

Metallurgical and mechanical characteristics of cryogenically treated tungsten carbide (WC–Co)

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Abstract This paper aims to present the metallurgical and mechanical characterization of cryogenically treated tungsten carbide (WC–Co) in terms of α -, β -, γ -, and η -phase particles and wear behavior, respectively. The specimens of commercially available uncoated WC–Co in the form of round turning inserts were procured and subjected to cryogenic treatment at two levels -110°C (shallow treatment) and -196°C (deep treatment) of temperature. The microstructures obtained after cryogenic treatments have been characterized with a prominence to comprehend the influence of cryogenic treatment on the nature, size, and distribution of α -, β -, γ -, and η -phase particles as compared to untreated specimen. The mechanical properties such as hardness and wear rate of the specimens have also been compared by performing Rockwell A hardness test and pin-on-disk wear test, respectively. Microstructures, hardness, wear rate, and analysis of worn surface divulge the underlying metallurgical mechanism responsible in improving mechanical properties of the WC–Co.

Keywords Tungsten carbide · Shallow cryogenic treatment · Deep cryogenic treatment · Turning insert · Rockwell A hardness test · Pin-on-disk wear test

1 Introduction

The life of tungsten carbide (WC–Co) inserts plays a major role in increasing productivity and consequently is an important economic factor. The original cost of inserts may be less, but to turn them means to interrupt the machining process which costs time and therefore money. The lifetime of a cutting insert is consequently an important economic factor, creating huge competition among cutting tool producers. The inserts have to withstand high temperature and stress during turning; they have to be shock-resistant during milling, corrosion-resistant, and chemically inert toward the workpiece material. Moreover, the metal working industry not only demands a long insert life but also is trying to push the working limits of the inserts still further, as higher and higher cutting speeds are required possibly even without lubrication and cooling liquids, which produces even more severe cutting conditions. From the material science point of view, the insert material must have combined properties typical for ceramics such as high hardness, temperature resistance, and chemical stability with typical metal properties as for example high toughness and good thermal conductivity. Tungsten carbides (WC–Co), which are composite materials with a dominant hard ceramic phase bonded by a soft metal binder, fulfill these requirements. Different machining applications demand different insert properties. A great variety of cutting insert materials were therefore developed during the last few decades, mostly by empirically changing the composition or microstructure. With these new possibilities and because

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of the strong competition, the cutting tool industry is highly interested in fundamental research to gain a better understanding of the mechanisms leading to the damage of the cutting edge and to find ways to prolong the lifetime of the tools. A big step in that direction is cryogenic treatment of WC–Co cutting inserts which has the capability to alter the morphology of WC–Co material in constructive manner.

Cryogenic treatment has been claimed to improve wear resistance of several steels and has also been implemented recently in WC–Co cutting inserts. Cryogenic treatment is the process of submitting a material to subzero temperatures (below 0°C) in order to enhance the service life through morphological changes that occurs during treatment. In recent years, many reports published which claim significant improvements in cutting life of WC–Co cutting inserts. However, scientific research on effects of cryogenic treatment on metallurgy and mechanical properties of WC–Co material has been spotty, and only a few academic papers have been published. It has been claimed by some researchers that cryogenic treatment enhances wear resistance of WC–Co inserts by virtue of changing the metallurgy.

Cryogenic treatment, the discipline upon which the present study is based, can be considered a recent development [1–7]. Sreerama Reddy et al. [8] observed the improvement in life of normal and deep cryogenically treated tungsten carbide inserts by an amount of 9.58% and 21.8%, respectively. They studied the improvement in tool life of cryogenically treated P-30 tungsten carbide inserts and concluded that precipitation and distributions of the η phase after cryogenic treatment have improved the flank wear resistance. Also, they observed slight increase in grain size which increases the toughness. In another study, Yong et al. [9] cryogenically treated tungsten carbide milling inserts and found 28.9% to 38.6% increase in tool life. They confirmed that, in contrary to steels, there is no martensite phase in tungsten carbide, as such; any improvement in tool life or wear resistance would be due to other mechanisms. Furthermore, Yong et al. [10] showed that cryogenic treatment no doubt improves the resistance to chipping of tools and, to a less significant extent, improves flank wear resistance. They stated that tools under mild cutting conditions stand to gain from cryogenic treatment, but heavy duty cutting operations with long periods of heating of the cutting tool will not benefit from it. Seah et al. [11] implemented the cryogenic treatment on cobalt-bonded tungsten carbide (Co–WC) inserts and found that the treated inserts were superior to those of the untreated as received inserts at high cutting speeds. From this study, they concluded that cryogenic treatment of tungsten carbide inserts increased the number of η -phase particles, a theory which they supported with photographs taken using a scanning electron microscope (SEM). They assigned this as

a reason for reducing transverse rupture strength hence greater resistance to chipping, improved resistance to plastic deformation during cutting, and lower toughness. After experimental evaluation of comparative performance of cryogenically treated TiCN-coated carbide inserts and Kennametal Grade KC 990 inserts by gas infusion process (dry process), Bonilla et al. [12] also succeeded in enhancing the tool life. Work by Quek [13] also agreed with the findings of these authors. Kao [14] also reported increase in abrasion wear resistance of sintered tungsten carbides inserts after cryogenic treatment. Bryson [15] attributed the wear resistance, and hence the increase in tool life, of carbide tools to the improvement in the holding strength of the binder after cryogenic treatment. He believes that cryogenic treatment also acts to relieve the stresses introduced during the sintering process by which carbide tools are produced. However, Bryson [15] also warned that under certain conditions, cryogenic treatment would have little or no effect on carbide tools, such as when reprocessed carbides are used. Stewart [16] applied cryogenic treatment to C2 tungsten carbide (WC–6% Co) inserts and compared with untreated carbide inserts to determine if tool wear could be reduced during turning tests with medium density fiberboard (MDF). Both the tool force data and observation of the cutting edges indicate that tool wear was reduced. He postulated that the cryogenic treatment appeared to have an effect upon the cobalt binder by changing phase or crystal structure so that more cobalt binder was retained during cutting. Gallagher et al. [17] analyzed the microstructural alterations of α (tungsten carbide), β (cobalt binder), γ (carbide of cubic lattice), and η (multiple carbides of tungsten and at least one metal of the binder) phases within the tungsten carbide (WC) inserts caused by the cryogenic treatment, and linked these changes to the corresponding enhanced tool life. In the recent study, Gill et al. [18] did comparative investigation of the wear behavior of cryogenically treated tungsten carbide inserts in dry and wet orthogonal turning conditions to excavate the affect of coolants on the performance of cryogenically treated tungsten carbide inserts. The authors claimed that the use of coolant coupled with cryogenic treatment of tungsten carbide inserts further improved the tool life. They also concluded that considerable increase in life of cryogenically treated tools can be attained for interrupted machining mode as compared with continuous machining mode. In another study, Gill et al. [19] recorded a substantial decrease in tool life of TiAlN-coated tungsten carbide deep cryogenically treated inserts as compared to untreated inserts indicating the destructive effect of deep cryogenic temperature (–196°C) on TiAlN-coated inserts which they further supported by VDI-3198 indentation test.

The review of the literature reveals the potential of use of cryogenic treatment in improving the performance of

WC–Co insert material from cutting tool point of view. But the available results in the literature pertaining to wear behavior of WC–Co insert material subjected to cryogenic treatment are not coherent, and the underlying postulated mechanisms for achieving improved tool life is not well crystallized [20]. The advantage of cryogenic treatment can only be suitably exploited if the underlying mechanism is carefully unfolded in a planned compartment. The present study therefore aims to examine the effects of cryogenic treatment on WC–Co insert material with respect to the nature, size, and distribution of α -, β -, γ -, and η -phase particles in the microstructure. The consequential mechanical properties viz. hardness and wear rate were also investigated.

2 Materials and methods

2.1 Material used

Tungsten carbide (WC–Co) material in the form of commercially available round-shaped ISO-P25 (RNMG 19-06-00-SR)-uncoated turning inserts was chosen for current study. The chemical composition of specimens is presented in Fig. 1.

2.2 Cryogenic treatment

All the WC–Co specimen inserts were classified in three different groups as untreated (UT), shallow cryogenically treated (SCT), and deep cryogenically treated (DCT). Each group contained three specimens. The group of specimens meant for SCT was subjected to cooling at -110°C and held at this temperature for 18 h and gradually brought back to room temperature. Similarly,

the group of specimens meant for DCT was subjected to cooling at -196°C and held for 38 h and gradually brought back to room temperature. The specimens were cryogenically treated (SCT and DCT) under direct cooling conditions where the tools being treated were exposed to a spray header system with atomizing nozzles that convert the liquid nitrogen into very cold gas thereby cooling the specimens. Uttermost care was taken to ensure that only the cold gas and not the fine droplets of liquid nitrogen could come in contact with the specimen's surface. The inbuilt controller ensured the monitoring of temperature in cold box by implementing a proper nitrogen flow. Figure 2a shows cryogenic treatment instrument schematically. Also, in order to avoid thermal shocks from rapid cooling and heating, the specimens were cooled down and heated up slowly, to and from the shallow cryogenic temperature (-110°C) and deep cryogenic temperature (-196°C), over an 4- and 7-h period, respectively, with the temperature being monitored by computerized control. This gave an average heating/cooling rate of $0.5^{\circ}\text{C}/\text{min}$. After this, two tempering cycles consisting of heating to 150°C were followed to relieve the stresses induced during cryogenic (SCT and DCT) treatment. All the specimens were cryogenically treated in cryogenic processor with tempering facility (Primero Enserve, India). Figure 2b shows the cryogenic treatment cycle used to treat the specimens.

2.3 Microstructural analysis

The microstructure of specimens were examined using both optical (Nikon: EPIPHOT 200, Japan) and scanning electron microscope (SEM, Quanta: F-200 FEI, Holland). Metallographic sample preparation was carried out in accordance with ASTM B665-03 standard, and micro-

Fig. 1 EDX spectra showing chemical composition of WC–Co material

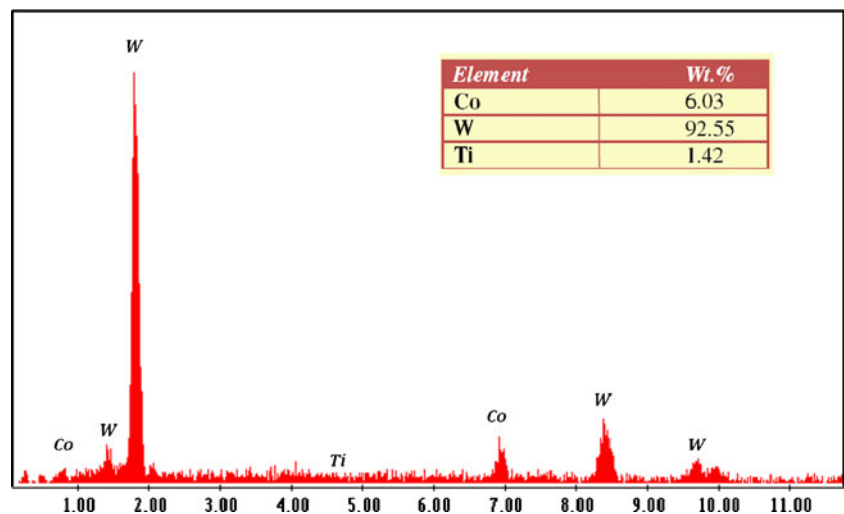
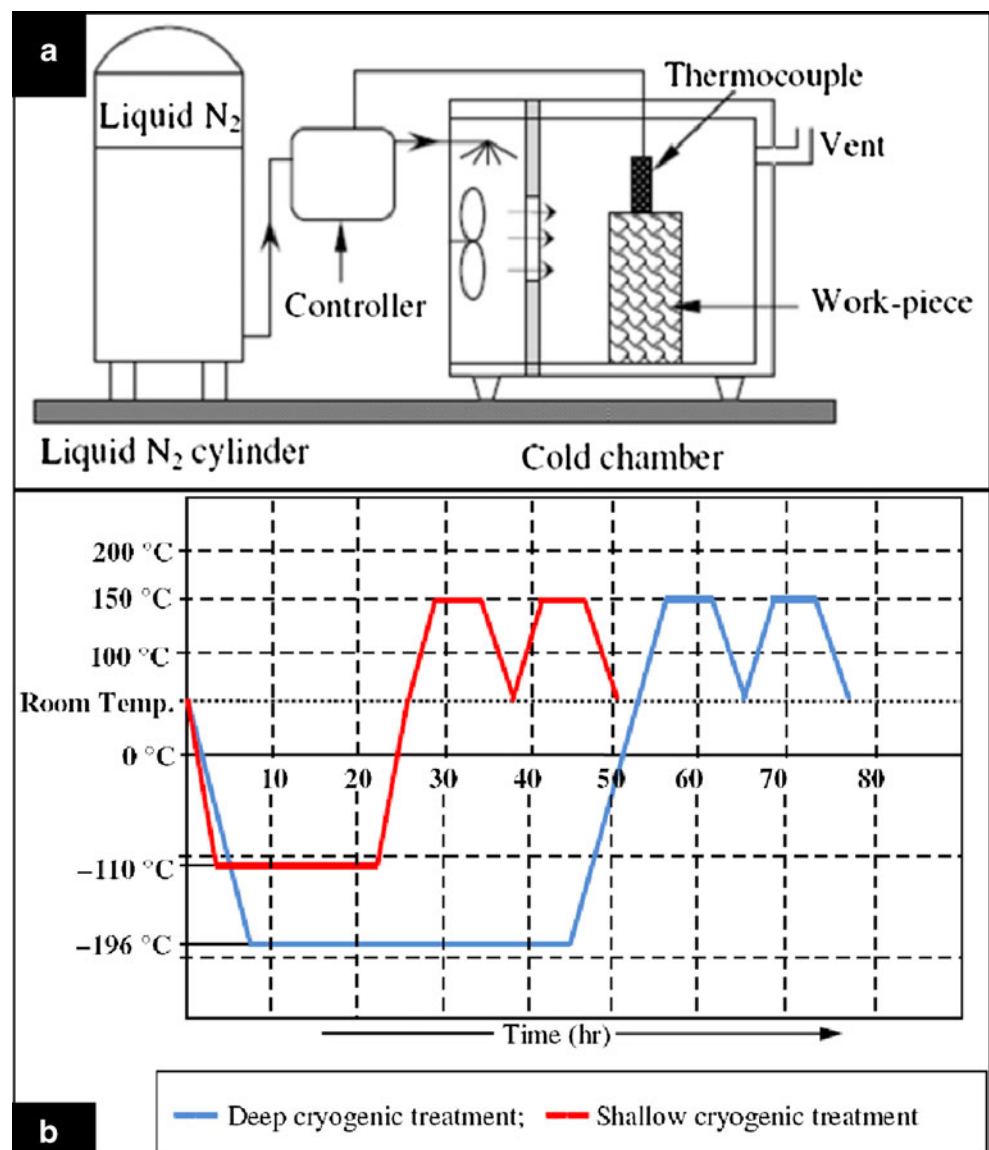


Fig. 2 **a** Schematic configuration of cryogenic treatment system. **b** Cryogenic treatment cycle used to treat the WC–Co specimens



structural evaluations were made in accordance with ASTM B657-92 standard. For the sample preparation, each specimen was grounded and polished by hand with different grades of diamond paste (15, 9, 3, and 0.25 μm) until a mirror finish was attained. Etching was then carried out in order to identify the various phases present in tungsten carbide. The etching techniques used is described in Table 1.

2.4 Hardness test

The specimens produced for microstructural analysis as discussed in Section 2.3 above were also used for hardness measurements. Digital Rockwell hardness tester interfaced with computer system was used to obtain the hardness values in accordance of ASTM B294-10 standard. A minor load of 98.07 N was first applied to seat the specimen. The

major load of 588.4 N was then applied for HRA scale for duration of 30 s. The hardness was measured at five different points evenly distributed on each specimen so as to get the average values of hardness.

2.5 Wear test

Sliding wear tests were performed using a pin-on-disk wear testing machine (DUCOM: TR 20, India) at ambient temperature under dry friction conditions. The contact conditions were generated by pressing the specimen in the form of a round turning insert to the narrow flat face of the rotating disk as shown in Fig. 3. Thus, the line type of the contact was always established at the beginning of each wear test performed.

The round faces of the specimens were cleaned in acetone prior to wear tests. These specimens were used as

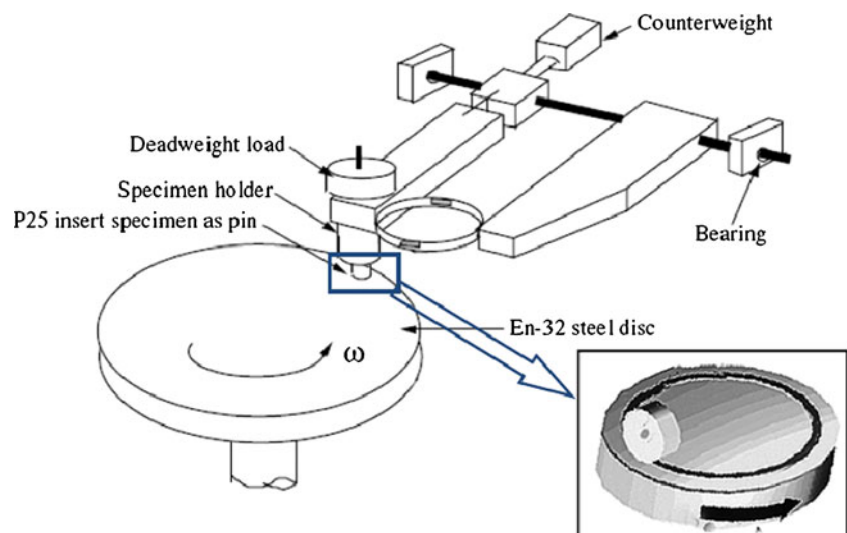
Table 1 Etching techniques to identify various phases in tungsten carbide (WC–Co)

Etching technique	Composition of etchants	Etching conditions	Identified phase
1	Mixture I: Freshly prepared mixture of equal quantities of 10% (mass/mass) aqueous solutions of $K_3Fe(CN)_6$ (III) (potassium ferricyanide) and potassium or sodium hydroxide.	Etch in mixture I at approximately 20°C for 2 to 10 s. Flush the test-piece section with water immediately, without removing the oxide layer. Dry the surface carefully with acetone or alcohol without wiping.	η
2	Mixture I: Same as in etching technique 1. Mixture II: A mixture of equal volumes of concentrated hydrochloric acid and water.	Etch at approximately 20°C in mixture I for 3 to 4 min. Then wash in water and etch in mixture II for approximately 10 s. Wash in water, then in alcohol and dry the test-piece section. Finally, etch in mixture I for approximately 20 s.	γ
3	Mixture I: Same as in Etching technique 1.	Etch in mixture I at approximately 20°C for 3 to 6 min.	α and β

static pins against En-32 steel disk ($\phi 100 \times 8$ mm thick) as rotating counterface as illustrated in Fig. 3. These tests were carried out at loads of 49, 68.6, and 88.2 N in dry condition at sliding speed of 1.5 m/s at the room temperature. Each specimen was tested for sliding distance of about 1,800 m. The wear rate of each pin (insert) was calculated from the weight loss, and each test was repeated three times for each condition to get the mean values of weight loss. The amount of wear is determined by weighing the specimen before and after the tests using a precision electronic weighing balance (Shinko Denshi: DJ-150SS, Japan) with an accuracy of 0.001 g. Wear rates (W_r) were calculated using the following equation:

$$W_r = \Delta m / (\rho L F) \times 10^3$$

In this equation, W_r is the wear rate in mm^3/Nm ; Δm , the weight loss in g; ρ , the density in g/cm^3 ; L , the wear distance in meter; and F , the normal load in Newton. A comparison has been made to identify the effects of each treatment (SCT and DCT) on wear improvement.

Fig. 3 Schematic of pin-on-disk wear test equipment

2.6 Wear mechanism

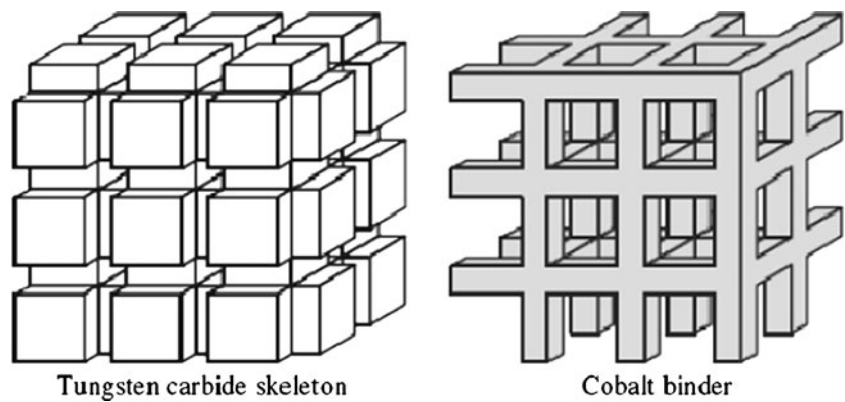
After wear tests, the worn-out surfaces of WC–Co specimen inserts were cleaned by acetone. The worn surfaces of specimens were then examined under optical and scanning electron microscope to evaluate the governing wear mechanism.

3 Results and discussion

3.1 Microstructure

Typical microstructure of WC–Co material contains the tungsten carbide (WC) hard phase which forms a continuous structure throughout the bulk of material, called the ceramic skeleton. Also the soft cobalt binder phase (Co) forms a continuous network structure. A schematic representation of the two major interconnected phases is shown in Fig. 4 and different phases in WC–Co material are summarized in Table 2.

Fig. 4 Tungsten carbide (WC–Co) is formed of hard tungsten carbide ceramic phase bonded by soft cobalt metal binder resulting in continuous interpenetrated skeletons



Several changes in the microstructure of the WC–Co material appear to be the contributing factor in improvement of durability as a result of cryogenic treatment. Gill et al. [20] summarize the changes occurred as: hard phase particles of tungsten carbide are refined into their most stable form via the phenomenon of spheroidization. It also aligns the hard phase carbide particulate structure into a durable, stress-free crystallographic configuration. This reduces the risk of stress-induced fractures. The fine eta (η) carbide particles precipitate during the cryogenic treatment. These are in addition to the larger carbide particles present before cryogenic treatment. These fine particles act as fillers along with the larger particles to form a denser, more coherent, and much tougher matrix in the material. Also, residual stresses in the material resulted due to sintering of tungsten carbide are relieved during cryogenic treatment. These microstresses are the leading cause of early carbide fracture. The stresses of manufacture, and bonding to the substrate are relieved throughout the material, permanently. Although the suggested reasons seem to justify the after effects of cryogenic treatment of WC–Co material, no advancement in scientific understanding of the mechanism involved has been reported even in recently published literature. Hence, in this section, an attempt has been made to dig out the mechanism responsible for abovementioned changes in metallurgy of WC–Co material.

Table 2 Phases in WC–Co

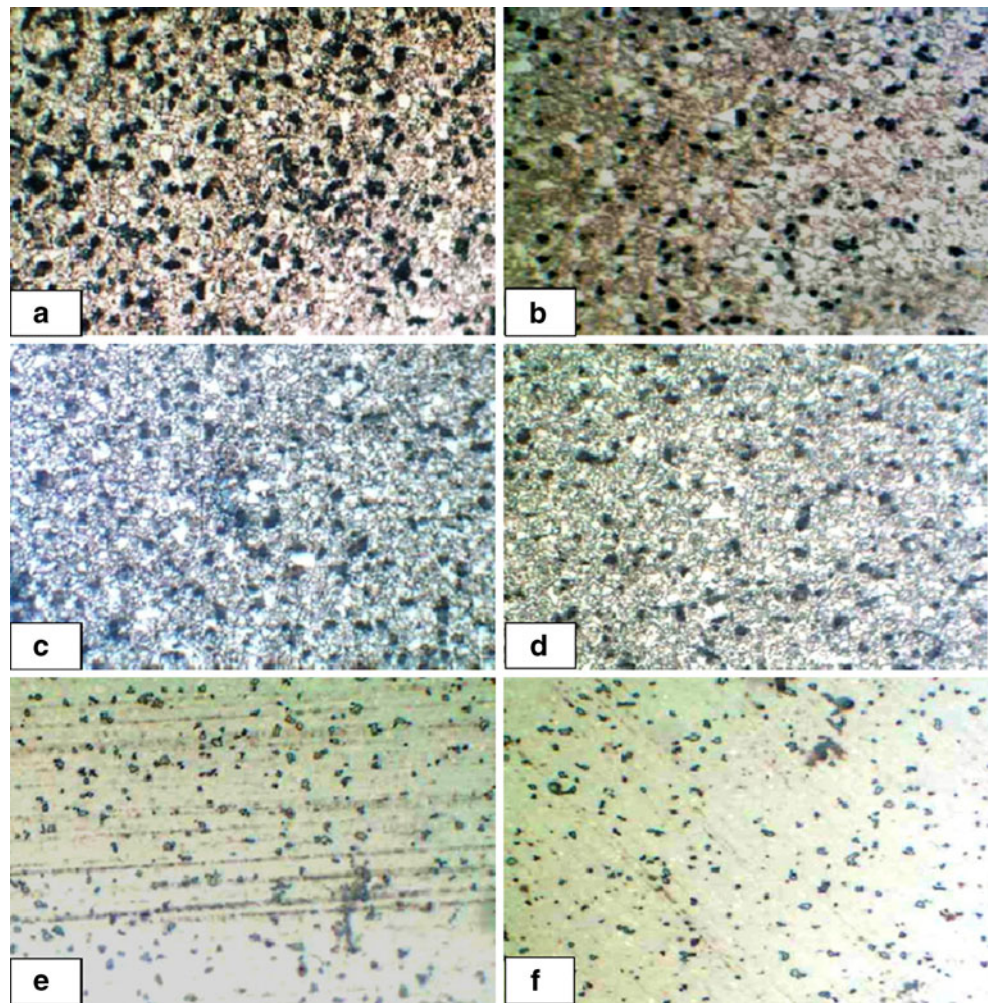
Phase	Definition of phase
α	Tungsten carbide (WC)
β	Cobalt metal binder (Co)
γ	Carbide of a cubic lattice (TiC, TaC, NbC) that may contain other carbides (e.g., WC) in solid solution
η	Multiple carbides of tungsten and at least one metal of the binder

The optical images (Fig. 5) were taken from the flat face of the UT and DCT WC–Co inserts to evaluate the metallurgical changes occurred during cryogenic treatment. According to the ASTM B657-92 standard, the γ phase, when etched, appears light yellowish-brown and has rounded shape particles which are evident from Fig. 5a, b for UT and DCT WC–Co specimen, respectively. From the optical photographs, it is apparent that there is a decrease in the γ phase after deep cryogenic treatment. In the optical image, the α phase, which is tungsten carbide, appears gray (Fig. 5c, d). The α phase makes up the bulk of the material as clear from Fig. 5c, d. However, the change in size and distribution of α -phase particles was not identifiable from the optical images. The β phase, which is the cobalt binder, appears as white specks (Fig. 5c, d). It can be very clearly seen that there is a significant decrease in the population and size of the β -phase particles after cryogenic treatment. Finally, the η phase, which contains multiple carbides of tungsten and binder, was identified as dark brownish specks in the optical photographs. There appears to be precipitation of fine particles in η phase after cryogenic treatment. However, it is thought that the different possible structures of η -phase particles may affect the mechanical properties differently.

Since the optical micrographs were not able to depict the size and distribution of the α -phase particles, higher magnification SEM images (Fig. 6) of the specimens were obtained. The α phase in treated WC–Co material (Fig. 6a) forms a continuous structure throughout the sample. Since the volume fractions of α phase are higher, α phase is present in the form of clusters of particles spread in entire bulk of material, which leads to mechanical properties dominated by this phase in treated WC–Co material. This is a very stable and absolutely stoichiometric phase. Whereas hard α -phase grain contiguity is relatively lower in case of untreated WC–Co material as evident from Fig. 6b.

The crystal structure of α phase (WC) is simple hexagonal with one tungsten and carbon atom per unit cell and an a/c ratio very close to unity (Fig. 7a). However, the

Fig. 5 Optical images of **a** untreated γ phase, **b** deep cryogenically treated γ phase, **c** untreated α and β phase, **d** deep cryogenically treated α and β phase, **e** untreated η phase, and **f** deep cryogenically treated η phase for WC–Co specimens at magnification of $\times 500$



stable shape of α -phase crystals is a triangular prism as shown in Fig. 7b [21, 22]. In untreated WC–Co material, the stable shape is not fully developed because of impingement with other particles as seen in Fig. 6b. Moreover, large particles of a more rectangular shape are found in the structure.

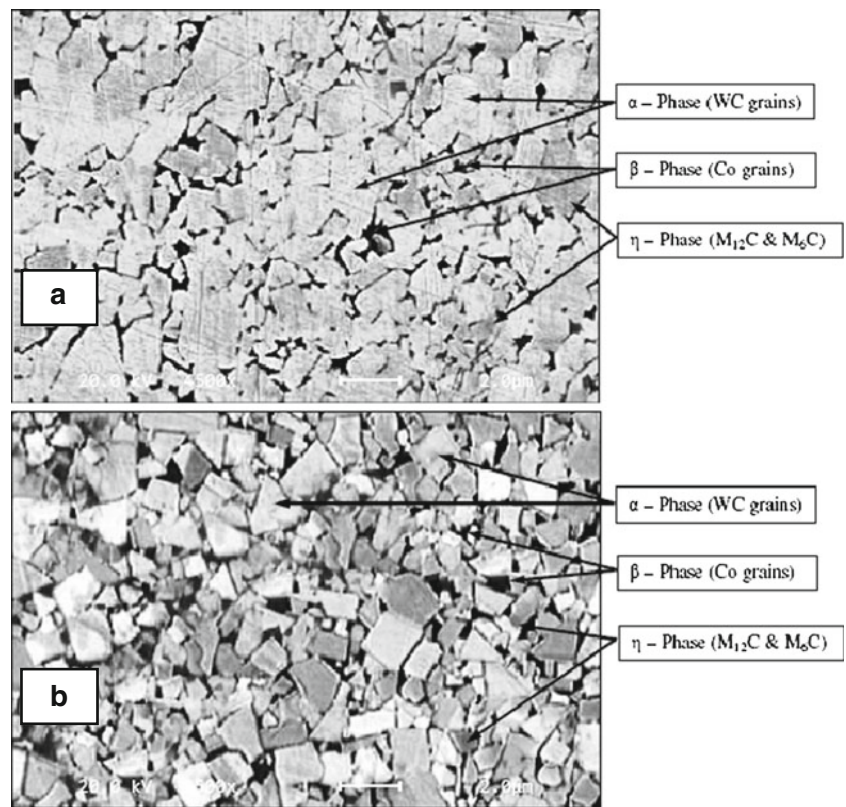
In contrary to untreated WC–Co material, it is thought that α -phase particles of tungsten carbide are refined into their most stable form via the phenomenon of spheroidization in cryogenically treated WC–Co material. The cryogenic temperature must have acted as catalyst for preferential growth of three of the six prismatic tungsten carbide $\{10\bar{1}0\}$ planes (Fig. 7b) which might have resulted in stable state of α -phase particles as triangular prism. It also crystallographically aligns α -phase carbide particulate structure into a durable, stress-free configuration which is apparent from the Fig. 6a. This reduces the risk of stress-induced fractures hence enhancing the wear resistance of WC–Co material.

Binder cobalt β -phase crystal is hexagonal at room temperature and undergoes a first order phase transition

from close packed hexagonal to face centered cubic at 416°C . Hence, in WC–Co material, cobalt β -phase crystals are generally present in its high-temperature face-centered cubic configuration after sintering process. It is thought that the face-centered cubic structure gets stabilized by the internal stresses resulted from the differential thermal contraction of α phase and binder β phase during sintering process [23]. The cryogenic treatment might have relieved the internal stresses [7, 19]. Hence, in the absence of internal stresses, binder β -phase crystals might have rearranged in their relatively stable close packed hexagonal shape thereby helping the α -phase crystals to align robust, stress-free crystallographic configuration as seen in Fig. 6a. It is important to note that the binder β phase is the transport medium for the hard α phase.

It is very vital to know the deformation behavior of α phase and cobalt binder β phase at elevated temperatures generally occurred during service life of WC–Co material. The separation of the deformation behavior of two phases into different temperature domains was proposed by S.

Fig. 6 Microstructure of **a** deep cryogenically treated and **b** untreated inserts

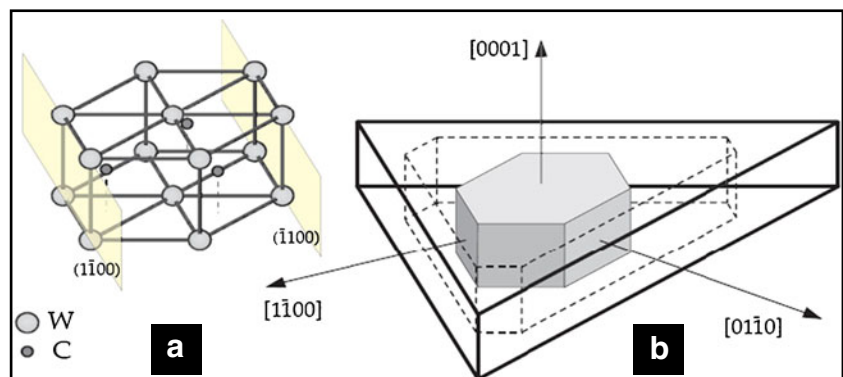


Bolognini [24]. In the first domain, up to temperatures 527° C, the α phase (WC) deforms elastically and shows brittle fracture. The second domain is characterized by the plastic deformation of the binder β phase. Even if dislocations have been observed in hard α phase, no considerable plastic deformation of α phase particles occurred. Third domain is characterized by extended creep at temperatures above 1,025°C and has been attributed to grain boundary sliding. Since in machining the temperature rarely rises up to 1,025°C during the service life of WC–Co material, this domain is not discussed in the present paper. The changeover temperatures of different domains furthermore depend on the cobalt binder β -phase content. By decreasing cobalt binder β -phase content, the transition between the different domains is shifted

toward higher temperatures thereby enabling the tungsten carbide to resist plastic deformation even at relatively higher temperatures. It is clear from the microstructure shown in Fig. 6 that cobalt binder β -phase content decreased significantly after cryogenic treatment thus enabling the WC–Co material to withstand relatively higher temperatures without failing by plastic deformation.

The η -phase carbides, which appeared after cryogenic treatment, can be identified as light gray areas (Fig. 6) and occupied the volume formerly occupied by cobalt binder β phase. It is obvious from Fig. 6 that the untreated WC–Co material contain little η -phase carbides. It is well established that two types of η -phase carbides can be obtained— $M_{12}C(Co_6W_6C)$ of substantially constant composition and

Fig. 7 a The hexagonal α -phase (WC) cell and **b** tungsten carbide grain shape resulting from preferential growth along prismatic planes [26]



M_6C in which the composition can vary within the range of $Co_{3.2}W_{2.8}C$ to Co_2W_4C . The M_6C type of the η -phase carbide is in equilibrium with the liquid phase and nucleates and grows during the sintering process. This not only makes the structure brittle by replacing the cobalt binder β -phase content with a brittle phase but also reduces the effective contribution of α phase to the strength of the composite. In order to identify any change of η -phase carbides, XRD analysis was done (Fig. 8). It is clear that the $M_{12}C$ (Co_6W_6C)-type carbide precipitated in the solid state during cryogenic treatment with small grains distributed throughout the matrix and therefore does not embrittle the structure as much as the former. These fine particles, along with the larger particles, form a denser, more coherent, and much tougher matrix in the material. The cryogenic treatment also reduces the chemical degradation of the cobalt binder β phase at higher temperatures. Lower binder β -phase contents in tungsten carbide material improved the overall thermal conductivity. An increase in α -phase particles size after cryogenic treatment of WC–Co material increases the thermal conductivity. This effect is attributed to an increase in hard α -phase grain contiguity and the dominant role of α -phase in thermal conduction in WC–Co material. The increase in thermal conductivity due to cryogenic treatment increases heat dissipation capacity of material. Thus, the cryogenic treatment results in increase in thermal conductivity of the WC–Co material.

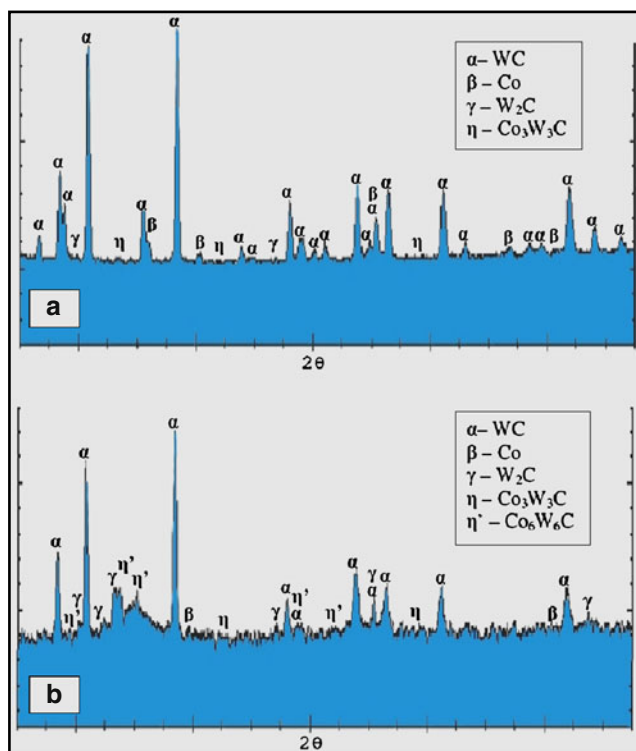


Fig. 8 XRD analysis of **a** nontreated and **b** deep cryogenically treated tungsten carbide

3.2 Hardness

The Rockwell A (HRA) hardness values were obtained for UT, SCT, and DCT WC–Co specimens at five equally spaced points. The purpose of taking hardness values at five different points was to obtain the mean hardness value so as to eliminate any possible error. The hardness values obtained are presented in Table 3. A plot of hardness as a function of type of heat treatment is shown in Fig. 9.

Shallow cryogenically treated WC–Co specimen has significantly higher hardness ($\approx 4.75\%$) compared with that for untreated specimen. Also, the improvement in hardness ($\approx 0.21\%$) for deep cryogenically treated specimen is trivial when compared with shallow cryogenically treated specimen. These findings are in line with the previous study by Kao [14] which also claimed increase in hardness after subjecting the tungsten carbide to cryogenic treatment. The application of shallow cryogenic treatment boosted the hardness of specimen by about 4HRA due to α -phase particles of tungsten carbide which got refined and aligned crystallographically into their most stable form via the phenomenon of spheroidization resulting in durable, stress-free configuration. The significant decrease in soft β -phase particles also contributes in enhancing the hardness. The fine η particles precipitated during cryogenic treatment act as fillers along with the larger particles to form a denser, more coherent, and much tougher matrix in the material. However, when the specimen was subjected to deep cryogenic treatment, no major improvement was recorded in hardness as compared to shallow cryogenically treated specimen. It is important to note that in many previous studies, it has been reported that deep cryogenically treated WC–Co material resists wear more effectively as compared to shallow cryogenically treated WC–Co material. Hence, it can be concluded that there may be two different processing temperature-dependent phenomena which govern the hardness and wear resistance properties independently. However, the identification of such phenomena is beyond the scope of the present study and can be taken up for further research. It is to be noted that hardness data do not always provide exact parameter to evaluate wear resistance of cryogenically treated WC–Co material. Also, it is inferred that cryogenic treatment causes morphological changes in the entire cross section of the WC–Co material. Evidently, cryogenic treatment is better to all type of coatings as the coatings become futile once it gets removed from the substrate.

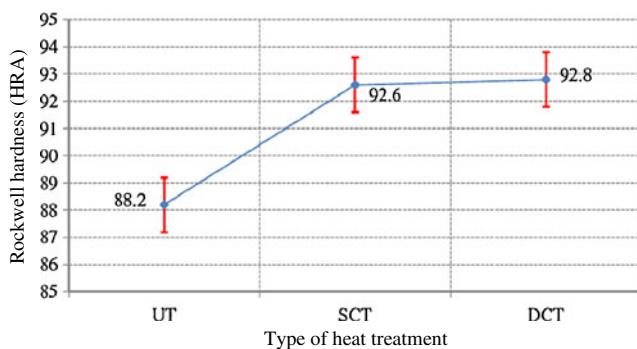
3.3 Sliding wear

Tribological characteristic of WC–Co material was evaluated by performing pin-on-disk sliding wear tests at three different loads using constant speed. The results obtained

Table 3 Hardness values for UT, SCT, and DCT WC–Co specimens

Type of heat treatment	Location of measurement	Hardness (HRA)	Mean hardness (HRA)
UT	Point 1	89	88.2
	Point 2	88	
	Point 3	88	
	Point 4	87	
	Point 5	89	
SCT	Point 1	92	92.6
	Point 2	93	
	Point 3	93	
	Point 4	93	
	Point 5	92	
DCT	Point 1	93	92.8
	Point 2	93	
	Point 3	93	
	Point 4	92	
	Point 5	93	

from the wear tests performed are presented in Table 4. Figure 10 shows the plot of wear rate (W_r) vs. normal load for the three types of specimens. It is evident from Fig. 9 that wear rate (W_r) of cryogenically treated (SCT and DCT) specimens is significantly lower than that of the untreated (UT) specimen at all the tested normal loads. Compared with the untreated specimens (UT), decrease in wear rate was about 12%, 19%, and 24% for SCT specimens and about 19%, 29%, and 42% for DCT specimens at normal load of 49, 68.6, and 88.2 N, respectively. It is interesting to note that decrease in wear rate for SCT and DCT specimens is in general more prominent at higher normal loads as compared to lower normal loads which is also evident from the graph shown in Fig. 10. The DCT specimens outperformed SCT specimens in terms of wear rate by about 7%, 9%, and 14% at normal load of 49, 68.6, and 88.2 N, respectively. Other very important observation is that the extent of improvement in hardness of DCT specimens over SCT specimens was merely about 0.21%, whereas improve-

**Fig. 9** Hardness values for different types of heat treatments

ment in wear rate varied from 6% to 14% which is quite significant. Apparently there is no straight correlation of wear rate with hardness. So, it can be concluded that mere hardness data do not provide exact parameter in evaluation of wear resistance of cryogenically treated WC–Co material. However, it can be accomplished that cryogenic treatment increases the wear resistance of WC–Co material appreciably, but the degree of increase is dependent on the applied load during these tests.

Augmentation of wear resistance by cryogenic treatment (SCT and DCT) is ascribed to the spheroidization of α -phase particles in durable and stress-free configuration, and decrease in soft β -phase particles and precipitation of fine eta (η) carbide particles. Figure 11 shows the optical micrographs of the worn surfaces of UT, SCT, and DCT WC–Co specimens. Under identical wear conditions, worn surfaces of SCT (Fig. 11b) and DCT (Fig. 11c) specimen appear much smoother than the UT specimen (Fig. 11a). This observation is consistent with the obtained results of wear rates as plotted in Fig. 10. However, the mechanism of wear could not be extracted from the optical micrographs; hence, SEM images (Fig. 12) were taken to understand the wear mechanism. Worn surfaces of untreated WC–Co specimen consist of two main regions: smooth areas with randomly scattered grooves and areas containing widespread surface fractures. The grooves and surface fractures can be identified as black and white areas respectively in the optical microphotograph shown in Fig. 11a. These two different regions are shown in close range SEM images in Fig. 12a, b, respectively. During the initial stage of wear, the binder β phase got removed from between the α -phase tungsten carbide particles by a combination of plastic deformation and microabrasion which appears as white patched layer (Fig. 12a) on the

Table 4 Tribological characteristics of WC–Co material for pin-on-disk wear tests at 1.5 m/s velocity

Type of heat treatment	Normal load (N)	Mean weight loss (g)	Wear rate $\times 10^{-5} W_r$ (mm ³ /Nm)	Wear resistance improvement w.r.t UT (%)	Wear resistance improvement w.r.t SCT (%)
UT	49.0	0.004	0.37	–	–
	68.6	0.007	0.44		
	88.2	0.010	0.51		
SCT	49.0	0.003	0.33	12.12	–
	68.6	0.005	0.37	18.91	
	88.2	0.008	0.41	24.39	
DCT	49.0	0.003	0.31	19.34	06.45
	68.6	0.005	0.34	29.41	08.82
	88.2	0.007	0.36	41.66	13.88

worn surface. It is thought that extrusions of binder phase from the bulk of material take place through continuous channels of binder material resulting in decrease in cobalt content in regions near surface. The binder material, which is extruded to the surface deformed plastically as cobalt metal, has ability to plastic deformation under shear stresses. H. Engqvist et al. [25] also confirm this phenomenon and named this surface layer of extruded cobalt as tribofilm. Because of the presence and widespread coverage of extruded cobalt layer, most of the surface deformation during sliding wear occurred within this layer. H. Engqvist et al. [25] identified this layer as thick paste consisting of small WC or WO_x particles in Co that is smeared out between the sliding surfaces. Cobalt extrusion preceded by cracking of the brittle α -phase particles. The high pressures on individual contact spots caused an initial fragmentation of α -phase particles since residual compressive stress of α -phase particles had lost because of plastic flow of cobalt binder β -phase. In the absence of cobalt binder β phase, these fractured α -phase particles got pulled out from the

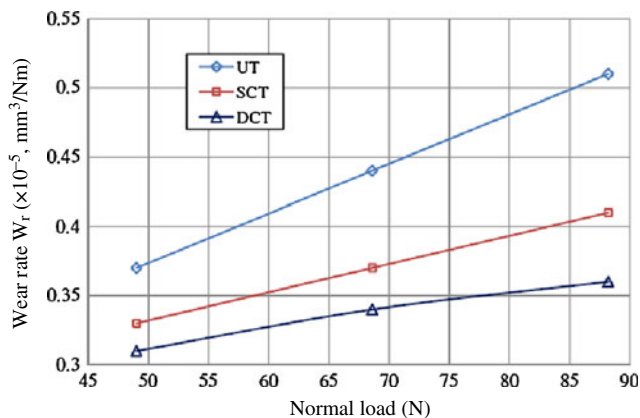


Fig. 10 Variation of estimated wear rate with applied normal load for UT, SCT, and DCT WC–Co specimens

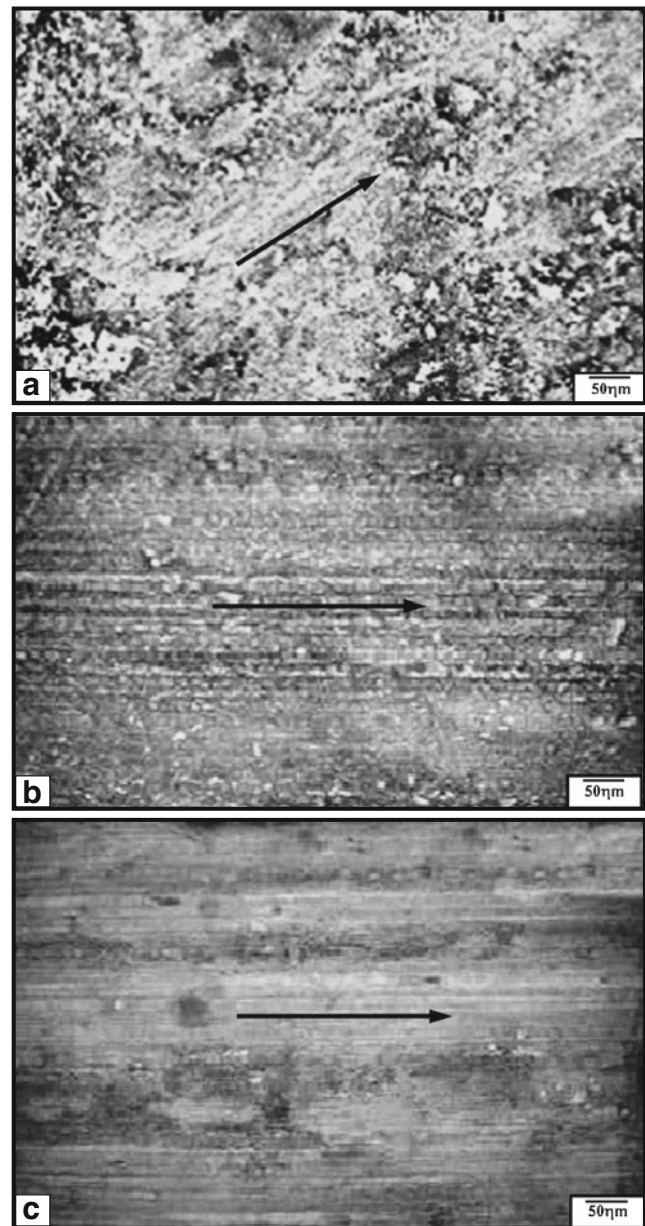


Fig. 11 Optical micrograph of worn surface of a UT, b SCT, and c DCT WC–Co specimen. The arrows show the sliding direction

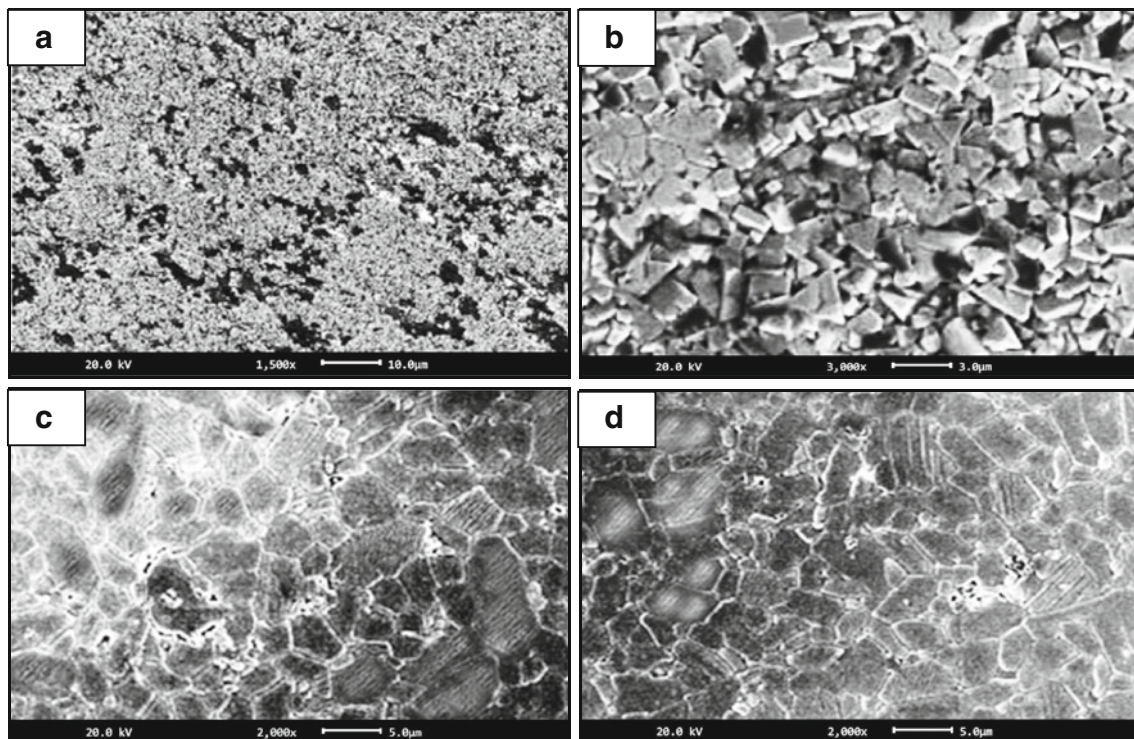


Fig. 12 SEM image of **a** UT, **b** UT etched with boiling HCl, **c** SCT, and **d** DCT WC–Co specimen worn surface

relatively feeble matrix structure resulting in grooves as evident from the SEM image shown in Fig. 12b. The α -phase particles deformed very little, and therefore, almost all the deformation is taken up by the cobalt binder β phase. From this discussion, it can be concluded that untreated WC–Co material wears primarily due to plastic deformation of cobalt binder β phase and secondarily due to fracture and pull-out of hard α -phase particles.

The optical micrographs of worn surface of SCT and DCT WC–Co specimen are relatively smooth as evident from Fig. 11b, c. In contrary to UT WC–Co specimen, the worn surface of SCT and DCT WC–Co specimen reported near absence of cobalt binder β -phase layer, though a little cobalt binder β -phase extrusions can be seen along the α -phase particle boundaries (Fig. 12c, d). The drastic reduction of cobalt binder β -phase extruded layer on the surface can be attributed to the fact that the cryogenic treatment decreases the cobalt binder β -phase contents in WC–Co specimen structure. Also, as discussed earlier, the application of cryogenic treatment causes the hard α -phase particles of tungsten carbide to get refined and aligned crystallographically into their most stable form via the phenomenon of spheroidization which results in durable, stress-free configuration. The hard α -phase particles interlocked with each other as can be seen in SEM images shown in Fig. 12c, d. In addition, the α -phase particles are observed to remain well bonded to the matrix during

sliding; thus, particle pull-out is less likely to occur in the specimens. The removal of particles is caused by intergranular fracture. Hence, the hard α -phase particles in relatively compact matrix structure neither could not easily be fragmented and nor got pulled out from the matrix. The dominating wear mechanism therefore is abrasion of α -phase particles as the abrasion marks can be seen in Fig. 12c, d. No evidence of plastic deformation was reported on cryogenically treated worn surfaces of WC–Co specimen.

4 Conclusions

From the present work based on mechanical and metallurgical characterization of cryogenically treated WC–Co material, the following conclusions can be drawn:

1. Hard phase particles of tungsten carbide are refined into their most stable form via the phenomenon of spheroidization after shallow and deep cryogenic treatment. It also aligns the hard phase carbide particulate structure into a durable, stress-free crystallographic configuration.
2. Precipitation of η -phase carbides is not the only reason for enhanced durability of tungsten carbide material. It is established that the cryogenic treatment causes the crystal structure changes in both hard and soft binder

phase of tungsten carbide material which may be responsible for the enhanced hardness and wear resistance properties along with precipitation of η -phase carbides.

3. The hardness of tungsten carbide material increases by 4.75% after subjecting the material to shallow cryogenic treatment, but no further significant improve in hardness (0.21%) was reported by further reducing the treating temperature to deep cryogenic temperature. Hence, there exists an optimum cryogenic treatment temperature for tungsten carbide material which may ensure the maximum possible enhancement in hardness. Identification of such temperature can lead to wider applications of cryogenic treatments.
4. Both types of cryogenic treatments substantially decrease the wear rate of the tungsten carbide material compared to the untreated ones. However, the improvement in wear rate by deep cryogenic treatment is significantly higher than that achieved by shallow cryogenic treatment though the reason for this is yet to be crystallized.
5. The significant improvement in wear resistance of shallow and deep cryogenically treated tungsten carbide material is attributed to the refinement and crystallographic alignment of hard α -phase particles, decreased amount of cobalt binder β phase, and precipitation of fine eta (η)-carbides.

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