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Enhancement in the microhardness of arc plasma melted tungsten carbide

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Microhardness is found to increase significantly in arc plasma melted tungsten carbide. To understand the mechanism for such increase, tungsten carbide powder was mixed with tungsten metal powder to prepare mixtures of seven different compositions. The mixtures with varying WC/W ratio were pelletized and melted in an arc plasma followed by cooling in the furnace. It is observed that microhardness value enhances in the product when WC/W_2C ratio becomes high. Based on our microstructural finding of ⟨100⟩ WC hard faces and lamellar/acicular structures (due to martensite transformation) carried out by XRD, optical microscope and SEM, an attempt has been made to understand the reason behind the enhancement in microhardness.

1. Introduction

Among the hard carbides, tungsten carbide occupies a prominent place. It is extensively used in making cemented carbide cutting tools and finds wide application for manufacture of wear resistance critical components such as spray injection nozzle, sand blasting nozzle, guide sleeve in machines, thread guide in textile industry, micrometer anvil, burnishing tool, centre for lathe and grinder, ball point tip, teeth and jaw of excavator, rock cutting drill bit etc. These components are generally made by adopting powder metallurgy process or by casting from melt. While the powder metallurgy process involves a number of process steps such as mixing with binder, compaction, sintering etc., the casting of melt into desired shape and size is less cumbersome and easy to adapt in industrial practice. The melting point of tungsten carbide is very high (∼2720°C). Hardly any conventional furnace (electrical or otherwise) reaches such high temperature to melt this carbide. Special type expensive furnaces like graphite tube furnace producing temperature in the range 3000–3500°C, electric induction furnace, arc furnace are used in industries [1, 2] to melt tungsten carbide for various specific applications. This, as a result, increases the processing cost which prevents wide scale application of tungsten carbide cast products. In recent years we have tried to exploit the arc plasma technology to melt high temperature carbide like tungsten carbide in an indigenously developed dc extended arc plasma furnace/reactor [3]. Since argon arc plasma is cheap, provides non-oxidizing medium and does not involve any sophistication or high technology, the arc plasma melting is expected to reduce the processing cost of cast tungsten carbide appreciably.

Keeping the above advantages of arc plasma in view, in this paper, effort has been made to melt tungsten carbide with varying WC/W ratio, in an arc plasma furnace and study the microstructural properties of the furnace cooled product. The significant increase in microhardness of the product is the highlighting feature in this study. Characterization by X-ray diffraction (XRD), optical microscope and scanning electron microscope (SEM) reveals that high microhardness results when phenomenologically the WC/W_2C phase ratio becomes high in the samples. A mixture of martensite structure and ⟨100⟩ hard faces of WC grains is identified to be the cause for the rise in microhardness.

2. Experimental procedure

Orban [4, 5] had reported in reactive carburisation of tungsten melt that carbon content and W_2C/WC ratio are the main factors that determine the microstructure, elastic modulus, flexural strength and Vicker's microhardness in quasi eutectoid mixture of tungsten carbide. It was therefore felt that if the proportion of W to WC was varied in the charge stage, the W_2C/WC ratio in the melted product would vary and the effect may be reflected in the microhardness. With such an objective in view, pellets were prepared by compacting mixtures of W and WC powders prepared at different W to WC ratios. W powder with particle size varying in the range 37–74 μm obtained from M/s. ROC/RIC, California, USA and WC powder with particle size in the range 1–15 μm purchased from M/s. Sandvik Asia, Pune, India were used for making the pellets. The ratio of W to WC was varied over seven different values to attain a carbon atomic% variation between 30 to 50. A 2% poly vinyl alcohol was used as binder. Pellets of 2.5 cm diameter and 1.5–2 cm thickness were prepared by uniaxial compaction of 500–800 MPa load. They were then dried to maintain 2–3% moisture and density of the green pellets varied between 8.05 to 8.97.

TABLE I Relative variation of W, WC and C percentage in the charge pellets vis-à-vis arc plasma melted and cooled products

Batch number of sample	wt% in charge			at.% of C in charge	Total wt% of C in product (expt. detnd.)
	W	WC	C		
30/01	55.50	44.50	2.72	30	3.15
33/01	48.30	51.70	3.17	33.40	3.52
38/01	37.20	62.80	3.85	38	4.60
40/01	32	68	4.16	40	4.54
45/01	16	84	5.15	45.40	5.23
48/01	5	95	5.82	48.64	5.88
50/01	0	100	6.13	50	6.84

TABLE II Relative variation of W, WC and C percentage in the charge pellets vis-à-vis WC powder backed pellets being arc plasma melted and cooled

Batch number of sample	wt% in charge			at.% of C in charge	Total wt% of C in product (expt. detnd.)
	W	WC	C		
33/01	48.30	51.70	3.17	33.40	3.12
38/01	37.20	62.80	3.85	38.00	3.75
45/01	16	84.00	5.15	45.40	4.98

Plasma melting was carried out in a 100 kW dc extended arc plasma furnace at 0.1–0.5 kg scale of charge. The details of the furnace have been reported in our earlier works [3, 6, 7]. It is a dc extended arc plasma furnace with graphite cathode and melting was carried out in a graphite crucible operating in the transferred arc mode. The pelletized charge was introduced into the graphite crucible and arcing was done between the vertical cathode and the charge to which positive polarity of electricity from power supply was transferred through the base of the crucible. Argon was used as plasma generating gas and passed at a rate of 1.5–2 litres per minute. It also prevented oxidation during melting and cooling. The following arc conditions were maintained during melting: voltage 40–120 V, current 300–600 A, arc length 5–7 cm. Two types of melting were done: in the first type, pellets were directly kept on the base of graphite crucible and melted by transferred arcing method while in the second type an insulating backing layer of WC powder (15–20 mm thick) was given at the base of graphite crucible to melt the pellets in the same transferred arc mode as above. The backing layer prevented heat transfer to the base as well as to the sides of the crucible, thereby increasing the size of melt pool by partly melting the backing WC powder and thus the final ingot size was increased. It took 5–15 min to completely melt the charge depending on the masses of the pellets. The temperature of the melt was monitored by a Raytek IR spectrometer (model: RAYR 3i 1 MSC) operating at 1 μm spectral range. The melt temperature was found to be recorded between 2800–3000°C. After melting was completed, the arc was switched off and argon flow at 0.5 lit/min was continued in the furnace to prevent oxidation of tungsten carbide. The melt was allowed to cool in the furnace for 2–3 hrs under the above argon flow. The solidified product (ingot) was then taken out for characterization.

XRD pattern of the plasma melted tungsten carbide was recorded for powder samples (prepared by crushing by impact hammer) by a Philips APD/1710 diffractometer. The indentification was done by Hanawalt's search-match method. Quantitative estimation of WC and W_2C phase was done by measuring area under respective peaks. Total carbon contents in the samples were determined by Strohlein apparatus. Surface morphologies of the polished products were observed under a Leitz optical microscope and a Jeol 35CF SEM. Vicker's microhardness was determined by using a Leitz Wetzlar hardness tester.

3. Results

Table I summarises the relative variations of W, WC and C percentage in the charge vis-à-vis arc plasma melted product for seven different compositions. While C wt%(total) in charge stage is seen to vary between

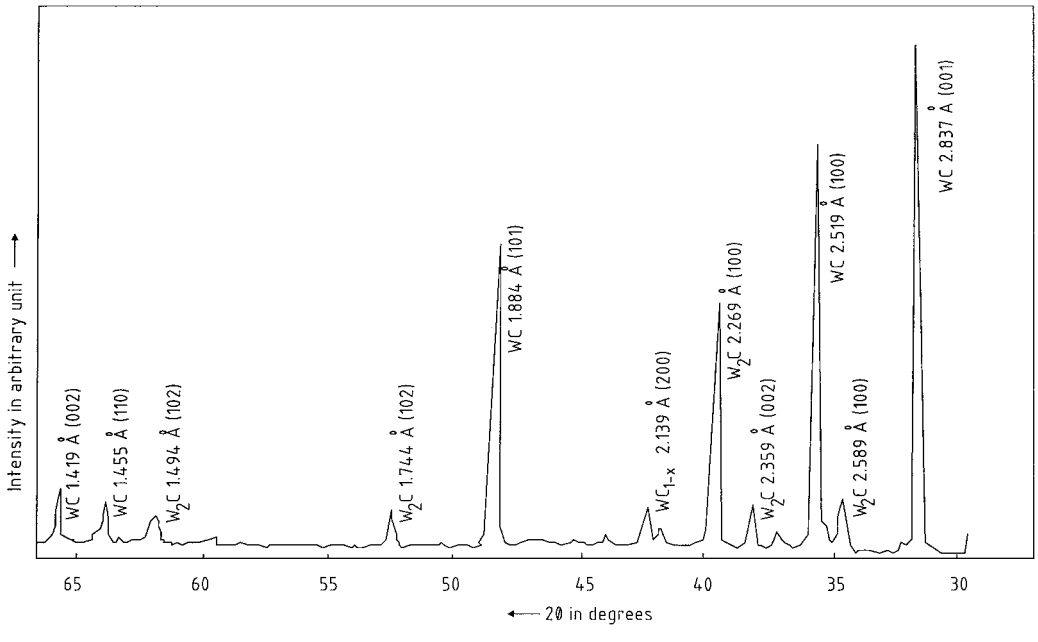


Figure 1 Typical XRD pattern of fused tungsten carbide.

2.72 and 6.13%, in the final product it is found to vary in between 3.15 and 6.84% due to carbon pick up from furnace sources such as graphite crucible and electrode. Table II shows similar relative variations for three different compositions where charge pellets were provided with WC powder backing and then arc plasma melted. Each composition (batch) of Tables I and II was analysed by XRD to identify the phases grown in the samples. WC and W_2C are the two major phases that are observed to grow at different ratios. WC/W_2C ratio is found to show a variation between 0.51 and 3.76. Fig. 1 shows a typical XRD pattern of an arc plasma melted and cooled sample (Table I, batch 50/01). Besides the major peaks due to WC and W_2C, a small peak around 2θ 42.5° appears in the XRD which is identified as due to WC_{1-x}.

Figs 2 and 3 depict the microhardness variation vs. C wt%(total) and WC/W_2C ratio for direct arc plasma melted, and WC powder backed and arc plasma melted samples respectively. Similar cooling in furnace was done in both the cases. From the above figures it is marked that high total carbon content alone does not ensure high hardness of grain. High microhardness results when WC/W_2C ratio becomes high and the highest value 3184 ($VHN_{0.1}$) is attained at 3.76 WC/W_2C ratio (Fig. 2). Similar trend with 3210 $VHN_{0.1}$ as highest microhardness value is observed in Fig. 3 for WC powder backed and arc plasma melted samples.

Microstructures of typical sample studied under optical microscope and SEM are shown in Fig. 4. A mixed morphology of two phase granular (Fig. 4a) and lamellar/acicular (Fig. 4b) (typical characteristic of hard martensite structure), is seen to grow. Triangular morphology is observed when the grains are further examined in the two phase granular region under SEM (Fig. 4c).

Electrical power consumption in the arc plasma melting process was recorded to vary in the range

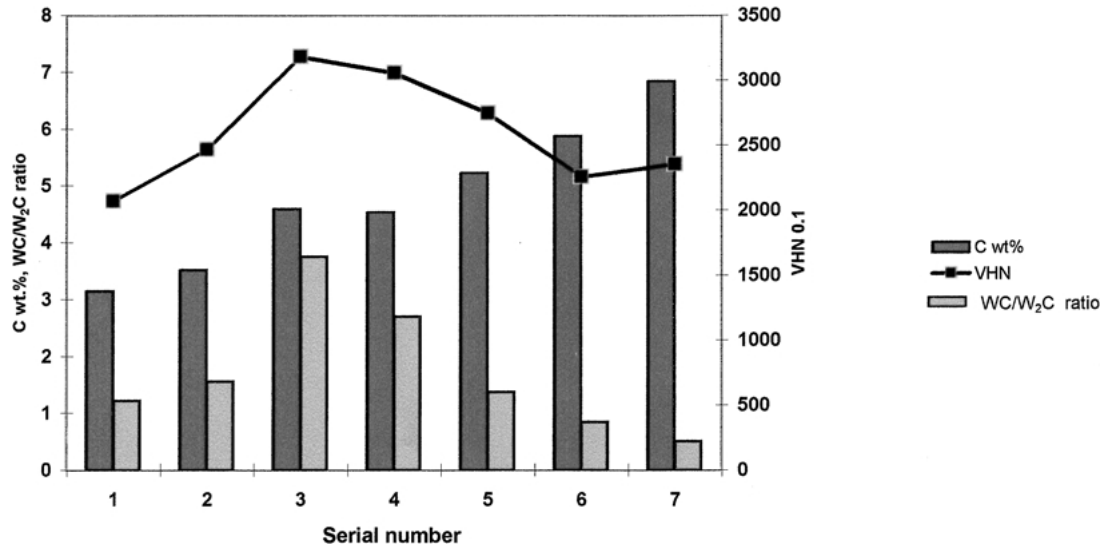


Figure 2 Microhardness variation in the samples produced by arc plasma melting of pellets and followed by cooling in furnace.

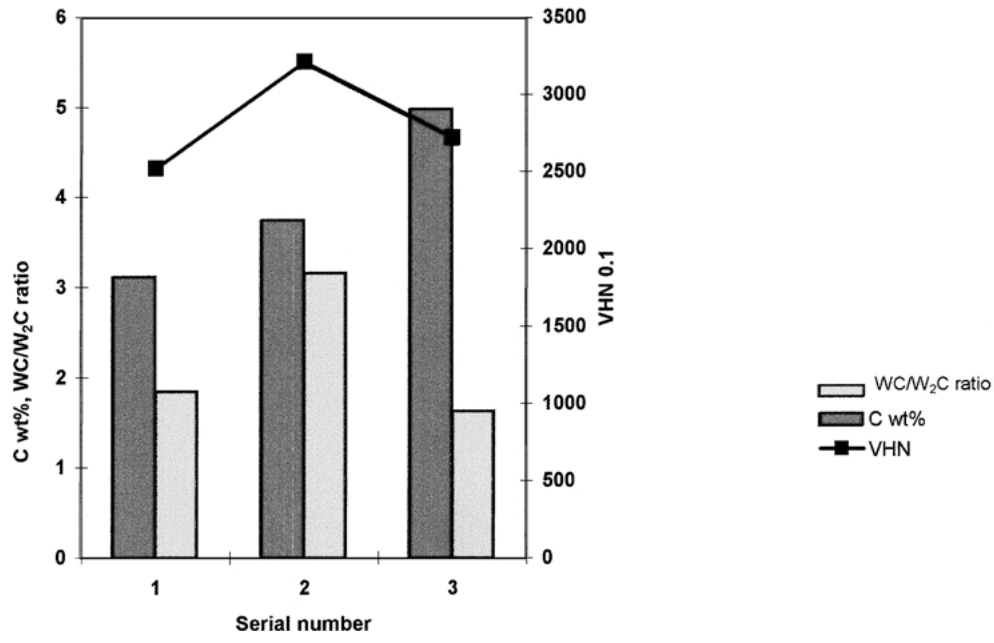
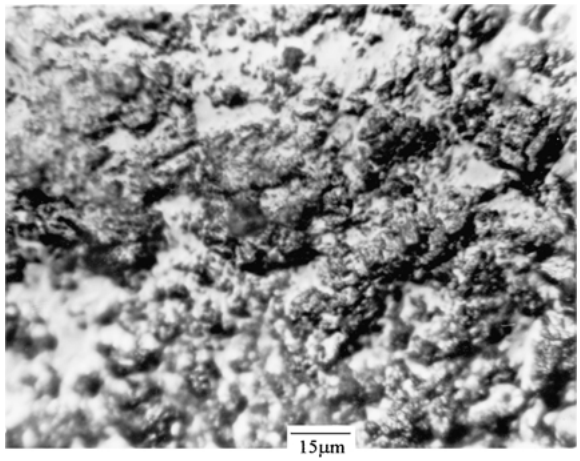
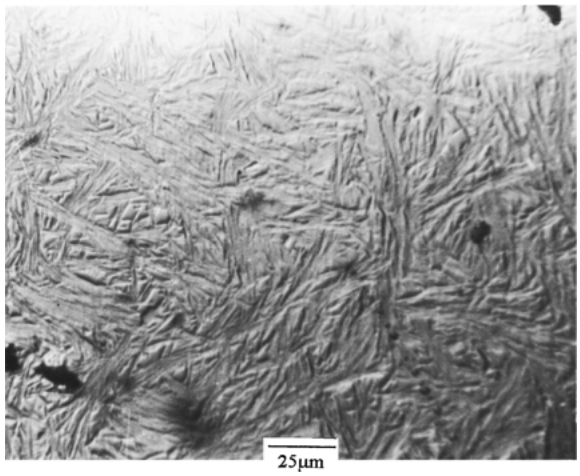


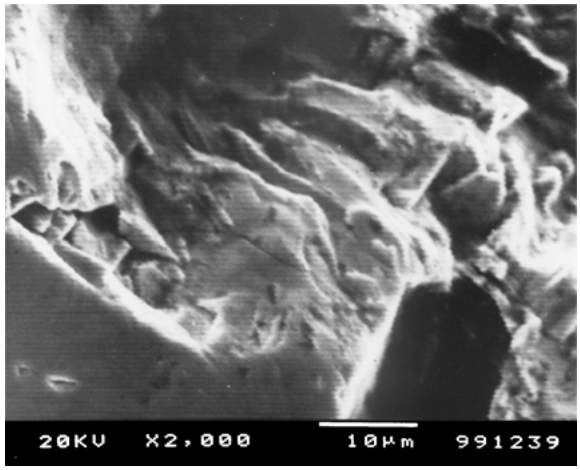
Figure 3 Microhardness variation in the samples produced by arc plasma melting of WC powder backed pellets and followed by cooling in furnace.



(a)



(b)



(c)

Figure 4 (a) Optical micrograph of FTC showing two phase granular structure; WC/W_2C ratio 3.76, total carbon 4.6%, (b) optical micrograph of FTC showing lamellar and acicular structure; WC/W_2C and C values are same as in the above Fig. (a), and (c) SEM micro structure of FTC grains of Fig. (a).

3–4 kWh/kg and the product yield was found more than 95%.

4. Discussion

Tungsten carbide is a commercially important abrasive material and has been in wide use for over last fifty years in metal cutting tool, grinding, and hard facing welding electrode applications. In industrial practice it is well known that when WC is melted and cooled or cast, W_2C phase grows as a minor phase along with WC and the resulting composite exhibits higher hardness than WC [1]. The composite is commercially known as fused or cast tungsten carbide and is mostly used in making drill bits for oil well digging, cutting rocks and RCC (reinforced concrete cement) structures. Our XRD result (Fig. 1) shows that the arc plasma melting has produced a composite of WC, W_2C and WC_{1-x} phases whose microhardness is found higher than constituent phases (Figs 2 and 3). Since intensity and area under the peak of WC_{1-x} is small, the presence of WC_{1-x} may not contribute significantly and hence the composite may be taken as fused tungsten carbide (FTC) consisting of WC and W_2C. Owing to commercial nature of interest involved in this area, most of the literature maintain secrecy about the details of FTC. It is therefore no surprise that only a few published works are now available on FTC. In such a background, the author has made an effort to understand the reason behind the occurrence of high micro hardness in FTC from a structural point of view.

FTC is reported to show hardness in the range 2250–3000 Kgf/mm^2 [8] whereas this value lies in the range 1200–2500 for WC [9] and is around 1450 for isolated W_2C [8]. The wide variation in the hardness values of WC could be due to random orientation of different grains in polycrystalline powder samples. One may wonder how the WC-W_2C composite exhibits higher/increased hardness than that of the constituent phases. To probe the reason behind this anomaly, following Orban [4, 5], we have systematically varied the C and WC contents (wt%) in the sample pellets by addition of W powder in green stage and melted the green and dried pellets in argon arc plasma, and the melt was cooled in furnace by switching off power under continuous argon flow. The melting was done by two different methods as described in Section 2 and highlighted in Tables I and II. Microhardnesses of the samples thus produced have been determined for different compositions and are plotted against C wt% and WC/W_2C ratio in Figs 2 and 3. While Orban considered W_2C/WC ratio and C% to be the two major factors to influence mechanical properties of FTC, we have found that WC/W_2C ratio but not the total C% is the parameter that influence microhardness of FTC. Figs 2 and 3 show the variation of microhardness for different samples at different WC/W_2C ratio and total C%. It is evident from the figures that high total carbon content does not ensure high microhardness due to presence of free carbon (seen to segregate in Fig. 4b). It is rather bound carbon in the form of WC/W_2C ratio which is the deciding factor to yield high microhardness. High values of microhardness above 3000 $VHN_{0.1}$ are seen to result in samples with relatively low carbon values but with high WC/W_2C ratio.

The microstructure of the samples having microhardness >3000 $VHN_{0.1}$ was studied under optical microscope. A mixed morphology consisting of two types of structures, viz., granular and lamellar/acicular, as shown in Fig. 4a and b respectively, is observed for

typical sample exhibiting microhardness 3184 $VHN_{0.1}$. The granular two phase structure grows due to co-existence of WC and W_2C. The lamellar/acicular morphology develops in carbon rich area when martensite structure grows by diffusionless transformation. Since, in the arc plasma process, cooling rate is high due to low thermal mass of the furnace and continuous flow of argon gas, it is quite feasible to produce martensite transformation. Similar morphology due to martensite structure has been reported by Grunenwalt and co-workers [10] in case of laser surface alloying of manganese steel (16 Mn Cr 55) with WC. The surface microstructure of our FTC grains seen under SEM (Fig. 4c) in the two phase granular region looks like the characteristic triangular structure of {0001} or (001) face of WC observed by Luyckx and Katzourakis [11]. It is known that the hardness of {0001}/(001) face of WC is up to two times higher than that of other faces [12]. XRD of our FTC (Fig. 1) corroborates the SEM finding. The (001) reflection of WC is seen to occur as the most dominant peak along with a small peak due to its equivalent plane (002). Taking into account the above findings, one may conclude that FTC grown by the arc plasma melting process develops a good number of ⟨001⟩ WC grains along with many lamellar/acicular crystals due to martensite transformation taking place by the fast rate cooling in arc plasma furnace. The high hardness of the ⟨001⟩ faces and the lamellar/acicular crystals jointly contribute towards significant enhancement in the microhardness of the WC-W_2C composite up to as high as 3210 $VHN_{0.1}$ (Fig. 3). It may be mentioned here that structural variation primarily results from differential cooling rate appearing from the surface and the core of the solid ingot undergoing transformation. Since core cools relatively slower than the surface, formation of granular structure is marked in the core zone of the ingot.

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