Effect of Deep Cryogenic Time on Martensite Multi-Level Microstructures and Mechanical Properties in AISI M35 High-Speed Steel

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Abstract: High-speed steel is widely used for cutting tools due to its convenience of preparation and cost-effectiveness. Previous research has shown that deep cryogenic treatments improve the mechanical properties of high-speed steel, due to the transformation of the residual austenite and the precipitation of carbide, while few studies have researched martensitic changes. The variations in martensite multi-level microstructures in AISI M35 high-speed steel, treated over different deep cryogenic time periods, were investigated in this study. Meanwhile, the effect of these variations on the mechanical properties of the selected steel was discussed. It was found that prolonging deep cryogenic time facilitated an increase in dislocation, low-angle grain boundary, and the coincident-site lattice boundary (especially the twin boundary) of martensite. The size of the martensite block ($d_b$) and lath ($d_l$) decreased with deep cryogenic time. However, the effect on the microstructure was limited when the cryogenic treatment time exceeded 5 h. The increase in dislocation decreased the temperature for carbide precipitation and promoted fine carbide precipitation during tempering. The refinement of martensite multi-level microstructures and the greater precipitation of fine carbides gave the tempered specimens excellent impact toughness. The impact toughness of the tempered samples undergoing deep cryogenic treatment for more than 5 h was about 32% higher than the sample without deep cryogenic treatment.

Keywords: AISI M35 high-speed steel; deep cryogenic treatment time; martensite multi-level microstructures; mechanical properties

1. Introduction

High-speed steel (HSS) was a widely used tool steel which is characterized by its high hardness, great wear resistance, superior impact toughness, and excellent cutting ability [1–3]. Deep cryogenic treatment (DCT) can further optimize the microstructure and enhance the mechanical properties of HSS to meet the efficiency and quality requirements of modern cutting [4–10]. As a supplementary process of heat treatment, DCT is widely used, environmentally friendly, and easy to operate [9,11,12]. According to the previous literature, DCT has a positive effect on the hardness [13], toughness [14], wear resistance [15], corrosion resistance [16], and service life [17,18] of HSS. M. Priyadarshini reported that the AISI P20 tool, when deep cryogenically treated for 9 h, increased 35% in micro-hardness hardness and 28% in wear resistance compared to the as-received untreated tool [19]. Düzce University showed that the AISI H11 steel, when deep cryogenically treated for 9 h, increased 35% in micro-hardness hardness and 28% in wear resistance compared to the as-received untreated tool [20]. It can be seen that DCT can improve the properties of steel, but the choices of DCT soaking time are various, according to different researchers.

As is well known, the matrix of HSS is martensite (M), which plays an important role in the mechanical properties of steel [21,22]. Martensite microstructures can be described via the descending levels of prior austenite grain (PAG), martensitic packet (MP), martensitic block (MB), and martensitic lath (ML) [23]. Each PAG is divided into several packets...
and the packet is then subdivided into the block with the same orientation; one block is composed of several laths [22]. Previous research has indicated that the toughness of the steel is enhanced with the decrease in the packet and block size under the conditions of the same prior austenite grain size [24,25]. Moreover, S.L. Long revealed that MB is the most effective control unit of strength, while ML is the most effective control unit of toughness in 20CrNi2Mo steel [26]. Martensite multi-level microstructures are one of the most important structures in martensitic steels.

However, most studies on the DCT of the HSS are mainly focused on the residual austenite (RA) stability and secondary carbide (SCs: 0.1–5.0 \( \mu \)m) precipitation [27,28]. There are few studies on the evolution and morphology changes of lath martensite with different DCT parameters. The relationship between the mechanical properties and martensite multi-level microstructures of the deep cryogenically treated HSS has not been revealed, which hinders the study of the toughening mechanism of DCT to the lath martensite microstructure and makes it difficult to predict the properties and microstructures according to DCT parameters. Therefore, the martensite multi-level microstructures of HSS with different DCT parameters needs further research.

This paper investigates the effect of different DCT processing times on the variation of the martensitic multi-level microstructures and the mechanical properties (including Vickers hardness and impact toughness) of the AISI M35 HSS. The relationship between microstructure evolution and mechanical properties is discussed. This work reveals the evolution of multi-level microstructures with DCT soaking time and provides some assistance in selecting the appropriate DCT soaking time.

2. Experimental Details

The selected material, AISI M35, is one of the most common HSSs used for cutting tools (including helical and spline broaches, hobs, shaving cutters, and shaping cutters) [15,29]. The chemical compositions of AISI M35 (W6Mo5Cr4V2Co5) were measured using an optical emission spectrometer (OES), and the results are given in Table 1. Figure 1 shows the schematic diagram of the heat-treatment procedure. First, the steel was pretreated (880 °C/5 min) and then quenched (1200 °C/3 min) in oil to room temperature (RT). The specimen was fully austenitized to obtain a martensitic matrix. The quenched sample was kept at \( -196 \) °C (achieved by liquid nitrogen) for various pre-selected durations (x minutes/hours) before being heated back to RT. Finally, all samples (Q and \( D_{x\text{min}}-D_{a\text{th}} \)) were triple-tempered at 550 °C to ensure SCs precipitation. Details of the heat-treatment parameters are given in Table 2.

| Table 1. Chemical composition of the AISI M35 high-speed steel. |
|---------------------------------------------------------------|
| Parameters | Element (wt %) |
|-------------|---------------|
| C           | 0.92          |
| W           | 5.97          |
| Mo          | 5.13          |
| V           | 1.84          |
| Cr          | 3.82          |
| Co          | 5.00          |
| S           | 0.03          |
| P           | 0.03          |
| Fe          | Balance       |

| Table 2. Different heat treatments and sample codes. |
|---------------------------------------------------|
| Groups | Detail of Treatment | Sample Codes  |
|--------|---------------------|---------------|
| 1      | Quenching           | Q             |
| 2      | Quenching + tempering (550 °C × 2 h × 3) | Q-T           |
| 3      | Quenching + DCT (x min/h) | \( D_{x\text{min}} \) |
| 4      | Quenching + DCT (x min/h) + tempering (550 °C × 2 h × 3) | \( D_{x\text{min}}-T \) |
Figure 1. Schematic diagram of the heat treatment procedure.

Microstructure characterizations were performed with an X-ray diffraction instrument (XRD, X Pertpro, Panaco, The Netherlands), a scanning electron microscope (SEM, ULTRA PLUS, Zeiss, Germany), electron backscatter diffraction (EBSD, Crossbeam550, Zeiss, Germany), and transmission electron microscopy (TEM, G20, FEI Tecnai, USA). The temperature of carbide precipitation was measured with a differential scanning calorimeter (DSC, 404F3, Nach, Germany). The XRD was conducted using an Ultima IV (Cu Ka radiation) at 40 kV, 40 mA, and 0.02° step size. The 20 angular interval from 20° to 90° was step-scanned with 5°/min. The operating voltages for SEM and TEM were 15 kV and 200 kV, respectively. The EBSD experiments were conducted at a 25 kV and 0.15 μm step size.

The sample was electrolytically polished by the electrolyte, composed of alcohol (70 vol. %), perchloric acid (20 vol. %), and glycerol (10 vol. %) to analyze the distribution of SCs. The sample to be analyzed by OM and SEM was etched for ~60 s using nital, which is made up of concentrated nitric acid (4 vol. %) and ethyl alcohol (96 vol. %). An EBSD sample of 8 mm × 8 mm × 3 mm was polished by argon ion-beam milling to prevent deformation-induced transformation. The TEM specimen was prepared by grinding down from 400-μm to 50-μm-thick and slicing into 3-mm disks, then they were twin-jet electrolytically polished in a solution of 5 vol. % perchloric acid and 87.5 vol. % glacial acetic acid at 20 °C and 20–30 V.

In addition, a sample of 10 mm × 10 mm × 10 mm was used to measure the Vickers hardness. A sample of 10 mm × 10 mm × 55 mm was used to test the impact toughness with a V-notch. The hardness and impact toughness were performed at RT, and three samples were used in each group to reduce the possibility of test error.

The lattice strain (ε_{hkl}) was analyzed by XRD data. The main calculation formulae are as follows [21,22]:

\[ d = \frac{n\lambda}{2\sin\theta} \]  

(1)

\[ \varepsilon_{hkl} = \frac{(d_{hkl}) - d_0}{d_0} \]  

(2)

where \( d_{hkl} \) (Å) is the lattice space after heat treatments; \( d_0 \) is the lattice space without deformation; \( \lambda \) is the wavelength of incident X-ray (\( \lambda_{Cu} = 0.15406 \) nm); \( n \) is the order of diffraction (\( n = 1 \)). Martensite with a tetragonal structure meets the following:

\[ \frac{1}{d^2} + \frac{1}{c^2} = \frac{1}{a^2} \]  

(3)

where \( a \) and \( c \) are the lattice parameters. The tetragonality (c/a) can be calculated from Equations (1) and (3), after which the carbon concentration (C_c) of M can be estimated by the following:

\[ C_c = \frac{(c/a - 1)}{0.046} \]  

(4)
SEM images of twenty randomly selected positions are studied using the Image-Pro Plus software, version 6.0. SCs with sizes of 0.1–0.5 μm (SSC), 0.5–1.0 μm (MSC), and 1.0–5.0 μm (LSC) are measured using different-magnification SEM images to reduce error [30]. However, the carbides with sizes of less than 0.1 μm could not be counted using SEM images but instead required TEM micrography.

3. Results
3.1. Mechanical Properties

Figure 2a shows the average Vickers hardness of the samples, treated for different deep cryogenic durations. The hardness of the deep cryogenically treated samples (D3min–D5h) has a slight increase when the DCT processing time is below 5 h. However, the difference in the hardness is slight when the DCT soaking time is over 5 h. The deep cryogenic time has little effect on the hardness when it exceeds 5 h. The hardness of D5h, namely, ~899.38 HV1, increases by ~44 HV1 more than the quenched samples (Q), namely, 855.56 HV1. The studied samples in the DCT were selected from the initial section, the turning point, and the stabilization zone, according to the hardness variation. These selected samples were used together with the quenched samples to study the effect of cryogenic duration. The effect of DCT immersion time on the microstructures and mechanical properties was investigated via the Q, D5min, D5h, and D12h samples (Figure 2a).

As shown in Figure 2b, the black line represents the average Vickers hardness of the tempered sample and the red line shows the average impact toughness of the tempered sample. Tempering reduces the hardness of the selected steel but obviously increases its toughness, resulting in better overall properties. The impact toughness and hardness of the tempered samples increase with DCT processing time, while the increase is slight when the DCT soaking time is higher than 5 h. The impact toughness and hardness of the D5h-T sample are 2.45 MJ/m² and 867.05 HV1, respectively. The impact toughness of D5h-T is 32.4% higher than that of Q-T, and the hardness of D5h-T increases by ~23.8 HV1 compared with Q-T (845.10 HV1). D5h-T has the highest value of impact toughness and hardness, which is 2.47 MJ/m² and 868.90 HV1, respectively.
3.2. Microstructure Characteristics

Figure 3 shows the diffraction peaks corresponding to the M (α-Fe), M₆C, and MC of samples subjected to different DCT soaking times [31,32]. The diffraction peaks of γ-Fe (RA) are present in the Q sample (red circle) but are absent in the DCT samples (D₅₅min, D₅h, and D₁₂h). Clearly, DCT promoted the decomposition of RA. Figure 4a,b show that the {211}M and [110]M diffraction peaks of all samples moved left, especially the DCT samples. The leftward movement of the DCT samples was more severe than that of the Q sample. The martensitic lattice space increased with DCT processing time. Moreover, the shift of the {211}M and [011]M diffraction peaks of D₅h and D₁₂h was more severe than that of D₅₅min.

![XRD pattern of Q, D₅₅min, D₅h, and D₁₂h.](image)

Figure 3. XRD pattern of Q, D₅₅min, D₅h, and D₁₂h.

![Enlarged view of (a) {211}M and (b) [011]M diffraction peaks, and (c) the lattice strain of {211}M.](image)

Figure 4. Enlarged view of (a) {211}M and (b) [011]M diffraction peaks, and (c) the lattice strain of {211}M.

The {211}M peak is used to calculate the lattice strain of M by Equations (1) and (2) since it is less disrupted by other peaks (Figure 4a). The lattice strain is shown in Figure 4c. The tetragonality (c/a) and carbon concentration (Cₛ) are calculated from Equations (3) and (4) using the diffraction peaks of [011]M and {211}M (Figure 4a,b). The selection of [011]M is the highest peak of M diffraction [33]. The value of c/a and Cₛ are shown in Table 3.
Table 3. The martensite tetragonality and carbon concentration.

| Groups  | Tetragonality (c/a) | Carbon Concentration (Cc)/wt % |
|---------|---------------------|-------------------------------|
| Q       | 1.001482            | 0.032                         |
| D5min   | 1.004918            | 0.107                         |
| D5h     | 1.005337            | 0.115                         |
| D12h    | 1.005473            | 0.119                         |

Table 3 indicates that the value of c/a and Cc increases with the DCT processing time. The M in the selected steel was subject to tensile stress due to the dissolution of high-alloying elements in the alloy (21.7 wt %) [34]. The tensile stress of M increased dramatically when the DCT processing time is from 0 to 5 h (Figure 4c). However, the tensile stress of M increased slightly when the DCT processing time lengthened from 5 h to 12 h. The values of c/a and Cc in the D5h and D12h samples were similar.

Although RA can be observed in the Q sample via XRD, its fraction in the deep cryogenically treated samples is less than the detection limits of XRD. Therefore, SEM and EBSD were adopted to further study the phase distribution and morphology of the Q, D5min, D5h, and D12h samples. Figure 5a1–d1 show that all samples are composed of needle-shaped M, carbide, and a small amount of RA. Figure 5a2–d2 show that RA decreases with DCT processing time, and RA is hard to identify in the D5h and D12h samples. The volume fractions of RA in Q, D5min, and D12h samples are ~8 vol %, ~3 vol %, and ~1 vol %, respectively (Figure 5e). The volume fraction of RA decreases when DCT processing time increases from 0 to 5 h, but it is similar in D5h and D12h samples at ~1 vol %. The increase in deep-cryogenic time has a limited effect on the decomposition of RA when the deep-cooling time exceeds 5 h.

Figure 5. SEM micrographs and phase distribution maps of (a1, a2) Q, (b1, b2) D5min, (c1, c2) D5h, and (d1, d2) D12h, and (e) the volume percentage of the phases.
3.3. Dislocation and Martensite Multi-Level Microstructure Size

As shown in Figure 6a–d, many dislocations in the Q and DCT samples can be observed due to high lattice strain and plastic deformation during DCT. The dislocation increases with DCT time, and most fine carbides (M₆C, MC, and M₂₃C₆) are present in the matrix of these samples. D₅₅h and D₁₂₅h have the most dislocation and fine carbides. Meanwhile, the dislocation is entangled with carbides forming dislocation tangles, which enhance the material performance.

For measuring the dislocation details, geometrically necessary dislocation (GND) maps of these samples are presented in Figure 6a₂–d₂. High GND indicates a high-strain region. Figure 6a₂–d₂ show that the high-strain regions are concentrated at the martensitic boundaries, including the high-angle grain boundary (HAGB > 15°) and low-angle grain boundary (LAGB ≤ 15°). Moreover, the interface between M and RA phases represents the high-strain region. The distribution (Figure 6e) and average value (Figure 6f) of the GND density show that the average GND density increases with DCT processing time. In addition, the value of the average GND density in D₅₅min increases around 1.16 × 10¹⁴ m⁻² compared to Q, while D₅₅h increases by 1.96 × 10¹⁴ m⁻² compared to D₅₅min. The value of average GND density in D₁₂₅h and D₅₅h is similar, at 40.4 × 10¹⁴ m⁻² and 40.3 × 10¹⁴ m⁻², respectively.

Figure 7a–d show that the PAG is divided by several MP, which is subdivided into different MBs with parallel directions and different orientations. The MPs in the deep cryogenically treated samples were not analyzed because the effect of this low-temperature
treatment on MP is negligible. The distribution of the martensite boundary orientation angles with the EBSD map is shown in Figure 8a. The MLs were observed via TEM, as shown in Figure 8a–d. The average diameter of the MBs and MLs was calculated from EBSD maps (Figure 7a–d) and TEM micrographs (Figure 8a–d), respectively. Table 4 shows that MBs and MLs are refined after DCT. The longer the DCT processing time, the more refined the martensite multi-level microstructures. The sizes of MBs (\(d_b\)) in the \(D_{5h}\) and \(D_{12h}\) samples are 1.135 \(\mu m\) and 1.106 \(\mu m\), respectively. The sizes of MLs (\(d_l\)) in the \(D_{5h}\) and \(D_{12h}\) samples are 0.124 \(\mu m\) and 0.119 \(\mu m\), respectively. However, the value of \(d_b\) and \(d_l\) in \(D_{5h}\) and \(D_{12h}\) samples changes slightly. The \(d_b\) in \(D_{5h}\) and \(D_{12h}\) samples are 1.028 \(\mu m\) and 1.021 \(\mu m\), respectively. The \(d_l\) in \(D_{5h}\) and \(D_{12h}\) samples are 0.107 \(\mu m\) and 0.103 \(\mu m\), respectively.

**Figure 7.** IPF (inverse pole figure) maps of (a) Q, (b) D_{5min}, (c) D_{5h}, and (d) D_{12h} (PAB—prior austenite boundary, PB—packet boundary, BB—block boundary).

**Figure 8.** TEM micrographs of (a) Q, (b) D_{5min}, (c) D_{5h}, and (d) D_{12h} (AVG: average value).

**Table 4.** The size of martensite block \((d_b)\) and martensite lath \((d_l)\) under different heat treatments.

| Size/\(\mu m\) | Q  | D_{5min} | D_{5h} | D_{12h} |
|--------------|----|----------|--------|---------|
| \(d_b\)      | 1.135 | 1.106   | 1.028  | 1.021   |
| \(d_l\)      | 0.124 | 0.119   | 0.107  | 0.103   |
Figure 9 shows that a large amount of twin martensite (TM) in Q and DCT specimens can be observed via TEM. The average sizes of the TM in Q, D_{5min}, D_{5h}, and D_{12h} samples are 7.338 nm, 6.557 nm, 3.853 nm, and 3.278 nm, respectively. Clearly, the TM is refined with DCT soaking time. The refinement is evident when the DCT treatment time goes from 0 to 5 h, but the TM sizes in D_{5h} and D_{12h} specimens are similar.

3.4. Martensite Boundaries

The grain boundary can be considered to be the LAGB and HAGB, based on the misorientation angle of the adjoining grains. LAGB is the ML boundary and HAGB is the boundary of the MB (55–65°), MP (45–55°), and PAG (15–45°). As shown in Figure 10c–f, LAGBs mainly concentrate in the range where the crystallographic orientation is less than or equal to 2°; the fraction of LAGBs in this range increases with DCT processing time. The LAGB fractions in Q, D_{5min}, D_{5h}, and D_{12h} samples are 46.3 vol %, 50.8 vol %, 55.9 vol %, and 56.4 vol %, respectively (Figure 10b). There is a dramatic increase in the LAGB fractions from Q to D_{5h} samples, yet there is only a little growth in the D_{5h} to D_{12h} samples. DCT promotes the production of LAGBs in M, and the fraction of LAGB increases slowly as the DCT soaking time reaches 5 h.

Figure 11a–d give the M boundary maps combined with the CSL boundary. The general grain boundary is marked by black lines, while the coincident-site lattice (CSL) boundary is represented by colors (red, yellow, green, and blue). The CSL boundary is a special interface wherein the lattice satisfies the requirement of the new space lattice by sharing several lattice points [35]. The CSL boundary is categorized by Σ, which is defined as the inverse of common lattice points in the boundaries between the two adjoining grains or crystals. Figure 11a–d show that all samples have CSL boundaries, especially the DCT samples. Σ3 indicates that one of the crystals with the same dot structure is rotated by 60° relative to the other crystal, to the [111] crystal band axis (Figure 11f). Therefore, Σ3 is also the twin crystal boundary in M. The frequency of Σ3 in D_{5h} and D_{12h} samples (namely, ~19%) is dramatically higher than that in the Q (Figure 11e) sample. The increase in Σ3 represents the increase in fresh TM. It can be inferred that finer TM was formed during the DCT process, increasing the Σ3 boundaries (Figure 11) and refining the TM size (Figure 9).
Figure 9. TEM micrographs of twin martensite in (a) Q, (b) D_{5min}, (c) D_{5h}, and (d) D_{12h}. (a) The distribution of the martensitic boundary details, the (b) proportions, and (c–f) the distribution of LAGBs.

Figure 10. (a) The distribution of the martensitic boundary details, the (b) proportions, and (c–f) the distribution of LAGBs.

Figure 11. Martensitic CSL (coincident-site lattice) boundary maps in (a) Q, (b) D_{5min}, (c) D_{5h}, and (d) D_{12h}. (a) The distribution of the martensitic boundary details, the (b) proportions, and (c–f) the distribution of LAGBs.

Σ11, Σ33c, and Σ41c represent the crystals, which are rotated with the same dot structure by 50.48°, 58.98°, and 55.88°, relative to the other crystal in the [111] crystal band axis, respectively. As shown in Figure 11e, the frequency of other CSL boundaries in M (Σ11, Σ33c, and Σ41c) is much less than Σ3. Σ11, Σ33c, and Σ41c, which also increase with DCT time, but they show a lower rise than Σ3.

4. Discussion
4.1. Effect of Microstructures Evolution on SCs Precipitation

Precipitation strengthening is mainly based on the precipitation of SCs (M₆C (M: Fe/W/Mo), MC (M: V/Fe), and M₂₃C₆ (M: Cr/Fe)) in AISI M35 HSS [21]. As shown in Figure 12e, the distribution of SCs (0.1–1 μm) in the Q and DCT samples is similar. The
interstitial diffusion coefficient of carbon and the self-diffusion coefficient of iron both tend to zero at \(-196 \, ^\circ\text{C}\) [36], indicating few SCs precipitations.

![Figure 12. (a) DSC curves of Q and DCT samples, (b-d) the density of SCs, and the distribution of SCs in the (e) untempered and (f) tempered samples.](image)

Although DCT hinders the diffusion activity of atoms, the supersaturated carbon atoms in M are extruded out of the M lattice owing to the high lattice contraction of M under ultra-low temperatures (Figure 4c) [22]. The fraction of fine SSCs (0.1–0.2 \(\mu\text{m}\)) in the DCT samples is a little higher than the quenched sample and increases with DCT processing time (Figure 12e). Plenty of dislocations generated by high plastic deformation (Figure 6) and the fresh M transformed from RA (Figure 5) [34] are beneficial to the precipitation of fine SSCs [14,37]. Nevertheless, the \(C_c\) increases after DCT, as shown in Table 3. On the one hand, the value of \(C_c\) in fresh M is higher than in the virgin one. On the other hand, the DCT sample that was heated to room temperature led to the increase in "c" and the decrease in "a", increasing the value of \(C_c\) [33]. In addition, the fraction of SCs with a particle size of 0.6–0.7 \(\mu\text{m}\) in the untempered samples dominates the SCs (0.1–1.0 \(\mu\text{m}\)).

The carbide precipitation in HSS mainly occurs during the tempering process, due to the diffusion coefficient, which is affected by temperature. Figure 12a shows that the peak temperatures of carbide precipitation in the Q, \(D_{5\text{min}}\), \(D_{5\text{h}}\), and \(D_{12\text{h}}\) samples are 525 \(^\circ\text{C}\), 515 \(^\circ\text{C}\), 485 \(^\circ\text{C}\), and 475 \(^\circ\text{C}\), respectively. SCs will precipitate sufficiently during tempering since the tempering temperature (550 \(^\circ\text{C}\)) is higher than the peak temperature of carbide precipitation in the Q and DCT samples. It can be seen that the temperature of carbide precipitation decreases with DCT process time. Fine carbides generated during DCT provide nucleation points for carbide precipitation during subsequent tempering (Figure 12e). Meanwhile, the increase in dislocation accelerates the diffusion process in the crystal, decreasing the temperature of carbide precipitation [38]. The dislocations increase with DCT soaking time (Figure 12e), so the peak of carbides precipitation declines accordingly.
Figure 12b–d,f display the density of SCs (0.1–5.0 \( \mu m \)) and the distribution of SCs (0.1–1.0 \( \mu m \)) in Q-T, D5min-T, D5h-T, and D12h-T samples. As most researchers reported [39–41], the density of SCs increases with the DCT processing time. In addition, the density of SCs has a significant improvement when the DCT time increases from 0 to 5 h. The increase in dislocation and the fine carbide precipitation during DCT promote the precipitation of SCs during tempering. However, the value of SC density in D5h-T and D12h-T is similar because the difference in microstructure (M and carbides) between D5h-T and D12h-T is slight. The densities of SSCs (0.1–0.5 \( \mu m \)) in Q-T, D5min-T, D5h-T, and D12h-T are 6.14 \( \times 10^{10} \) m\(^{-2} \), 6.48 \( \times 10^{10} \) m\(^{-2} \), 7.05 \( \times 10^{10} \) m\(^{-2} \), and 7.15 \( \times 10^{10} \) m\(^{-2} \), respectively. The densities of MSCs in Q-T, D5min-T, D5h-T, and D12h-T are 8.78 \( \times 10^{10} \) m\(^{-2} \), 9.01 \( \times 10^{10} \) m\(^{-2} \), 9.15 \( \times 10^{10} \) m\(^{-2} \), and 9.20 \( \times 10^{10} \) m\(^{-2} \), respectively. Clearly, the rise in the SSCs is more dramatic than that in the MSCs. The densities of LSCs in Q-T, D5min-T, D5h-T, and D12h-T are 3.64 \( \times 10^{10} \) m\(^{-2} \), 3.70 \( \times 10^{10} \) m\(^{-2} \), 3.81 \( \times 10^{10} \) m\(^{-2} \), and 3.82 \( \times 10^{10} \) m\(^{-2} \), respectively. The density value of the LSCs in all samples differs little. Figure 12f shows that the fractions of SSCs (0.1–0.2 \( \mu m \)) in D5h-T and D12h-T are higher by ~4% than those in Q and D5min-T. These results show that the increase in DCT processing time has a more obvious effect on the precipitation of fine SCs. Similarly, the fraction of SCs with a particle size of 0.6–0.7 \( \mu m \) in the tempered samples dominates the SCs (0.1–1.0 \( \mu m \)).

4.2. Effect of Martensite Multi-Level Microstructures on Mechanical Properties

According to the above results, the hardness of untempered samples that were deep-deep cryogenically treated for more than 5 h improved by ~44 HV\(_1\) more than the quenched sample due to the combined action of RA transformation (Figure 5) and dislocation increases (Figure 11). However, the hardness in the D5h-T sample only increased by ~23.8 HV\(_1\) more than that in the Q-T sample (Figure 2). Although the precipitation of fine SCs enhances the precipitation hardening process, the weakening of dislocation strengthening and the reduction in alloying elements in M leads to a decrease in hardness [22,42]. The increase in SC (0.1–5.0 \( \mu m \)) density with the DCT processing time simultaneously contributes to the homogeneity of hardness [18].

Previous studies reported that there is always an opposite relationship between hardness and impact toughness [12,43]. However, the impact toughness in D5h-T is ~32.4% higher than that in Q-T (Figure 2). The tempered samples exhibited a dramatic improvement in impact toughness, based on a few increases in hardness after the DCT process. The increase in SCs precipitation is one reason [44], while the evolution of M multi-level microstructures also plays a significant role.

M has a certain ductility compared with carbides [21], making a great contribution to impact toughness. Plenty of dislocation lines that are generated from vacancies and carbon atom segregation will occur during DCT, due to the lattice contraction of M and drastic temperature changes (Figure 6). The fresh MLs are formed with the dislocation lines as the boundary [22,45], which represents the refinement of M (Table 4). Meanwhile, the fresh M formed from RA is more refined than the original M.

The addition of dislocation lines and LAGBs during DCT promotes the generation of new martensitic boundaries (BBs and LBs). The formation of the new boundary contributes to the refinement of M multi-level microstructures, including MB and MP. Previous research showed that the cracks have large deflections at the martensitic boundaries, which means that the crack propagation is hindered by all the PBs, BBs, and LBs [22]. The increase in MB and MP can hinder the crack propagation path, which is more effective than ML [45]. Because both PB and BB boundaries are high-angle grain boundaries (HAGBs), HAGBs are high-energy boundaries and require more energy consumption to propagate across the boundary. Therefore, large deflections may occur at the PB and BB boundaries, while the crack propagation at the ML boundaries (LAGBs) mainly exhibits small deflections. The hindering effect of MB boundaries on crack propagation is similar to the MP boundaries, yet the size is far smaller than the pack size [22]. Meanwhile, LAGBs are less likely to cause stress concentrations and have fewer crack initiation points, due to their lower energy.
boundaries and stronger interfacial binding forces [26]. In addition, several investigations show that low-$\Sigma$ CSL boundaries (e.g., $\Sigma 3$) exhibit higher resistance to various types of intergranular degradation compared with random boundaries, enhancing the properties of the materials [35,46]. In conclusion, the refinement of M multi-level microstructures improves the impact toughness of tempered samples.

5. Conclusions

This study presents the evolution of martensitic multi-level microstructures for AISI M35 HSS that was deep cryogenically treated, with different DCT soaking times (0–48 h). Meanwhile, the effect of these microstructural variations on the mechanical properties (Vickers hardness and impact toughness) of the tempered samples was also discussed. The following conclusions can be derived:

1. The transformation of RA and the high plastic deformation that occurs during the DCT process increase the martensitic lattice strain and dislocations, reducing the temperature of carbide precipitation. The effect of DCT soaking time on the SCs precipitation of the DCT samples is limited. However, the increase in deep cryogenic time notably promotes the precipitation of fine carbides in tempered samples when the time is less than 5 h.

2. The rise in DCT processing time has a remarkable refinement of the martensite multi-level microstructures (including $d_b$ and $d_l$) due to the formation of numerous fresh martensite and martensitic laths. However, DCT immersion time has a limited effect on the martensite multi-level microstructures when the DCT processing time is longer than 5 h. The addition of dislocations and LAGBs promotes the generation of new boundaries (BBs and LBs), contributing to the impact toughness of tempered samples.

3. The hardness of untempered samples that were deep-cryogenically treated for more than 5 h was ~900 HV$_1$, improved by ~$44$ HV$_1$ compared to the Q samples because of the transformation of RA and the increase in dislocation. The hardness in $D_{5h}$-T is 867.05 HV$_1$, which rose by ~$22$ HV$_1$ more than that in Q-T, due to the precipitation of the SCs. Moreover, the impact toughness in $D_{5h}$-T is 2.45 MJ·m$^{-2}$, which is 32.4% higher than Q-T, owing to the refinement of M multi-level microstructures and the massive precipitation of SCs (especially the SSCs). When the DCT processing time is higher than 5 h, the increase in DCT immersion time has little effect on the other properties (Vickers hardness and impact toughness) of the selected steel.

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**References**

1. Chaus, A.S.; Bračík, M.; Sahul, M.; Dománková, M. Microstructure and properties of M2 high-speed steel cast by the gravity and vacuum investment casting. *Vacuum* 2019, 162, 183–198. [CrossRef]
2. Jiao, W.C.; Li, H.-B.; Feng, H.; Wang, H.-J.; Jiang, Z.-H.; Wu, W. High-temperature annealing significantly enhances intrinsic hot workability of the as-cast high-nitrogen M42 high-speed steel. *Metall. Mater. Trans. A* 2022, 53, 2426–2451. [CrossRef]
Materials 2022, 15, 6618

3. Peng, H.; Hu, L.; Li, L.; Zhang, L.; Zhang, X. Evolution of the microstructure and mechanical properties of powder metallurgical high-speed steel 5390 after heat treatment. J. Alloys Compd. 2018, 740, 766–773. [CrossRef]

4. Qu, M.; Wang, Z.; Li, H.; Lv, Z.; Sun, S.; Fu, W. Effects of mischmetal addition on phase transformation and as-cast microstructure characteristics of M2 high-speed steel. J. Rare Earths 2013, 31, 628–633. [CrossRef]

5. Xiao, L.; Li, S.; Xu, J.; Zhao, Z.; Xiang, H.; Bao, X.; Fiao, S.; Peng, Z.; Pan, L.; Liang, X.; et al. Failure mechanism and improvement process of preparing carbide coating on high speed steel by thermal diffusion reaction. Surf. Coat. Technol. 2020, 404, 126398. [CrossRef]

6. Martins, P.S.; Gonçalves Carneiro, J.R.; Ba, E.C.T.; Vieira, V.F. Study on roughness and form errors linked with tool wear in the drilling process of an Al-Si alloy under high cutting speed using coated diamond-like carbon high-speed steel drill bits. J. Manuf. Process. 2021, 62, 711–719. [CrossRef]

7. Gsellmann, M.; Klünsner, T.; Mitterer, C.; Krobath, M.; Wurmshuber, M.; Leitner, H.; Ecker, W.; Marsoner, S.; Maiер-Kiener, V.; Kien, D.; et al. Strength ranking for interfaces between a TiN hard coating and microstructural constituents of high speed steel determined by micromechanical testing. Mater. Des. 2021, 204, 109690. [CrossRef]

8. Pan, Y.; Pi, Z.; Liu, B.; Xu, W.; Zhang, C.; Qu, X.; Lu, X. Influence of heat treatment on the microstructural evolution and mechanical properties of W6Mo5Cr4V2Co5Nb (825 K) high speed steel. Mater. Sci. Eng. A 2020, 787, 134980. [CrossRef]

9. Akınçoğlu, G. Investigation of the effect of cryogenic treatment cubic boron nitride turning insert tools. J. Mater. Eng. Perform. 2021, 30, 1280–1288. [CrossRef]

10. Đurica, J.; Pačinová, J.; Dománková, M.; Čapliovič, L.; Čapliovičová, M.; Hrušovská, L.; Malovcová, V.; Jurčí, P. Changes in microstructure of leadeduritic tool steel due to vacuum austenitizing and quenching, sub-zero treatments at −140 °C and tempering. Vacuum 2019, 170, 108977. [CrossRef]

11. Li, J.; Min, Y.; Wang, P.; Cai, X.; Wu, X. Analysis of distortion mechanism of a cold Work tool steel during quenching and deep cryogenic treatment. Met. Mater.-Int. 2018, 25, 546–558. [CrossRef]

12. Bai, X.; Zheng, L.; Cui, J.; Wu, S.; Song, R.; Xie, D.; Wang, D.; Li, H. Effect of cryogenic treatment on microstructure and mechanical properties of 0Cr12MnSn4Mo3Al steel. J. Mater. Eng. Perform. 2017, 26, 5079–5084. [CrossRef]

13. Jovičević-Klug, P.; Podgornik, B. Comparative study of conventional and deep cryogenic treatment of AISI M3:2 (EN 1.3395) high-speed steel. J. Mater. Res. Technol. 2020, 9, 13118–13127. [CrossRef]

14. Katoch, S.; Singh, V.; Sehgal, R. Mechanical properties and microstructure evaluation of differently cryogenically treated AISI-H11 steel. Int. J. Steel Struct. 2019, 19, 1381–1392. [CrossRef]

15. Jovičević-Klug, M.; Jovičević-Klug, P.; Kranjec, T.; Podgornik, B. Cross-effect of surface finishing and deep cryogenic treatment on corrosion resistance of AISI M35 steel. J. Mater. Res. Technol. 2021, 14, 2365–2381. [CrossRef]

16. Shinde, T.; Pruncu, C.; Dhokey, N.B.; Parau, A.C.; Vladescu, A. Effect of deep cryogenic treatment on corrosion behavior of AISI H13 die Steel. Materials 2021, 14, 131790. [CrossRef]

17. Hariharan, K.B.; Saravanaan, S.; Parkunan, N. Life time improvement of D7 tool steel by cryogenic treatment. Mater. Today Proc. 2020, 21, 619–621. [CrossRef]

18. Kumar, T.V.; Thirumurugan, R.; Viswanath, B. Influence of cryogenic treatment on the metallurgy of ferritic alloys: A review. Mater. Manuf. Processes 2017, 32, 1789–1805. [CrossRef]

19. Priyadarshini, M.; Behera, A.; Biswas, C.K. Effect of sub-zero temperatures on wear resistance of AISI P20 tool steel. J. Braz. Soc. Mech. Sci. Eng. 2020, 42, 212. [CrossRef]

20. Özbek, N.A. Effects of cryogenic treatment types on the performance of coated tungsten tools in the turning of AISI H11 steel. J. Mater. Res. Technol. 2020, 9, 9442–9456. [CrossRef]

21. Lyu, C.; Zhou, J.; Zhang, X.; Yao, Y.; Zhang, Y. Effect of heat treatment on microstructure and impact toughness of a Tungsten-Molybdenum powder metallurgical high-speed steel. Mater. Sci. Eng. A 2021, 815, 141268. [CrossRef]

22. Fan, S.; Hao, H.; Meng, L.; Zhang, X. Effect of deep cryogenic treatment parameters on martensite multi-level microstructures and properties in a lath martensite/ferrite dual-phase steel. Mater. Sci. Eng. A 2021, 810, 141022. [CrossRef]

23. Mostaghimi, M.; Safyari, M. Temperature mitigates the hydrogen embrittlement sensitivity of martensitic steels in slow strain rates. Vacuum 2022, 202, 11187. [CrossRef]

24. Jun, L.Z.; Chang, S.J.; Hang, S.; Hua, D.Y.; Fu, Y.C.; Xing, Z. Effect of substructure on toughness of lath martensite/bainite mixed structure in low-carbon steels. J. Iron Steel Res. Int. 2010, 17, 40–48.

25. Swarr, T.; Krauss, G. The effect of structure on the deformation of as-quenched and tempered martensite in a Fe-0.2 pct C alloy. Metall. Trans. A 1976, 7, 41–48. [CrossRef]

26. Long, S.L.; Liang, Y.L.; Jiang, Y.; Liang, Y.; Ming, Y.; Yi, Y.L. Effect of quenching temperature on martensite multi-level microstructures and properties of strength and toughness in 20CrNi2Mo steel. Mater. Sci. Eng. A 2016, 676, 38–47. [CrossRef]

27. Cardoso, P.H.S.; Israel, C.L.; da Silva, M.B.; Klein, G.A.; Soccol, L. Effects of deep cryogenic treatment on microstructure, impact toughness and wear resistance of an AISI D6 tool steel. Wear 2020, 456–457, 203832. [CrossRef]

28. Fantinelli, D.G.; Parcianello, C.T.; Rosendo, T.S.; Reguly, A.; Tier, M.D. Effect of heat and cryogenic treatment on wear and toughness of HSS AISI M2. J. Mater. Res. Technol. 2020, 9, 12354–12363. [CrossRef]

29. Xu, G.; Huang, P.; Wei, Z.; Feng, Z.; Zu, G. Microstructural variations and mechanical properties of deep cryogenically treated AISI M35 high-speed steel tempered at various temperatures. J. Mater. Res. Technol. 2022, 17, 3371–3383. [CrossRef]
30. Das, D.; Dutta, A.K.; Ray, K.K. Sub-zero treatments of AISI D2 steel: Part II. Wear behavior. Mater. Sci. Eng. A 2010, 527, 2194–2206. [CrossRef]

31. Peng, H.; Hu, L.; Ngai, T.; Li, L.; Zhang, X.; Xie, H.; Gong, W. Effects of austenitizing temperature on microstructure and mechanical property of a 4-GPa-grade PM high-speed steel. Mater. Sci. Eng. A 2018, 719, 21–26. [CrossRef]

32. Chaus, A.S.; Sahul, M. On origin of delta eutectoid carbide in M2 high-speed steel and its behaviour at high temperature. Mater. Lett. 2019, 256, 126605. [CrossRef]

33. Kurdjumov, G.V. Martensite crystal lattice, mechanism of austenite-martensite transformation and behavior of carbon atoms in martensite. Metall. Trans. A 1976, 74, 999–1011.

34. Villa, M.; Pantleon, K.; Somers, M.A.J. Evolution of compressive strains in retained austenite during sub-zero celsius martensite formation and tempering. Acta Mater. 2014, 65, 383–392. [CrossRef]

35. Akhiani, H.; Nezakat, M.; Sanayei, M.; Szpunar, J. The effect of thermo-mechanical processing on grain boundary character distribution in Incoloy 800H/HT. Mater. Sci. Eng. A 2015, 626, 51–60. [CrossRef]

36. Gale, W.F.; Totemeier, T.C. Smithells Metals Reference Book, 8th ed.; Elsevier Butterworth-Heinemann: Oxford, UK, 2004.

37. Kumar, S.; Nagraj, M.; Bongale, A.; Khedkar, N. Deep cryogenic treatment of AISI M2 tool steel and optimisation of its wear characteristics using taguchi’s approach. Arab. J. Sci. Eng. 2018, 43, 4917–4929. [CrossRef]

38. Li, S.; Min, N.; Li, J.; Wu, X.; Li, C.; Tang, L. Experimental verification of segregation of carbon and precipitation of carbides due to deep cryogenic treatment for tool steel by internal friction method. Mater. Sci. Eng. A 2013, 575, 51–60. [CrossRef]

39. Xu, X.; Ren, X.; Hou, H.; Luo, X. Effects of cryogenic and annealing treatment on microstructure and properties of friction stir welded TA15 joints. Mater. Sci. Eng. A 2021, 804, 140750. [CrossRef]

40. Yan, Z.; Liu, K.; Eckert, J. Effect of tempering and deep cryogenic treatment on microstructure and mechanical properties of Cr–Mo–V–Ni steel. Mater. Sci. Eng. A 2020, 787, 139520. [CrossRef]

41. Jurčí, P.; Šurica, J.; Dlouhý, I.; Horník, J.; Planieta, R.; Kralovič, D. Application of −140 °C sub-zero treatment for Cr-V ledeburitic steel service performance improvement. Metall. Mater. Trans. A 2019, 50, 2413–2434. [CrossRef]

42. Shi, Z.M.; Gong, W.; Tomota, Y.; Harjo, S.; Li, J.; Chi, B.; Pu, J. Study of tempering behavior of lath martensite using in situ neutron diffraction. Mater. Charact. 2015, 107, 29–32. [CrossRef]

43. Li, S.; Yuan, X.; Jiang, W.; Sun, H.; Li, J.; Zhao, K.; Yang, M. Effects of heat treatment influencing factors on microstructure and mechanical properties of a low-carbon martensitic stainless bearing steel. Mater. Sci. Eng. A 2014, 605, 229–235. [CrossRef]

44. Sarkari Khorrami, M.; Mostafaei, M.A.; Pouraliakbar, H.; Kokabi, A.H. Study on microstructure and mechanical characteristics of low-carbon steel and ferritic stainless steel joints. Mater. Sci. Eng. A 2014, 608, 35–45. [CrossRef]

45. Weng, Z.; Gu, K.; Wang, K.; Liu, X.; Wang, J. The reinforcement role of deep cryogenic treatment on the strength and toughness of alloy structural steel. Mater. Sci. Eng. A 2020, 772, 138698. [CrossRef]

46. Tummalapalli, M.K.; Szpunar, J.A.; Prasad, A.; Bichler, L. EBSD studies on microstructure and crystallographic orientation of UO2-Mo composite fuels. Nucl. Eng. and Technol. 2021, 53, 4052-4059. [CrossRef]