The effect of deep cryogenic treatment on hardness and wear behavior of the H13 tool steel

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In recent decades, cryogenic treatment has been used as the finishing operation between the quenching and tempering treatment on tool steels for the purpose of increasing hardness and wear resistance. H13 tool steel is a hot working steel widely used in manufacturing molds and hot working tools. In this research, the effect of deep cryogenic treatment at -196 °C for 24 hours has been investigated in comparison with the quenching-tempering treatment on hardness, structure and wear resistance. In addition, the effect of TiC coating after cryogenic treatment on hardness and wear resistance has been studied. The results of this research showed that cryogenic treatment with or without coating leads to an increase in hardness levels of 5.7 % and 9.6 %, respectively, and an improvement in the wear resistance levels of 33 % and 60 % respectively, in comparison with the quenching-tempering treatments. Investigating the wear surfaces by scanning electron microscopy (SEM) showed that the wear mechanism is adhesive.

Keywords: Deep cryogenic treatment - H13 tool steel - Hardness - Wear behavior

INTRODUCTION

The martensitic transformation start and finish temperatures in steels are reduced by increasing the percentages of carbon and the alloying elements. Even in high-alloy steels with high carbon contents, the martensitic transformation finish temperatures may reach less than zero degrees Celsius. Because of this, the retained austenite will exist in the steel structure after quenching to the environmental temperature. Retained austenite is a soft phase that reduces hardness, wear resistance, and dimensional stability [1]. It is an unstable phase that may be converted into martensite in working conditions and under stress. The recently formed martensite is not tempering; hence, it is very brittle. Also, the mentioned transformation is accompanied with a 4% increase in volume. This undesirable increased volume can lead to distortion and dimensional instability [1-2]. Therefore, one of the important issues in heat treatment of steels is the reduction or elimination of the retained austenite.

One of the methods of the reduction or elimination of the retained austenite is using cryogenic treatment [3-4]. Technically, cryogenic treatment is divided into two categories based on the temperature of the treatment: shallow cryogenic treatment (cooling to temperatures of -80 °C and deep Cryogenic Treatment (cooling to temperatures of -196 °C. Most of the improvement in properties is obtained when cryogenic treatment is performed immediately after quenching and before tempering [4]. In deep cryogenic treatment, in addition to the transformation of retained austenite to martensite, the secondary and highly fine carbides are formed in the structure after the tempering treatment [4-5]. Conducted researches show that in deep cryogenic treatment in comparison with conventional heat treatment, the number of carbides increases and a more suitable distribution of carbides is formed [4-6]. Huang showed that in high-speed steel M2, the carbides volume fraction becomes two-fold due to the effect of deep cryogenic treatment [6]. Meng reported 110 – 600% improvement in wear resistance at different speeds by performing cryogenic treatment on steel Fe-12Cr-Mo-V-1,4C using sample on the wheel test [5]. Meng also showed that despite the lack of change in the percentage of martensite at temperatures of -50 °C and -185 °C, the wear resistance of a sample on which the deep cryogenic treatment is per-

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formed improves due to the deposition of fine carbides η (Eta). The reason for the deposition of these carbides is the lattice contraction and the pressuring of the carbon atoms to leave the primary places. These carbides increase the strength and toughness of steel [5]. The conducted researches show that cryogenic treatment improves hardness [7-9], wear resistance [10-11], and increases bending strength [12], dimensional stability [13], fatigue resistance [9], and fracture toughness [12] in the steel pieces. H13 tool steel is a hot working steel that is widely used in manufacturing molds and hot working tools. In the present study, the effect of deep cryogenic treatment on microstructure, hardness and wear resistance of this steel with and without TiC coating has been investigated in comparison with the conventional quenching-tempering heat treatment. The steel investigated in the present study is the H13 tool steel which is a hot working steel Due to the sensitiveness of using this steel and the existence of the retained austenite in its structure, using deep cryogenic treatment after performing common austenite - quenching treatment is necessary. However, there is not much available information about deep cryogenic treatment of this steel. The current study has been performed to investigate the effect of holding duration of the H13 tool steel at the temperature of deep cryogenic treatment (-196 °C for 24 hours, and coating this steel as well as investigating the effect of this treatment on its hardness and wear behavior. Also, the effect of deep cryogenic treatment on the wear mechanism and distribution of carbides was studied.

EXPERIMENTS

A H13 rod with adiameter of 20mm was cut into disks with height of 55 mm. The nominal composition of the rod is introduced in Table 1. To perform heat treatment, the samples were preheated at the rate of 30 °C / min up to 650°C and kept at this temperature for 20 minutes. Then, for austenitizing, these samples were heated at the rate of 20 °C / min up to 1030° C and kept at this temperature for 30 minutes. Then the samples were removed from the furnace and were immediately quenched in the oil environment. After that, two of the samples were immediately placed in the furnace under tempering treatment at 550 ˚C for 50 minutes (QT) and the other two samples were placed under cryogenic treatment at -196 °C (Deep Cryogenic treatment) for 24 hours.

After warming to ambient temperature, one of the cryogenic samples was immediately tempered for 50 minutes at temperature of 550 °C (DCT24). In order to investigate the effect of the coating treatment, two other samples were prepared after warming to the ambient temperature. For this purpose some of the DCT and QT samples were coated by a 50 mm-thick layer of TiC via the PVD method and were placed under tempering treatment at 550 °C for 50 minutes (DCT24P and QTP respectively). The heat treatments of the samples and their abbreviation signs are given in Table 2.

A programmable heat-operating furnace (Carbolite, RHF1400, England) was used for austenitizing and tempering the samples. After the austenitizing and quenching heat treatment, in order to remove surface oxides and calculate the hardness carefully, the samples were sanded to a 600 grit. After tempering, the samples were sanded to a 1200 grit to be polished and the uniformity of the surface in the wear test and their surface roughness reached 0.3 µm. Then they were put under the hardness and wear tests. The hardness of the samples was measured in Rockwell scale (HRC) and based on the ASTEM E18 standard. The samples were analyzed via XRD to evaluate the effect of the deep cryogenic heat treatment on the retained austenite percentage. For this evaluation, a Cu Kα radiation was used, and the retained austenite percentage was determined according to the ASTM E975-00 standard. Metallography of the samples was conducted by using the common method of sanding and polishing with the emulsion of a device containing alumina of 0.5 µm. 4% Nital Etching solution was used for etching the samples and the structure was studied by optical microscopy (Olympus, PGM3) and field emission scanning electron microscopy (FSEM JEOL2010).

The wear test samples were cut from the original sample as discs with a diameter of 50 mm and by using the wire cut method before the heat treatment and they were ground by magnetic stone for uniformity of surface. The wear test was conducted according to the ASTM G99 standard by using the wear machine with the Pin-On-Disk method with a force of 60 Newton and the speed of 0.15 m/s. During the experiment, the samples weight reduction was calculated by a digital scale with 0.0001 g precision milligram. The abrasion test was conducted at a distance of 1000 meters in the humidity of 30±5 %, and at the temperature of 25±5 . In the wear test, the graphs of weight reduction versus distance and wear rate versus distance were drawn. The wear rate was calculated by using the following formula.

$$W_r = \Delta m / (\rho \times l \times F) \times 10^6 \qquad (1)$$

where, W_r is the wear rate (mm^3 /Nm), m is the weight reduction (mg), ρ is the density of steel (g/cm^3) l is the sliding distance (meter), F is the applied force (Newton) and the coefficient of 10^6 is for the unit conversion.

Scanning electron microscopy (SEM Philips-XI30) was used to study the surface and wear mechanisms.

C	Si	Mn	P	S	Cr	Mo	V	Fe
0.35	1.2	0.35	0.03	0.03	5	1.5	1	90.5

Table 1 - Chemical composition of the H13 tool steel (Wt.%)

RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis of the samples show that the deep cryogenic heat treatment eliminates the retained austenite completely. It was also clarified that the rate of carbides dispersion in the samples which have been

Sample number	Heat treatment	Abbreviation sign
Sample 1	Preheating at 650 °C for 20 minutes; Austenitizing at 1030 °C for 30 minutes; Quenching in oil; Tempering at 550 °C for 50 minutes; Air cooling	Austenitizing; Quenching in oil; Tempering (QT)
Sample 2	Preheating at 650 °C for 20 minutes; Austenitizing at 1030 °C for 30 minutes; Quenching in oil; Cooling to -196 °C; Keeping at this temperature for 24 hr; Warming to ambient temperature; Tempering at 550 °C for 50 minutes; Air cooling	Austenitizing; Quenching in oil; Deep cryogenic treatment; Tempering (DCT24)
Sample 3	Preheating at 650 °C for 20 minutes; Austenitizing at 1030 °C for 30 minutes; Quenching in oil; Coating with TiC using the PVD method, Tempering at 550 °C for 50 minutes; Air cooling	Austenitizing, Quenching in oil, Tempering, Coating (QTP)
Sample 4	Preheating at 650 °C for 20 minutes; Austenitizing at 1030 °C for 30 minutes; Quenching in oil; cooling to -196 °C; Keeping at this temperature for 24 hr; Warming to ambient temperature; Coating with TiC using the PVD method Tempering at 550 °C for 50 minutes; Air cooling;	Austenitizing, Quenching in oil, Deep Cryogenic Treatment, Tempering, Coating (DCT24P)

Table 2 - Heat treatment condition of the H13 tool steel

under deep cryogenic treatment is much more than the samples of quenching-tempering (Figs 1and 2 (a, b)). This is one of the main reasons for increasing the hardness and wear resistance of cryogenic samples in comparison with the samples of quenching-tempering.

These tiny carbides are created due to the microscopic internal tensions caused by factors such as difference in the thermal contraction coefficient of different phases or transformation of the retained austenite to martensite and crystalline defects such as twinning and dislocation. Under these conditions, the temperature must be sufficiently low for these microscopic internal tensions to reach the point of the forming of the mentioned crystalline defects. If sufficient time is available under this condition, the local influence leads to the clustering of carbon and the alloying elements near the lattice defects. On the other hand, by decreasing temperature, super-saturation in martensite increases. Thus, the lattice distortion and thermodynamic instability in martensite increases. Both of the above mentioned factors are the driving force for the movement of carbon atoms and the alloying elements around these crystal defects [6, 14-15]. Therefore, very tiny nuclei are formed, leading to sediment of very fine carbides even the nano-sized ones in the tempering treatment [14-16]. Clustering of carbon atoms around these dislocations is to reduce the final energy of the system [6, 14].

In a study on steel 80 CrMo 125 conducted by Amini et al., a 2% increase in the volume fraction of carbides due to cryogenic treatment in comparison with the common heat treatment (quenching-tempering) was reported. They also reported more homogeneous distribution of the carbides due to the cryogenic treatment [15].

In another research performed by the same researchers on tool steel 1.2080, due to cryogenic treatment, the carbide volume fraction increased, the distribution of these carbides was more appropriate, and the nano-sized carbides were observed in the structure [16].

These researchers have considered the mentioned carbides as the main factor in the improvement of hardness and wear resistance of steel 1.2080 due to the cryogenic treatment [14-16].

Results of the hardness tests of different samples are given in Tables 3 and 4. As can be seen, hardness has increased by 5.7 % due to the cryogenic treatment and has increased by 9.6 % due to coating after the cryogenic treatment. It was also revealed that the dep cryogenic heat tretament did not affects the hardness of PVD samples (DCT24P and QTP) (table 3) due to the similar top layer.

The reason for increasing hardness due to the cryogenic treatment is related to the conversion of the retained austenite to martensite and the sediment of the tiny nanometer-sized carbides, and more appropriate distribution of carbides. Increasing hardness due to the cryogenic treatment has also been reported by other researchers [8-10, 14-17].

Sample	Hardness of Average (HRC)
DCT24	55 ± 1
DCT24P	57 ± 1
QTP	57 ± 1
QT	52 ±2

Table 3 - Hardness of experimental samples

Sample	DCT24	DCT24P
Percentage of increase of the hardness (in comparison with the QT sample)	5.76	9.61

Table 4 - Percentage rate of the increase of the hardness of the samples

Fig. 3 shows the curve of the mass loss versus the sliding distance under a force of 60 Newton. As can be seen, in the samples which have been under deep cryogenic treatment, less weight reduction was observed in comparison with the conventional heat treatment samples due to the elimination of the retained austenite and the sediment of very tiny carbides. In the comparison between these four samples, the samples of the conventional quenching-tempering treatment have the highest weight reduction. Lowest weight reduction has been observed in the 24 hr deep cryogenic and coated samples. The curves of the wear rate versus distance under the force of 60 Newton and at the speed of 0.15 m/s for all the samples are drawn in Fig. 4. The lowest wear rate has been observed in the deep cryogenic and coated samples. Also, due to the increase in the distance and cold working of the layers under wear, the wear rate has been reduced [4]. As can be seen in Table 5, the improvement of wear resistance for the DCT24 and DCT24P samples in comparison with the QT sample is 30% and 60%, respectively. The reason for the improvement of wear behavior in the cryogenic samples in comparison with the QT sample is the transformation of the retained austenite to martensite and the sediment of the tiny carbides. However, in the coated samples, the wear behavior improves by increasing the hardness of the surface due to the TiC coating after deep cryogenic treatment. The

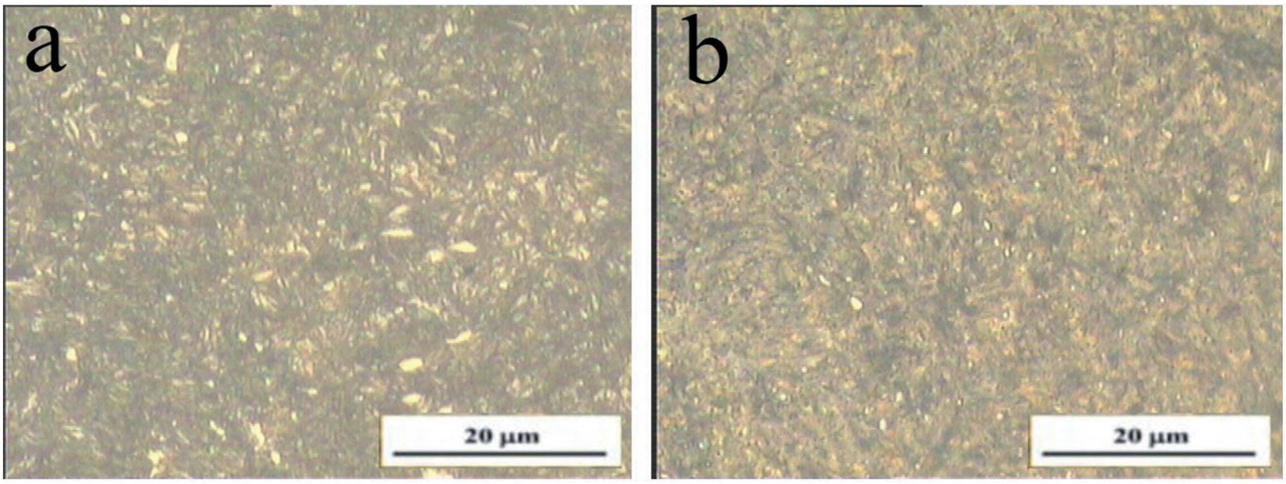

Fig.1 - Optical micrographs of carbides: (a) DCT24 and (b) QT samples

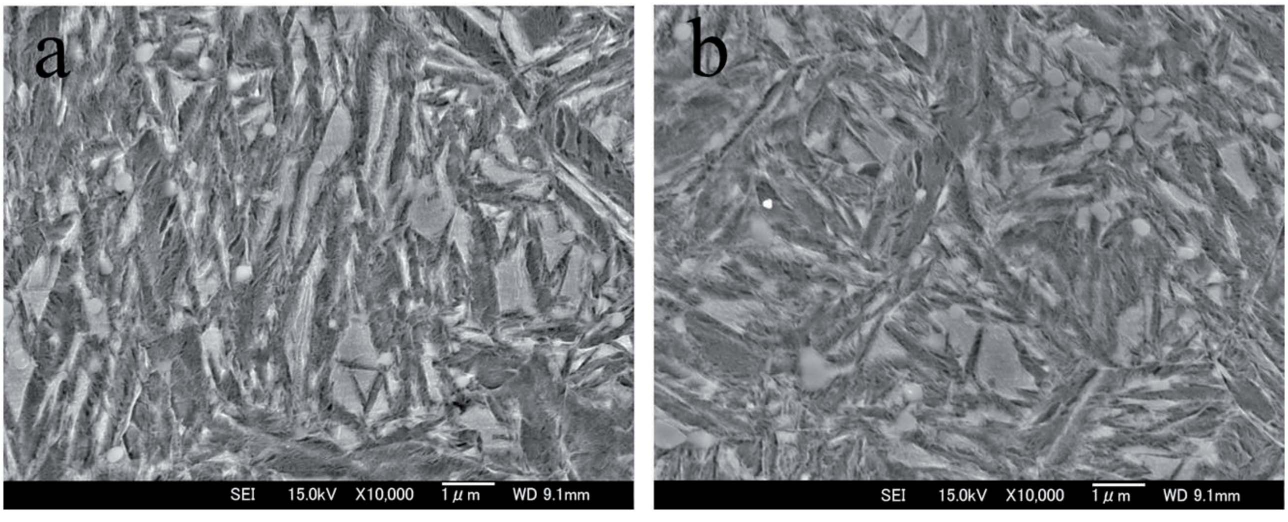

Fig. 2 - FSEM micrographs of the carbides: (a) CHT and (b) DCT24 samples

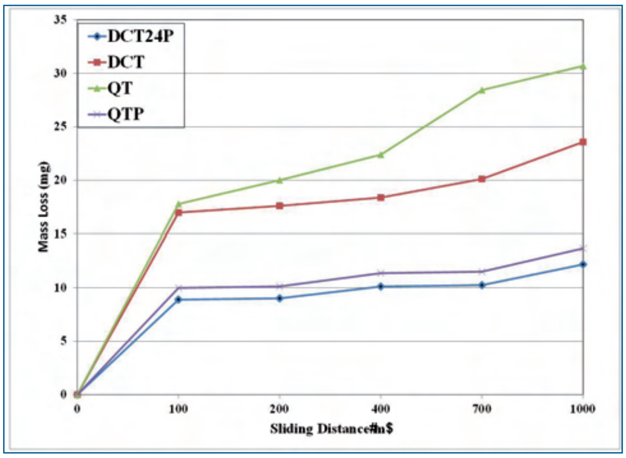

Fig.3 - Variations of the mass loss of the heat treated H13 tool steel versus the sliding distance under 60 N at V = 0.15m/s

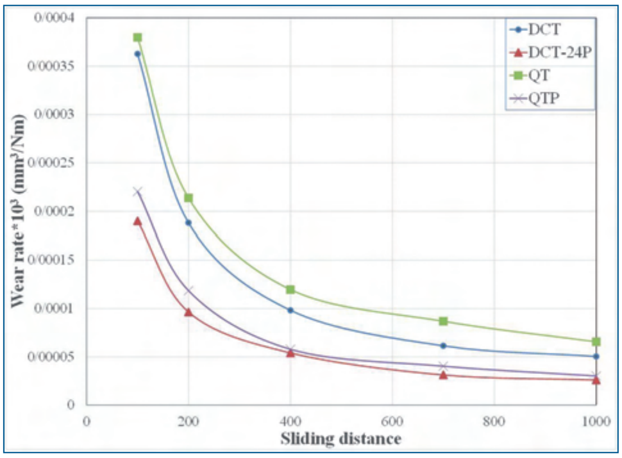

Fig. 4 - Variations of the wear rate of the heat treated H13 tool steel versus sliding distance under 60 N at V = 0.15m/s

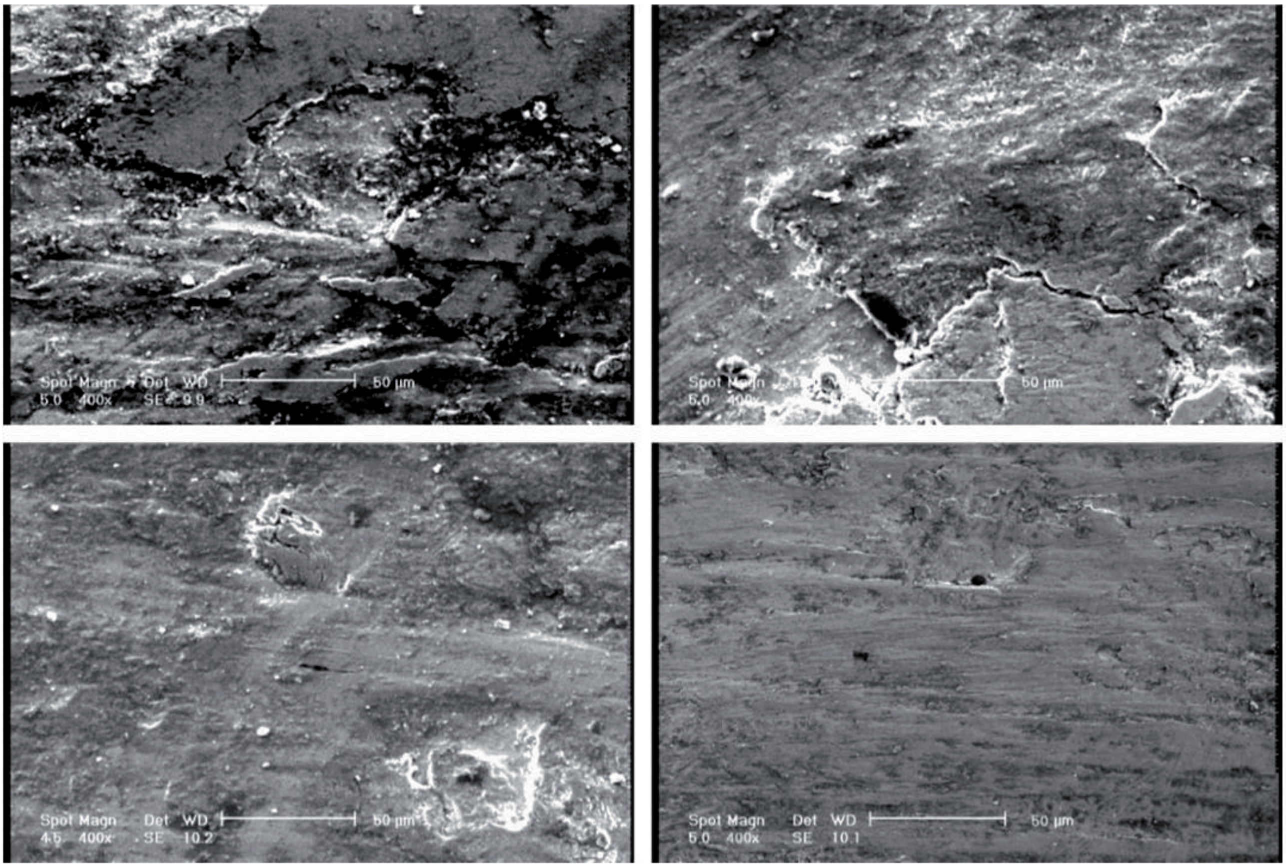

Fig. 5 - SEM image of the worn- out surface of the H13 tool steel under 60 N load and 0.15 m/s sliding velocity after 1000m sliding: (a) QT,(b)DCT24, (c)DCT24P, (d)QTP.

Sample	DCT24	DCT24P
Percentage of the increase of the wear resistance (in comparison with the QT sample)	33	60

Table 5 - Percentage rate of the increase of the samples wear resistance

PVD coating improves the wear resistance remarkably. In comparison between the PVD samples (DCT24P and QTP) the DCT24P shows a slightly higher wear resistance. This behavior is a consequence of a harder sub-layer beneath the coating top layer. After the erosion of the coating the DCT sub-layer shows a higher degree of resistance against wear and hence the wear resistance of the DCT24P samples is higher than that of the QTP ones. Studying the wear surface given in Fig 5 indicates an adhesive mechanism in the worn out surface of the samples.

As can be seen, less adhesive wear is observed in the cryogenic samples. In the studies conducted by Fantalvo [18] on tool steels, increasing the volume fraction and reducing the distance between carbides have reduced the adhesive wear. On the other hand, Yang et al. [19] have considered increasing the hardness of the steel surface as the main actions of the resistance to adhesive wear. Therefore, resistance to adhesive wear increases in the deep cryogenic treatment because of the increase in hardness due to increasing of the volume fraction of carbides.

For more studies the wear derbies was also examined via the SEM. Results show that the wear derbies of the DCT sample are smaller in size as compared with the QT ones. This behavior is a consequence of harder surface of the DCT samples as compared with the conventionally treated ones (Fig. 6).

Fig. 6 - SEM micrograph of wear derbies of the heat treated samples under 60 N load and sliding velocity of 0.15 m/s: (a) QT and (b) DCT24.

CONCLUSION

1. It was observed that deep cryogenic treatment with and without coating with TiC resulted in the increase of hardness and wear resistance in comparison with conventional heat treatment. The increasing of the hardness and wear resistance in the samples of deep cryogenic treatment, respectively, is 5.8% and 33% and with regard to the samples of deep cryogenic treatment and coating is 9.6% and 60%. The increasing of the hardness and wear resistance in deep cryogenic treatment is related to the conversion of the retained austenite to martensite, more sediment and more uniform distribution of carbides.
2. The predominant wear mechanism in the sample of conventional heat treatment is adhesive. It was also observed that by performing the deep cryogenic treatment the wear mechanism did not change and the collected wear derbies of the cryogenically treated samples were more brittle and smaller

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