Effect of deep cryogenic treatment on microstructure and properties of M35 high speed steel

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Abstract: The effects of cryogenic treatment on microstructure, hardness, red hardness and wear resistance of M35 high speed steel(HSS) were studied by means of scanning electron microscope, X-ray diffractograph, friction and wear tester and Rockwell hardness tester. The results show that with the increase of tempering temperature, the residual austenite in M35 HSS decreases and the grain size increases gradually. After deep cryogenic treatment (DCT), the grain size of M35 HSS is refined and the wear volume is reduced. DCT at 525℃ has the best wear resistance. With the increase of tempering temperature, the hardness of M35 HSS decreases first and then increases, and finally decreases sharply. The Rockwell hardness of M35 HSS at 525 ℃ is the highest, which is 67.1 HRC. The peak hardness of Rockwell increased by 0.7 HRC and the tempering temperature decreased from 550 ℃ to 525 ℃, which showed good stability of red hardness.

1. Introduction
High-speed steel is a very important tool material in industrial production. It has high hardness, high strength, good red hardness and wear resistance, and is widely used in the manufacturing of milling cutters, taps, presser and other products. The traditional heat treatment realizes the control of the content of residual austenite and carbide in HSS by optimizing the process parameters, so as to improve the service performance of the material, but a slight careless in the production may lead to the scrap of the whole batch of materials [1]. In order to further improve the comprehensive performance of HSS and solve the process pain point, it has very important practical significance for the process research of HSS. Cryogenic treatment has opened up a new way to improve the comprehensive properties of high speed steel. Cryogenic treatment generally refers to the process of insulating materials at temperatures below -130℃, which can promote the transformation of residual austenite in steel and the precipitation and dispersion distribution of secondary carbides, thus helping to further improve the microstructure of the material and improve the hardness and wear resistance [2-4]. Research shows that the introduction of cryogenic treatment [5-7] will change the action law of tempering temperature on the properties of HSS, promote the carbide precipitation in HSS, and further
improve the hardness and wear resistance of HSS. However, the effect of cryogenic treatment technology is still controversial at present. For example, the difference of cryogenic equipment, cryogenic mode and pre-heat treatment of materials will lead to great differences in the microstructure and mechanical properties of the same material under the same cryogenic parameters\cite{8-10}. Using the characteristics of cryogenic treatment, it is expected to reduce the tempering temperature and times of the traditional high speed steel heat treatment, which has the positive significance of energy saving and high efficiency. Taking M35 high speed steel as the research object, this paper combines cryogenic treatment with traditional heat treatment process to explore the influence law of cryogenic treatment on microstructure, phase composition, hardness and friction and wear behavior of M35 high speed steel.

2. Test materials and methods
In this paper, the experiment uses annealed state \(\phi20.5\) mm M35 high speed steel bar material as the research object, its main chemical composition as shown in table 1. After surface purification, the annealed samples were heated to 1210 \(^\circ\)C for 12 min in vacuum gas quenching furnace (VUQ557H-10), and then quenched to room temperature with nitrogen. The quenched samples were treated with tempering isotherm for 1 h (Qt) in a tubular furnace (OTF-1200X). The temperature range was 200 ~ 650 \(^\circ\)C, and the samples were divided into 12 groups, respectively 200, 300, 400, 450, 475, 500, 525, 550, 575, 600, 625, 650 \(^\circ\)C; After that, the samples were cooled to -180 \(^\circ\)C at a cooling rate of 5 \(^\circ\)C / min in a programmed liquid nitrogen deep cold chamber (cryometal-50), and held for 6 h for cryogenic treatment (DCT).

| Table 1 Chemical composition of M35 high-speed steel (mass fraction %). |
|------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| C  | Mn  | Si  | Cr  | Mo  | W   | V   | Co  | Fe |
| 0.91-0.95  | 0.2-0.4 | 0.25-0.45 | 3.8-4.5 | 4.7-5.2 | 6.0-6.5 | 1.7-2.0 | 4.5-5.0 | Bal. |

The QT and DCT samples were processed into 4 mm thick samples by wire cutting, respectively. After grinding and polishing, the phase structure was determined by XRD. The samples were corroded by 4% nitric acid alcohol and the microstructures were observed by Sigma 300 field emission scanning electron microscopy (SEM) with energy spectrometer. A Future-Tech Rockwell Hardness Tester with a loading force of 150 kg was used for the sample hardness test. Each sample was tested with 7 indentation, and the average value was obtained after removing the maximum and minimum values. At room temperature and atmospheric environment, relative humidity of 40%, the ball disc friction and wear tests of QT and DCT samples were carried out by SFT-2 M high-speed pin-disc friction and wear tester. Si3N4 with a diameter of 4 mm was selected to grind the ball with a rotation radius of 3 mm. The rotational speed was 300 r/min, the test load was 40 N, and the test time was 1 h. After friction and wear tests, the wear profile of the samples was measured and the wear volume was calculated using a 3D optical profilometer of RTEC UP DUAL MODEL. Finally, QT and DCT samples were put into a tubular furnace for four tempering treatments at 600 \(^\circ\)C for 1 h to test their red hardness.

3. Results and analysis

3.1 hardness
Fig. 1 shows the hardness change rule of M35 high speed steel after different treatments. With the increase of tempering temperature, the hardness of both QT and DCT samples decreased firstly, then increased, and finally decreased sharply. In the tempering range of 300 ~ 400 \(^\circ\)C, the hardness of DCT samples is lower than that of QT samples. With the increase of tempering temperature, the hardness difference between the two processes increases gradually. In the tempering range of 400 ~ 550 \(^\circ\)C, the peak hardness of the QT sample is 66.4 HRC at 550 \(^\circ\)C, which is consistent with that obtained by repeated tempering\cite{11}. The peak hardness of the DCT sample is 66.1 HRC at 525 \(^\circ\)C. As the tempering temperature continues to increase, the hardness values decrease sharply. It can be found that the peak
hardness of M35 steel increases by 0.7 HRC and the tempering temperature to obtain peak hardness decreases by nearly 30 ℃.

Fig. 1 Effect of deep cryogenic treatment on Rockwell hardness of the M35 high-speed steel

It is worth noting that the Rockwell hardness of DCT samples changes more rapidly with tempering temperature. When tempered at 200 ~ 400 ℃, part of the internal stress caused by quenching in the steel is eliminated, and most of the microcracks are healed, leading to a decrease in hardness but an increase in toughness\[12\] . The local stress generated by cryogenic treatment eliminates the internal stress generated by partial quenching by movable dislocation\[4\], and the hardness continues to decrease. When the tempering temperature exceeds 400 ℃, fine granular carbides are precipitated, and with the increase of temperature, the number of carbides gradually increases\[13\], and the hardness increases as a result of precipitation strengthening. Cryogenic treatment promotes the precipitation of fine carbides\[14\], increases the precipitation strengthening effect of carbides, increases the peak hardness, and reduces the tempering temperature for obtaining peak hardness. When the tempering temperature is higher than the peak point of hardness, the hardness decreases as the carbide grows up. The cryogenic treatment promotes the transformation of the residual austenite and the precipitation of carbide in the matrix, which delays the rate of hardness decline. Red hardness test and analysis were performed on QT and DCT samples at four tempering temperatures of 200, 400, 525 and 650 ℃, as shown in Figure 3. Compared with Figure 2, after tempering at 600 ℃ for 1 h for 4 times, hardness of QT and DCT samples after tempering at 400 ℃ increased while hardness of other samples decreased. The red hardness of DCT samples with different tempering temperatures is basically the same as that of QT samples, with a difference of about 0.1 HRC. Among the DCT samples, the red hardness of 525℃-DCT sample was the highest and had good stability of red hardness.
3.2. Microstructure

Figure 3 shows the XRD patterns of M35 HSS after different treatments. As the tempering temperature increases, the content of retained austenite in QT and DCT samples decreases significantly. When the tempering temperature increases to 525 °C, the diffraction peak of retained austenite in M35 high speed steel basically disappears. On the contrary, with the increase of tempering temperature, the diffraction peaks of martensite and carbide increase, indicating that the content of generated tempered martensite and precipitated carbide increases. In addition, the diffraction peaks of martensite become narrow and accompanied by the shift of peak positions, indicating that the carbon content in the martensite matrix in M35 high-speed steel changes. Under the same tempering temperature, the intensity of residual austenite diffractive peak in QT and DCT samples is not significantly different, but the martensite diffraction peak of DCT samples becomes wider, which may be due to the increase of dislocation and vacancy in M35 high-speed steel due to cryogenic treatment, resulting in the diffraction peak broadening.

Fig. 4 shows the microstructure of M35 high speed steel after different treatments. When tempered
Fig. 4 Effect of deep cryogenic treatment tempering and temperature on microstructure of the M35 high-speed steel (a) 200 °C-QT; (b) 400 °C-QT; (c) 525 °C-QT; (d) 200 °C-DCT; (e) 400 °C-DCT; (f) 525 °C-DCT; (g) 650 °C-QT; (h) 650 °C-DCT

at 200 °C, a large number of acicular martensite and residual austenite were found in both QT and DCT samples. Carbides were mainly precipitated at grain boundaries and agglomerated, and a small amount of carbides were precipitated inside the grain. The distribution of carbide and grain size was very uneven (see Fig. 5a and 5d). With the increase of tempering temperature, the transformation of residual austenite to tempered martensite in QT and DCT samples is more complete. The quantity of tempered martensite in both QT and DCT samples increases, and there is a certain angle between the lath, and the residual austenite decreases significantly. Large amount of carbide precipitates inside the grain, and the grain size distribution is more uniform. At 400 °C, some carbides agglomerate at the grain boundary, and a large number of nearly spherical carbides with the size of 1-5 μm and some carbides with the size of less than 1 μm are precipitated in the grain boundary. The grain interior of DCT samples is dominated by fine carbides with a size less than 1μm, and the distribution of carbides on grain boundaries is more uniform (see Fig. 5b, 5c). When tempered at 525 °C, the carbides in the QT sample were evenly distributed, and a large number of fine carbides were precipitated in the grain, while the large carbides in the DCT sample were reduced (see Fig. 5c and 5f). When tempering at 650 °C, a large amount of carbides were precipitated in the QT sample, and the size of the carbides was more than 1 μm. The number of large irregular carbides in the DCT sample decreased (see Fig. 5g, 5h). Continuous cooling or long-term heat preservation at a temperature far lower than the formation temperature of martensite (-100 °C or below) can produce crystal defects and improve the lattice distortion range of supersaturated martensite on the matrix[17], and carbon and alloying elements gather at the defects.During the subsequent rise to room temperature, these clusters may act as or grow into nucleation sites of carbides and promote the precipitation of carbides[18].
Figure 5 shows the statistical results of grain size of M35 high speed steel after different treatments.

Fig. 5 Effect of deep cryogenic treatment on the grain size of the M35 high-speed steel

With the increase of tempering temperature, the grain size of M35 HSS increases monotonically, and the growth rate of grain size of QT sample is lower than that of DCT sample. When tempered at 200 °C, the grain size of DCT sample is higher than that of QT sample, which may be due to the uneven grain size distribution and the range is large. However, the grain size of DCT sample is relatively more uniform and the range is small, and the average grain size after calculation is slightly higher than that of QT sample. When tempering at 525 ~ 650 °C, the grain size of DCT sample is lower than that of QT sample. When tempering at 650 °C, the grain size of DCT sample decreases by 9.2%. This is because during cryogenic treatment, the stress generated by lattice shrinkage of martensite and retained austenite and the difference in thermal expansion coefficient promote the migration of movable dislocations, thus leading to grain refinement [3].

3.3. Friction and wear

Table 2 shows the friction coefficients of M35 high speed steel after different treatments. The friction coefficient of M35 high speed steel has no obvious difference with different tempering temperature and cryogenic treatment, which indicates that tempering temperature and cryogenic treatment have little influence on the friction reducing property of M35 high speed steel.

Table2 Friction coefficient of the M35 HSS after different DCT and QT.

| Treatment | Friction coefficient |
|-----------|----------------------|
| 200 °C -QT | 0.68                 |
| 200 °C -DCT | 0.65               |
| 400 °C -QT | 0.68                 |
| 400 °C -DCT | 0.67               |
| 525 °C -QT | 0.69                 |
| 525 °C -DCT | 0.69               |
| 650 °C -QT | 0.69                 |
| 650 °C -DCT | 0.69               |
The wear volume of the sample is shown in Fig.6. When the tempering temperature is 525 ℃, the hardness and wear volume of the QT sample are the highest and the wear volume is the lowest, and the wear volume of the DCT sample decreases by 7.1%. The wear volume of DCT samples decreased with different tempering temperatures, but the decreasing amplitude was different. According to the SEM photos of M35 high speed steel, when tempered at 525 ℃, the carbide precipitation content is high and evenly distributed. After cryogenic treatment, a large number of fine spherical carbides are distributed inside the grain, which improves the wear resistance of high speed steel.

Figure 7 shows the wear morphology of M35 high speed steel after different treatments. Both QT
and DCT samples with different tempering temperatures show scaly surface with different depth of furrow and a small amount of wear debris, showing typical characteristics of adhesive wear and abrasive wear. When tempering at 400 ℃, the furrow on the surface of Qt sample is deeper and more, and abrasive wear occurs, but the oxygen content is the lowest, and the degree of oxidative wear is less (see Fig. 8b). In the DCT sample, the furrows on the surface of the wear marks were shallow, mainly adhesive wear, and the abrasive wear was relieved (see Fig. 8e). When tempered at 525 ℃, the wear surface of the Qt sample presents fine scales and a very small amount of shallow furrows, showing adhesive wear, slight abrasive wear and oxidation wear (see Fig. 8c). The oxygen content in the DCT sample decreased slightly, but the area of the dark oxide layer increased (see Fig. 8f), which had an anti-wear effect to a certain extent[19]. When tempered at 200 and 650 ℃, there are slight furrows on the surface of Qt samples, which are mainly adhesive wear, abrasive wear and oxidation wear (see Fig. 8a, 8g). In the DCT sample, the furrow became shallow and was dominated by adhesive wear (see Fig. 8d and 8h).

4. Conclusion
1) With the increase of tempering temperature, the Rockwell hardness of M35 high speed steel after QT and DCT decreases first, then increases, and finally decreases sharply. The introduction of cryogenic treatment technology increases the peak hardness of M35 high speed steel by 0.7 HRC, and the tempering temperature for obtaining peak hardness decreases by nearly 30 ℃. In addition, the Rockwell hardness of DCT samples changes more rapidly with tempering temperature, and has good stability of red hardness.

2) With the increase of tempering temperature, the content of retained austenite in M35 high speed steel decreases gradually, and the tempering martensite is formed. The distribution of carbides is more uniform, and the grain size increases gradually and the distribution is more uniform. After deep cryogenic treatment, the grain size and irregular bulk carbides are reduced, and a large number of spherical carbides with size less than 1 μm are precipitated in the grain.

3) The friction coefficients of QT and DCT steel with different tempering temperatures are almost the same, which indicates that cryogenic treatment has little effect on the friction reducing property of HSS, but the wear resistance of DCT steel is obviously improved. The main wear mechanism of Si3N4 friction is adhesive wear and abrasive wear. When tempered at 525℃,QT and DCT high speed steels have the smallest wear volume and the best wear resistance.

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