC	0	100	11.8	99.4	4.5
WC-TiC (0.5 wt.%)	0.5	99.5	12.4	99.2	4.5
WC-TiC (2 wt.%)	2	98	14.3	98.3	4.5
WC-TiC (4 wt.%)	4	96	14.1	98.6	4.5