Industrial Engineering Journal
ISSN: 0970-2555
Volume : 51, Issue 04, April : 2022

Effect of Soaking Periods on Tungsten Carbide Cryogenic Treatments.

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Abstract

Improvement in wear resistance and hardness of cutting tool material is one of the most important challenges in machining operation. This issue can be overcome by improving the wear resistance and hardness by cryogenic treatment of tungsten carbide. In this work it is tried to study the effect of different soaking periods in cryogenic treatment of tungsten carbide. The experiments were conducted at temperature of 88K at different soaking periods of 8hrs, 16hrs, 24hrs and 30hrs on commercially used tungsten carbide. Further efforts were made to quantify and confirm the effect of different soaking period along with the mechanism responsible for change in the hardness and wear resistance by measuring Rockwell hardness and weight loss during wear test. In addition to this OM, SEM, EDX and XRD tests were also conducted to support the results..

The obtained result shows that there is a significant decrease in weight loss of 8hr soaked sample out of different soaking periods but, there was no change in bulk hardness. In addition to this the formation of carbide and change in particles size was observed in SEM and XRD after cryogenic treatment. The weight loss during sliding wear test indicates the cryogenically treated tungsten carbide is more wear resistance due to increase in population density of carbides. Microstructure analysis of worn surface reflects the mechanism behind the improvement of mechanical properties.

Keywords: Cryogenic treatment, Tungsten carbide, Hardness, SEM, XRD.

1. Introduction

In the machining process, the tool's material life is crucial [1]. It is based on the material's wear properties for the cutting tool [1]. Several researchers have thoroughly explored the use of CT to enhance the wear characteristics of different materials [3–7]. The cryogenic treatment procedure comprises gradually lowering the temperature of the material to below zero degrees Celsius, holding it there for a predetermined amount of time known as the soaking period, and then gradually bringing it back up to normal temperature.

Barron saw an improvement in the steels' wear properties following CT [8]. The presence of iron (Fe) in steels led to an improvement in wear characteristics [3–7]. Researchers have spent the last ten years thoroughly examining the CT of ferrous alloys, including tool steels and nonferrous materials [3]. Song [7] noted that deep cryogenic treatment of several materials increased tool life by 9% to 22%. Stewart [9] noted that after cryogenic treatment of tungsten carbide tools used in the milling of medium density fiberboard, normal tool force and parallel force were both reduced by 25% and 20%, respectively. Cryogenic treatment was performed for this work at 86 K during a 24-hour soaking period [9]. Cryogenically treated WC-Co tools showed a 38% increase in flank wear

resistance. The CT was performed at 88 K for a 24-hour soaking period, and the tool life was determined using the ISO standard's 0.5 mm flank wear criterion [10]. In evaluating the effectiveness of cryogenically treated tungsten carbide tools in turning carbon steels, A. Y. L. Yong [11] discovered a 20% reduction in flank wear following the CT. When tungsten carbide inserts were subjected to CT, Gill et al. [12] discovered a 27% reduction in flank wear when cutting at 110 m/min in both dry and wet turning operations. CT was performed for 24 hours at 77K throughout this investigation [12].

Performance analysis of cryogenically treated carbide drills for drilling white cast iron was done by Ramji et al. [13]. Reduced tool forces, improved tool wear resistance, and improved surface polish of the drilled holes are all benefits of the cryogenically treated drills. It was noted that the carbides produced following CT. CT was performed for this investigation at 94K for 24 hours [13]. The impact of shallow CT (SCT) and deep cryogenic treatment (DCT) on the WC-Co tool has been researched by Gill et al. [14]. Over an 18-hour soaking session at 163K, it was shown that bulk hardness improved by 4.75% at SCT [14]. The impact of a tempering cycle following CT on cobalt-bounded tungsten carbide inserts has been researched by Kalsi et al. When CT was done at 77K for 24 hours, there was a noticeable increase in tool life. As the treated sample undergoes its first tempering cycle, the material's hardness also increases [15].

The powder metallurgy process is used to create the tungsten carbide (WC-Co) tool material for commercial usage. Cobalt serves as the binding component. Iron and cobalt are located in the periodic table's VIIB group [8, 9]. Hence, it was assumed that WC-Co, which uses cobalt as a binder, would react to CT in a manner similar to that of steels. Also, it is yet unknown what process led to the improvement in wear characteristics. The gape to survey the impact of various soaking periods in CT on WC-Co material was therefore conducted in addition to these investigations. The mechanisms underlying the alteration in wear characteristics brought on by CT are being studied.

2. Material and Methods

Material samples

The sintered WIDIA product of tungsten carbide (WC-Co) material commercial available in the form of P-30 (CNMG 120-408-TTR) square uncoated turning inserts was chosen for this study. The chemical analysis of samples was carried by positive material identification at ELCA Quality System and Calibrations Pvt. Ptd. Pune. The chemical composition of samples is presented in Table 01.

Table 1. Chemical composition

Name of element	Chemical composition %
W	77.20
Co	11.30
Ti	00.60
Ta	03.80
Nb	00.60

Cryogenic treatment

All the samples were named as UT, CT with different soaking periods (CT1-8hr, CT2-16hr, CT3-24hr and

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ISSN: 0970-2555
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CT4-30hr). The samples were subjected to CT (Deep Subzero processor Model Shell & tube SC-50 Dura Cyl.) with step cooling at 88 K and hold at this temperature for different soaking period. After CT, sample was gradually brought to room temperature by step cooling at 2 ºC/min rate. The samples were placed in cryogenic chamber where the gases nitrogen entered at 88k. After this, tempering cycle was carried out at 423K for 4hr to relieve the stresses induce in cryogenic treatment.

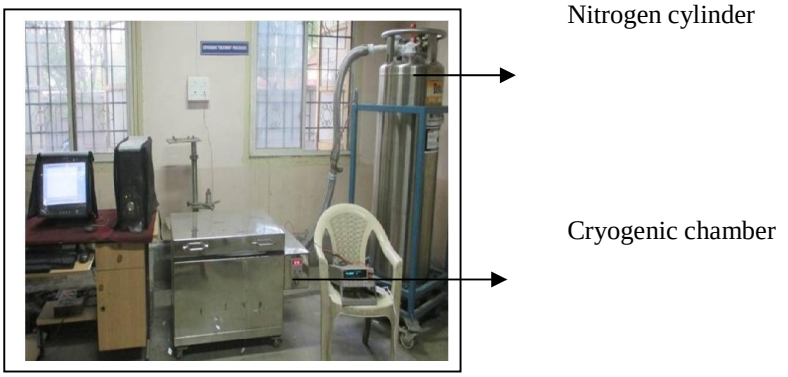

Fig. 1. Cryogenic treatment setup; (Deep Subzero processor Model Shell & tube SC-50 Dura Cyl.)

Hardness test

Rock well hardness tester was used to measure the hardness according to ASTM B294-10 standard. A minor load of 98.07N was applied to set the sample and major load of 588.4 N was then applied to measure hardness for 30s duration for HRA scale. The hardness was measured for five times to get average value.

Pin on disc wear test

Sliding wear tests were performed using a 'Pin-on-disk' wear testing machine at room temperature as shown in Fig 02. The contact conduction generated by pressing the sample on alumina disk without use of coolant means under dry friction conduction. The rectangular surface of sample with the dimension 12 x 5 mm ^{2} is in contact with the Alumina disc during the wear test. These tests were carried out common conduction for every sample at 68N load, 800 rpm and 42 mm wear track diameter for 15 min. Weight loss of each sample was measured on weighting machine.

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ISSN: 0970-2555
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Fig. 2. Pin- On-Disk wear testing machine;

Microstructure analysis

Micro structural evaluation was carried out under optical microscope (OM) and Scanning Electron Microscopy (SEM). The morphology of plane sample and worn sample are investigated by Scanning Electron Microscopy (SEM-JEOL 6380A). All the sample were polished by diamond paste (3 μm) to reach mirror finish and etched with dilute NaOH (20%) solution. The elemental composition of phases carried out by energy dispersive spectroscopy (EDS-Bruker X flash 6130). The worn surface of samples was observed under the SEM to evaluate the wear mechanism. The effect of cryogenic treatment on critical structure of samples at various structures was studied by using X-ray diffraction (XRD philps X'Pert pro PAN –alytical Pw3040/60 X-Ray Diffractormeter). The sample were scanned for a 2θ angle of 10^0 to 40^0 using nickel filtered Cu K α radiation (λ=1.54°A) generated at 40KV and 30mA with steps size employed was 0.010 with time per step of 10sec.

3. Result and discussion

Wear characteristics have contribution significantly in the enhancement of the material tool life. Wear characteristics of all samples were measured by Rockwell hardness tester and Pin-on-disk machine.

Hardness

The hardness values of UT and CT obtained are presented in Table 2. It shows that, the average hardness for UT sample is 88.8 HRA and CT2 sample (8hr soaking period) is 89.4HRA. Further increase in soaking period shows no significant change in hardness. From this result it can be concluded that there is no significant impact of different soaking periods on bulk hardness.

Table 2. Hardness value for UT and CT samples.

Type of sample	Hardness in HRA at different location					Mean hardness (HRA)
	1	2	3	4	5	
UT	89	89	88	89	89	89.9
CT1	90	89	90	89	90	89.4
CT2	89	91	90	90	90	90.0
CT3	89	89	90	89	89	89.2
CT4	90	90	90	90	90	90.0

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Pin on disc wear test

The below Table 3 shows that there is 67% reduction in wear of CT1 sample (8hr soaking period) as compared to wear of UT sample. It was found that further increase in the soaking period shows increase in wear up to 24 hr soaking period for CT3 sample. Beyond the 24 hr soaking period there is 79% reduction in wear of CT4 sample (30hr soaking period) as compared to wear of UT sample.

Table 3. Wear test on Pin on Disc.

Type of sample	Average weight loss in g/cm^2	% Reduction in weight loss
UT	0.0168	-
CT1	0.0055	67.60
CT2	0.0087	48.49
CT3	0.0105	37.5
CT4	0.0035	79.52

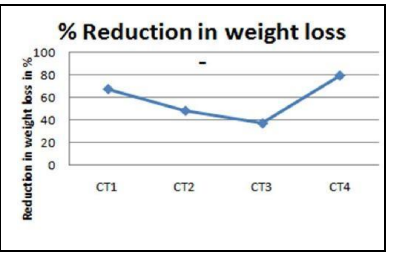

Fig. 3 Reduction in weight

This indicates that 8hr is one of the optimum soaking periods. Soaking period of 8hr requires less nitrogen for CT as compared to soaking period of 30 hr. It also saves the cost of CT. It shows that the relation between wear characteristics and influence of soaking period in CT of WC-Co sample is of non linear type.

To find out the mechanism of change in wear characteristics, further microscopic analysis of untreated and treated samples was carried out. The UT and CT1 samples were used for this stu

Micro structural analysis

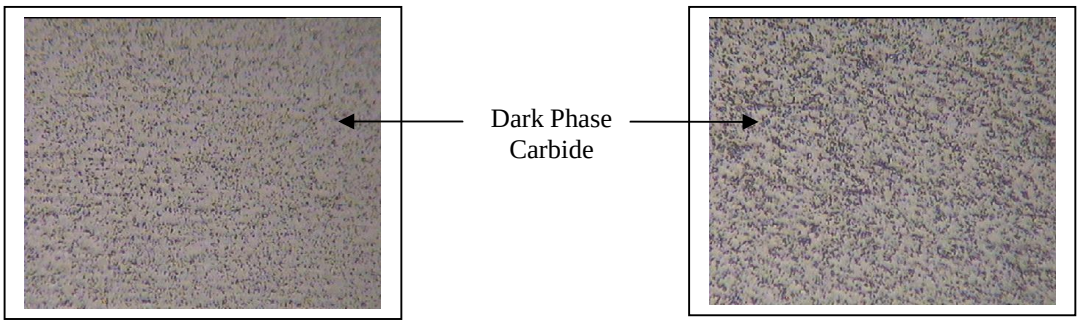

Fig. 4. OM images at 400 X magnification of WC-Co samples (a) UT; (b) CT1

Microstructure of polished UT and CT1 samples was observed under the Optical Microscope as shown in Figure 4. It is seen that population of carbide phase (volume fraction of dark phase) has increased after CT by 12% as shown in Table 4.

Table 4. The volume fraction of dark phase

Type of sample	Volume fraction of dark in%	Average volume fraction of dark in%
UT	39.8 38.9 37.9	38
	49.4	

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ISSN: 0970-2555
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CT1	51.2 49.7	50

Optical microscope was not able to show the image at higher magnification so further analysis was carried out using SEM. Surface morphology of UT and CT1 sample was studied at 4000x magnification under SEM as shown in Fig 5 .

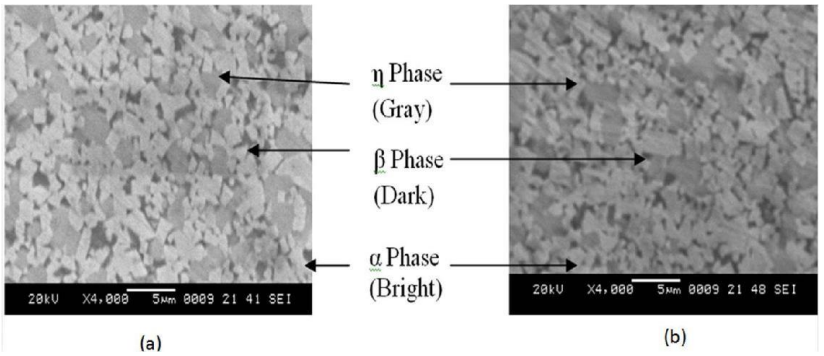

Fig 5 .SEM images at 4000X magnification of WC-Co samples (a) UT; (b) CT1

As gills [14] indentified different phases in the WC-Co material same image were observed in this study. In this SEM image of both samples shows that there are three different phases such as Bright (α) phase, Dark (β) phase and Gray (η) phase. In addition to this Further EDS was carried out to find out the elemental content of different constituents (phases and particles) which was found in SEM image, as shown Fig 6 and in Table 5.

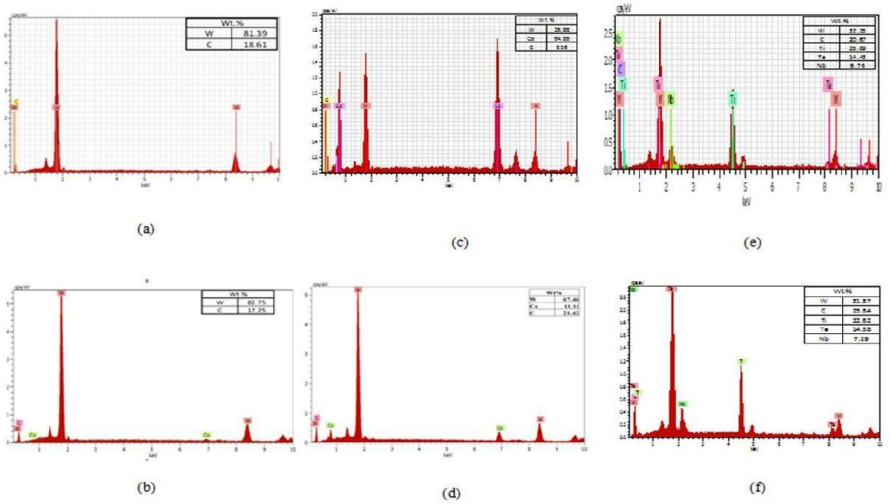

Fig 6. EDS of WC-Co samples (a), (c), (e) UT; (b), (d), (e) CT1; (a), (b) α phase; (c), (d) β phase; (e), (f) η phase

Table 5. Elemental contents of different phases in % wt.

Different phases	Contents	% wt. from EDS Analysis	
		UT	CT1
α phase	W	81.39	82.75
	C	18.61	17.25
β phase	W	26.98	67.46
	CO	64.86	11.11
	C	8.16	21.42
η phase	W	32.25	31.87
	C	20.67	23.84
	Ti	25.89	22.62
	Ta	14.43	14.38
	Nb	6.76	7.29

The Fig 6 and Table 5 shows that, α phase contains tungsten and carbon, β phase contains tungsten carbide and cobalt, and η-phase contain tungsten, carbon, titanium, niobium and tantalum. Notable changes include the reduction in cobalt in β phase (Cobalt or dark phase) from 64% to 11%. This shows that refinement and densification of structure takes place after the CT1. As a result surface morphology of CT1 sample gets changed as shown in Fig 5.

The XRD was used to find out the presences of different phases and relative intensity of UT and CT1 sample. The Fig 7 can be used to compare the XRD pattern for UT and CT1sample. It clearly indicates the presence of η carbide (Co_6W_6C) in both cases.

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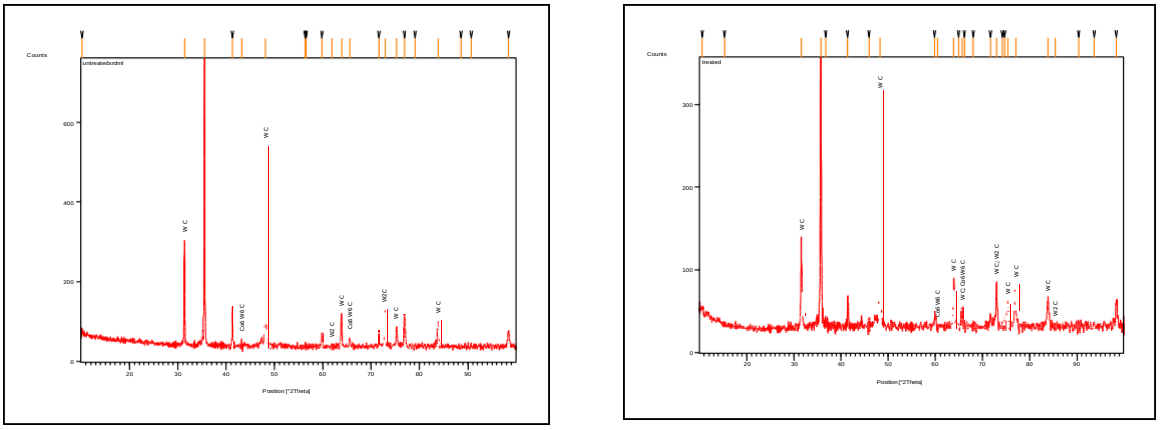

Fig 7. XRD of WC-Co samples (a)- UT; CT1-(b)

It indicates that relative intensity of η carbide increases from the insignificant in UT sample to significant in CT1 sample as shown in XRD profile. The average diameter of different particles was calculated using by Scherrer's formula [16]

$$\text{Average Diameter, } D = 0.9\,\lambda/(B\cos\theta)$$

Where,

D-Average diameter in nm, B-FWHM (Full width half maxima)-Instrumental error (0.01),
λ- Wave length of X-Ray, θ- Diffraction angle

Table 6. Average particles size from the Scherer's formula

Samples	Phases	Average diameter in nm
UT	α phase	9.5031
	η carbide	13.1922
CT1	α phase	5.1333
	η carbide	4.922

The above Table 6 indicates that before CT1 the average diameter of α phase and η phase particles were 9.5031nm and 13.1922 nm and after the CT1 it is observed as 5.1333nm and 4.922nm respectively. This is indicative of the formation of stable structure and proper alignment of particles after the CT1. It also implies that reduction in residual stresses, formation of denser and tougher matrix is taking place. This shows homogenous distribution of phases because of CT1. Such refined structure reduces the chances of fracture thereby improving the wear resistance. From the EDS and XRD results it may be concluded that reduction in cobalt content results in the formation on η carbide. CT1 has impact on Co in β phase due to deficiency of carbon in WC-Co material. Deficiency of carbon results in the formation of a η carbides by diffusion of cobalt in CT of WC-Co [2]. Relative intensity of η carbide increased from insignificant in UT sample to significant in treated (8 hr soaking period) sample as shown in XRD profile 7.

Worn surface analysis

Worn surface of UT and CT1 sample was observed to study the wear track.SEM images of worn surface are shown in Fig 8.

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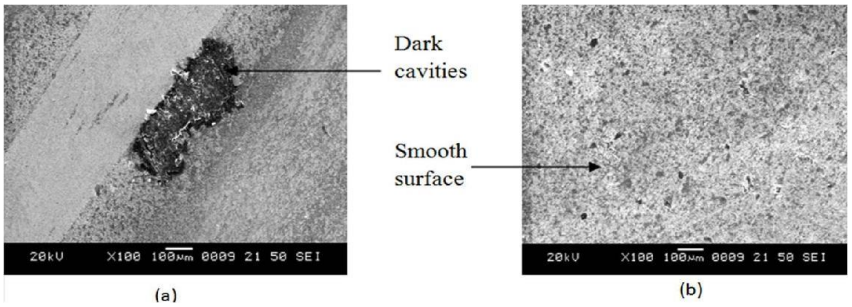

Fig 8. SEM image at 100X magnification of worn sample (a) UT; (b) CT1

From the above images it is seen that UT sample have some grooves. The random fracture area was found near the grooves on UT worn surface as shown in Fig 8. In the case of CT1 sample surface grooves were not found. Worn surface of the treated sample is smoother than UT sample. Worn surface of treated sample does not have any fracture area.

In WC-Co material cobalt is used as a binder in matrix. It also contains brittle and hard α phase WC. Cobalt matrix binds α phase as shown in SEM image from Fig 5. Cobalt extrudes from the surface due to plastic deformation during wear. Cobalt gets pulled out from the surface with the bounded hard α phase resulting in formation of grooves on the surface of the untreated sample as seen in Fig 8.

It indicates that wear of UT WC-Co martial is due to plastic deformation of soft cobalt and fracture of α phase. Presence of cobalt on the surface of UT sample has contribution in wear of samples. From this result it is clear that the CT affects cobalt in β phase. Notable changes include the reduction of Co contents in β phase of WC-Co matrix Table 5. Due to insufficient amount of cobalt present on the surface of the treated sample, grooves are not formed after wearing of the treated sample as shown in Fig 8.

3.4 Basic mechanism behind the effect on hardness and wear resistance

Cobalt is used as a binder for manufacturing of tungsten carbide tools. It also contains brittle and hard α phase (WC) in the cobalt matrix. Cobalt matrix binds α phase in the untreated sample as shown in Fig 5. Co has the property to deform during wear conduction. Alpha (α) phase has property to fracture during the wear process due to its brittle nature. Cobalt extrudes from the surface due to plastic deformation during wear as shown in Fig 8. Cobalt gets pulled out from the surface with the bounded hard α phase resulting in the formation of grooves on surface of UT sample as seen in Fig 8. It indicates that wear of WC-Co martial is due to plastic deformation of soft cobalt and fracture of α phase in untreated sample. Presence of cobalt on the surface of the sample contributes in the wear of samples.

The EDS results show (Table 5) that there is reduction in cobalt from 64% to 11% from β phase after CT of tungsten carbide tool as a result of diffusion process. Due to insufficient amount of cobalt present on the surface of treated sample grooves are not formed after wearing of CT1 sample as shown in Fig 8. The result of this experiment shows that that cobalt content reduction results in formation of η phase on the surface of treated sample. This formation of η phase involves the dissolution of the original carbides into the cobalt binder as a result of diffusion process [2].

The XRD results show reduction in the diameter of η phase and α phase after the CT. The formation of η phase increases the relative intensity of η phase on the surface of CT1 treated sample Fig 5. This is indicative of the formation of stable structure and proper alignment of particles Fig 5. Change in the cobalt content in cobalt matrix and formation of η carbide causes refinement of structure which has contribution in the improvement of wear resistance of WC-Co sample.

5. Conclusion

Following conclusions regarding the impact of various soaking periods on wear characteristics and the mechanism of

change in the improvement of wear characteristics after the CT of tungsten carbide may be made based on the study's findings.

1. CT reveals a 67% reduction in weight loss of WC-Co instruments after an 8-hour soaking time.
2. The bulk hardness has not much improved.
3. After the (CT1), the cobalt proportion in the WC-Co matrix decreased by 53%. The surface of the treated sample forms the phase as a result of the drop in cobalt content.
4. In treated samples (CT1-8 hr soaking period) the relative intensity of carbide increased from negligible in untreated samples to substantial.
5. The average diameter of phase and phase particles in the untreated sample is 9.5031 nm and 13.1922 nm, respectively. After the CT, it is found to be 5.1333 nm and 4.922 nm.
6. The structure's refining also leads to an improvement in the wear characteristics

Fundamental mechanisms for increasing wear resistance: The results of the metallurgical investigation show that phase carbide is formed following cryogenic treatment when the cobalt % is reduced. Following cryogenic treatment, this phase of carbides (Co6W6C) is harder than any other phases that were previously present on the surface of sample CT1. The XRD finding is supplemented by the development of reduced-dimension carbides, which leads to the formation of fine structures and improves mechanical characteristics after cryogenic treatment.

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