Effects of deep cryogenic treatment on the microstructure and friction performance of M35 high-speed steel

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Abstract. The tempered M35 samples were deep-cryogenically treated (DCT) at temperature -240℃ for a long time. The microstructure and hardness were characterized by SEM, and Rockwell together with Vicker’s indenter respectively. The wear resistance was tested by a ball-on-disc friction and wear testing against Si3N4 balls. Comparing to high-speed steel without further treatment, the size of grains was reduced to 9.94 μm and promoted the formation of carbides after DCT. However, it was found that the hardness of the samples before and after DCT kept almost the same. Under high load, the wear resistance was slightly improved. This was probably responsible for carbides precipitation and Co precipitated from the α-Fe matrix during DCT.

1. Introduction
In industrial production, reducing production cost and improving product quality are important means to improve core competitiveness. High-speed steel is an important material in advanced machining area, which is widely used in aerospace, automotive and electronics industries [1]. However, almost high-speed steels were simply quenched and triple tempered (QT), their mechanical properties and their service life are not as the expected, which limited their extensive application in industry.

Some strategies, such as controllable heat treatment [2], surface modification [3, 4] and alloying [5], are carried out to improve the properties of high-speed steel. A large number of studies show that cryogenic treatment (CT) is an important way to enhance various material’s practical performance. As far as the high-speed steel is concerned, there are three strengthening mechanisms: 1) transformation of retained austenite into martensite; 2) refinement of grain size; 3) precipitation of ultrafine dispersed carbides [6-8]. The DCT is different from a traditional cold treatment, the former treatment temperature is below -130℃, while the latter is from -60℃ to -80℃ [9]. Especially DCT can reach -196℃ in liquid nitrogen, which makes DCT convenient [10]. Over the last several decades, there are many studies in the deep cryogenic treatment of high-speed steel. The strengthening effect of cryogenic treatment on materials is still controversial. Less research is focused on the treatment below -200℃. In addition, The Co evolution during DCT is not yet known for those high-speed steel with high Co.

In this paper, liquid helium was used as the cooling medium, and samples of M35 steel were treated at -240℃ ultra-low cryogenic temperature. The morphology, composition and mechanical properties of
M35 before and after cryogenic treatment were explored basically by means of X-ray diffraction, SEM, the rotating sliding wear test, Rockwell and Vickers indenter.

2. Materials and methods
The chemical composition of the M35 high-speed steel used in this work was listed in Table 1. Samples were cut into 25 mm in diameter and 5 mm in thickness from steel rods. The DCT, as shown in Fig. 1, was given in a computer controlled cryoprocessor after quenching and triple tempering (QT). The temperature of the samples was brought down from room temperature to -240°C by liquid helium (DCT). Since the loss of recycling of the liquid helium, enclosed in the cavity, was very little, the specimens were cryogenically treated for 24 hours for better performance, as shown in Fig. 1.

| Element | C   | Si  | Mn  | Cr   | Mo  | V   | W   | Co  |
|---------|-----|-----|-----|------|-----|-----|-----|-----|
| Concentration | 0.806 | 0.347 | 0.389 | 4.221 | 4.950 | 1.643 | 5.572 | 4.835 |

Table 1 Chemical composition of the M35 high-speed steel used in this work (wt. %).

Fig. 1. Processing routes of the cryogenic treatment.

| Parameters                          | Value        | Unit |
|-------------------------------------|--------------|------|
| Load                                | 10, 60       | N    |
| Sliding speed                       | 300          | r/min|
| Sliding time                        | 60, 90       | min  |
| Wear track diameter                 | 6            | mm   |
| Dimension of disc (diameter × thickness) | Φ25×5       | mm   |
| Diameter of balls                   | 4            | mm   |

Table 2 The experimental conditions of ball-on-disc of M35 against Si₃N₄ balls.

These samples were lapped and polished and then etched with freshly prepared 4% nital for 13 seconds. Microstructures of specimens were characterized by scanning electron microscopy (SEM) (FEI, Nova NanoSEM 430, Netherlands) with analyses of energy dispersive Spectrometer (EDS). In addition, the X-ray diffraction (XRD) technique using Cu-Kα radiation was employed for identification of different phases presented in specimens. Hardness tests were performed by Rockwell C, and micro-hardness by Vickers method with 1 kg load. An average of seven readings was noted as the final value of hardness. Samples for the wear tests were the discs, having been lapped and polished. Ball-on-disc test was conducted by Si₃N₄ balls with a diameter of 4 mm using a ball-on-disc friction and wear testing machine (SFT-2M, China) under dry condition. Before tests, the steel disc and the Si₃N₄ balls were ultrasonically cleaned in ethanol for 5 min to avoid the impact of the impurity on their surface. The detailed experimental conditions of wear tests were shown in Table 2. After the wear tests, the wear marks were observed by SEM, and the wear mechanism of the different treated samples was compared.
3. Result and discussion

Microstructural Features. The SEM was used to observe the microstructure and carbide distribution of samples. As shown in Fig. 2, it was found that the surface of high-speed steel contained a lot of gray carbides (V-rich) and white carbides (W-rich). After deep cryogenic treatment, the grain size was reduced from 10.22 μm to 9.94 μm. In addition, it was clearly observed that the coarse carbides were mainly at the grain boundary and a quantity of fine carbides (size ≤ 1 μm) were precipitated and dispersed in the grains. Dhokey et al. [1] reported that with the cryosoaking time increasing, the tendency of merging of W-rich and V-rich carbides increased. However, there was no obvious difference in the merging of two carbides between the QT and DCT.

Fig. 2. SEM images: (a) QT; (b) DCT.

XRD was used to observe content of coarse and fine carbides. From Fig. 3, it could be observed that high-speed steel contains α-Fe, M₆C, MC, M₇C₃ and Co, which was matched with the result of Table 1. Moreover, the peak intensity of M₆C and M₇C₃ carbides were enhanced apparently, which could be considered as an increase in the amount of carbides after deep cryogenic treatment. In a word, results of SEM and XRD revealed that deep cryogenic treatment can reduce the size of grains and stimulate the carbides precipitating.

Fig. 3. X-ray diffraction line profiles of specimens.

Hardness. According to Table 3, the change of the average hardness was negligible before and after deep cryogenic treatment. When M35 steel was cryotreated at the degree of -185℃ for 24 h, the samples had almost the same Rockwell hardness as before cryogenic treatment, and the hardness changed with carbides and residual stress [11]. It was proposed that if the materials had only few retained austenite, it
would dramatically increase the wear resistance compared to its original state, but without altering the hardness [12]. This was contributed to the residual stress, impact toughness, the cooling rate of experiment and so on. Obviously, the above explanation deserved deep discussion.

Table 3. Average hardness (HRC and HV) in M35 high-speed steel before and after the DCT.

| Treatment | Hardness HRC | Microhardness HV |
|-----------|--------------|-----------------|
| QT        | 65.4 ± 0.2   | 866 ± 15        |
| DCT       | 65.1 ± 0.2   | 875 ± 15        |

In our study, strengthening mechanisms and degradation coexisted during DCT. One side, carbide precipitation and grain refining were beneficial to improve the M35 steel hardness; the other side, dissolution of Co out from Fe matrix and Co phase dispersion would soften the alloy. The cooperation of both sides was responsible to the almost negligible hardness change in this study.

Wear. Fig. 4 showed the friction coefficients of two loads used for M35 wear tests. It can be seen that the friction coefficient of DCT samples at the load of 10 N was not very smooth and steady than that of QT specimens. In a research on M2 high-speed steel [13], the wear resistance of samples was practically the same and the wear corresponded to mild wear region. However, at high loads, the wear resistance of the samples was significantly different. Hence, the load of 60 N was performed in the wear tests, as shown in Fig. 4 (b). Compared to the Fig. 4 (a), the friction coefficient at the load of 60 N was stable relatively and higher. The friction coefficient increased with the wear load during YG6 cemented carbide sliding against Si3N4 ceramics [14], which was similar to the wear tests in this work. Generally, the friction process can be divided into two stages: wear in stage and stable wear stage [15]. In the wear in stage, there was the crushing of oxide film and formation of abrasive particles, resulting in the increasing of the friction coefficient. From Fig. 4 (b), the friction coefficients of QT and DCT were very close but there was a downward trend after stabilization of the DCT value and the one of QT was gradually increasing. This was due to the low wear resistance of the QT sample surface, and the formation of a large number of abrasive particles during the wear process, resulting in the increasing friction coefficient. This suggested that the wear resistance of the M35 steel could be improved by DCT.

![Fig. 4. Friction coefficient of M35 in experiments at two selected loads: (a) 10N and (b) 60 N.](image)

The worn faces of specimens tested at low load were shown in Fig. 5. It was obvious that the surfaces suffered little damage and the dark area of DCT sample was smaller than that of QT sample, as shown in Fig. 5 (a) (b). From the Fig. 5 (c) (d), there were many fine debris and a proportion of O atoms with 32.58% atomic percentage was detected by EDS in the dark area. Due to the relative motion of the friction pair, the oxide film formed on the worn surface. Meanwhile, some carbide particles were dropped from the matrix material, moved across the surface and caused the macro-traces [16]. It revealed that the wear mechanism at low load primarily involved formation of the oxide film and the abrasive particles. Compared with the QT samples, the DCT samples showed better wear resistance.
Fig. 5. Worn surface of (a) (c) QT-10N; (b) (d) DCT-10N

It also can be seen that the worn surfaces of samples under high load were quite different with those at low load. From the Fig. 6 (a) and (b), it was obviously noticed that there were an amount of smearing and clear visible sliding marks on the worn surface. In addition, the dark smearing had a larger proportion of O atoms with 58.10% atomic percentage and was approximately three times as many as that in the scratch region, indicating that the process of wear at high load was along with serious oxidation wear. Meanwhile, the oxide film was crushed and fell off from the worn surface under high load, resulting in a reduction of the dark area [17]. From Fig. 6, it was observed that QT samples showed deeper ploughing and were easier smeared. The worn surfaces of QT and DCT samples indicated more severe adhesion and abrasive wear, which was consistent with the friction coefficient results. Hence, the wear resistance of M35 high-speed steel was improved with the DCT.
During M35 steel sliding against Si₃N₄, abrasive, adhesive and surface oxidation presented simultaneously. It is well known that Co transforms easily into Co-oxides, which is beneficial for the oxidation resistance of the steel. Probably Co dispersion in the matrix can also enhance the thermal conductivity of the steel. The degree difference of worn track surface oxidation between before and after DCT might come from these effects.

4. Conclusions

M35 high-speed steel was treated at -240°C ultra-low cryogenic temperature for 24 h. After deep cryogenic treatment, the carbides on the surface of M35 steel increased and the average size of grains reduced. Co dissolved in Fe matrix precipitated during this ultra-low cryogenic treatment. Under the cooperation of dispersive, fine-grained strengthening, along with dissolution and soft phase degradation, the hardness after DCT kept almost the same as QT for M35 steel. At the load of 60 N, the wear resistance of the DCT M35 became higher than that of the QT. Abrasive, adhesive and surface oxidation played role simultaneously during friction. This mechanism will be investigated deeply.

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