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Abstract

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Full Text

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3DAP Study of C Segregation Behavior during Deep Cryogenic Treatment of High-Carbon High-Alloy Steel*

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Abstract High-carbon high-alloy steel SDC99 was austenitized at 1030 °C for 30 min and then oil-quenched, deep cryogenically treated in liquid nitrogen at −196 °C for 8 h, and tempered at 210 °C for 2 h. Three-dimensional atom probe (3DAP) technology was used to analyze the spatial distribution of C atoms in the quenched, deep-cryogenic, and tempered states; XRD was used to study the changes in martensite axial ratio and C content in martensite under the three heat-treatment conditions; and SEM was used for in situ observation of carbide morphology before and after deep cryogenic treatment. The results show that during deep cryogenic treatment, C atoms segregate at martensite twin boundaries, forming segregation zones with a thickness of 5–10 nm. During low-temperature tempering at 210 °C, C further segregates, forming a carbon-rich phase or forming $M_{23}C_6$-type carbides with alloying atoms.

Keywords high-carbon high-alloy steel; deep cryogenic treatment; C segregation; carbide morphology; three-dimensional atom probe (3DAP)

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CARBON SEGREGATION BEHAVIOR OF HIGH-CARBON HIGH-ALLOY STEEL DURING DEEP CRYOGENIC TREATMENT USING 3DAP

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ABSTRACT Deep cryogenic treatment (DCT) is a supplement to conventional heat treatment, which usually involves cooling the material to liquid nitrogen temperature around −196 °C for a given soaking time and then heating back to the room temperature. As claimed in many pioneering researchers, DCT can evidently improve the hardness and wear resistance of high-carbon high-alloy steel and has been widely used to die steels, cutting tools, carburizing steels and barrels. The improvement of mechanical properties by DCT can be attributed to the transformation from retained austenite to martensite, the fine dispersion of nanoscale carbide precipitate and the removal of residual stresses. However, the nanoscale carbide precipitate is still lack of evidence and the interpretation of carbon segregation behavior during DCT is still unconvincing. In this work, the high-carbon high-alloy steel SDC99 is first austenized at 1030 °C for 30 min and then immersed in liquid nitrogen for 8 h and finally tempered at 210 °C for 2 h. The spatial distributions of carbon atom and alloy element concentration in quenched, DCT treated and tempered samples are analyzed by three dimensional atom probe (3DAP), respectively. In addition, the axial ratio and carbon content of martensite are studied using XRD and the carbide morphology before and after DCT are also observed in situ by SEM. The results indicate that after quenching from 1030 °C to room temperature, the volume fraction of retained austenite in SDC99 is about 21.1%. The retained austenite is soft and unstable which can easily transfer to martensite at lower temperatures. Carbon atoms will segregate slightly due to self-tempering. However, other alloy atoms do not segregated with carbon atoms. After quenching from 1030 °C to room temperature and then cooling in nitrogen for 8 h, the volume fraction of retained austenite in SDC99 will decrease to 7.4%. Carbon atoms will segregate along the twin boundary of martensite and form a segregation area with a thickness about 5~

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10 nm. There is no carbide precipitate after DCT. Furthermore, carbon atoms segregate again during heating up back to room temperature from −196 ℃. After tempering at 210 ℃ for 2 h, the volume fraction of retained austenite is almost 5.4%. Both carbon and alloy atoms will segregate during tempering at 210 ℃. With the increase of tempering time, the carbon segregation will aggravate and result in a C-rich phase or form the $M_{23}C_6$ carbide combined with other alloy element. This is one of the main reasons increasing the wear resistance of tool steels.

KEY WORDS high-carbon high-alloy steel, deep cryogenic treatment (DCT), carbon segregation, carbide morphology, 3DAP

Deep cryogenic treatment (DCT) refers to a heat-treatment process in which a workpiece is placed in a low-temperature environment below −130 ℃ (usually liquid nitrogen) and held there, thereby improving its hardness, wear resistance, and dimensional stability. This process can markedly improve the wear resistance of high-carbon high-alloy steels such as cold-work die steels, bearing steels, carburizing steels, and high-speed steels; however, its microscopic mechanism remains unclear and has become one of the research hotspots at home and abroad[^1]. Clarifying the effect of the deep cryogenic process on carbide precipitation is the key to studying the mechanism by which wear resistance is improved. Huang et al.[^2] statistically analyzed the carbide size distribution of M2 high-speed steel before and after deep cryogenic treatment and found that the carbide particle size decreased from 0.9 μm before deep cryogenic treatment to 0.6 μm after deep cryogenic treatment. Das et al.[^3] used scanning electron microscopy to analyze the size and distribution of carbides in D2 steel after deep cryogenic treatment. Meng et al.[^4] observed carbides in Fe-12Cr-Mo-V-1.4C after deep cryogenic treatment by transmission electron microscopy and concluded that expansion and contraction of the martensite lattice promoted the precipitation of fine η-carbides. Li et al.[^5–8] used internal-friction methods to study the effect of deep cryogenic treatment on the Snoek peak and SKK peak of cold-work die steel, and considered that deep cryogenic treatment enhanced the interaction between C atoms and dislocations. Current studies all support the view that deep cryogenic treatment promotes the precipitation of nanoscale carbides. However, the diffusion ability of C atoms decreases exponentially with decreasing temperature, and it is generally believed that C atoms cannot move below −100 ℃[^9], which makes it impossible to explain the phenomenon of carbide precipitation after deep cryogenic treatment. In addition, the above characterization methods are not sufficiently accurate or intuitive for analyzing nanoscale carbides precipitated during the deep cryogenic process; more precise equipment is needed to directly observe carbon segregation during deep

cryogenic treatment.

Three-dimensional atom probe (3DAP) can provide the distribution of atoms of different chemical elements in a specimen in nanoscale space, and is one of the microanalytical techniques with the highest analytical precision at present. Zhu et al.[^10] studied C segregation during low-temperature tempering of Fe-Ni-C alloy and AISI 4340 (40CrNi2Mo) alloy steel, and for the first time revealed the three-dimensional structure of C-rich regions and microscale defects. Wilde et al.[^11] used 3DAP to study Cottrell atmospheres in three low-carbon steel specimens with different C contents after quenching from 1000–1100 ℃ and subsequent room-temperature aging. Liu Qingdong et al.[^12-14] studied the nucleation, growth, and coarsening of alloy carbides in tempered martensite. It can therefore be seen that three-dimensional atom probe can directly reveal the microscopic morphology of nanoscale precipitates. However, no 3DAP characterization of C segregation behavior during deep cryogenic treatment of high-carbon high-alloy steel has yet been reported. Therefore, in this work, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were combined with 3DAP to study the spatial distribution of C atoms in a high-carbon high-alloy steel during quenching, deep cryogenic treatment, and tempering; the microstructural evolution and the diffusion, segregation, and precipitation processes of C were investigated, and the mechanism of C segregation/carbide precipitation during deep cryogenic treatment was discussed.

1 Experimental Method

The experiment used SDC99, a high-strength and tough cold-work die high-carbon high-alloy steel independently developed by this research group. Its chemical composition (mass fraction, %) was: C 0.83, Si 0.57, Mn 0.51, Cr 9.37, Mo 1.46, V 0.28, balance Fe; its atomic fractions (%) were: C 3.73, Si 1.01, Mn 0.50, Cr 9.72, Mo 0.82, V 0.30, balance Fe. The three heat-treatment processes are shown in Table 1. The annealed specimens were austenitized at 1030 ℃ for 30 min and then oil-quenched; some of the quenched specimens were retained, while the remaining specimens were taken out after being held in a liquid-nitrogen tank for 8 h. Some specimens after deep cryogenic treatment were retained, and the remaining specimens were tempered at 210 ℃ for 2 h.

Table 1 Heat treatment processes of SDC99 steel and hardness, volume fraction of retained austenite

Process	Heat treatment	Hardness / HRC	V_γ / %
Quenching	Quenching, 1030 ℃, 30 min	62	21.1

Process	Heat treatment	Hardness / HRC	V_γ / %
DCT	Quenching, 1030 ℃, 30 min+DCT, −196 ℃, 8 h	64	7.4
Tempering	Quenching, 1030 ℃, 30 min+DCT, −196 ℃, 8 h+tempering, 210 ℃, 2 h	63	5.4

Note: DCT—deep cryogenic treatment, V_γ—volume fraction of retained austenite.

The three heat-treated specimens were cut by wire electrical discharge machining into samples with dimensions of 10 mm × 10 mm × 10 mm. An HD 9-45 hardness tester was used to measure Rockwell hardness, so as to characterize changes in the macroscopic properties of the material. Phase analysis was carried out using a D/max-2200 XRD instrument. A rotating Cu target was used, with a wavelength of 1.5418×10^{-10} m, a scanning angle range of $30^\circ \sim 110^\circ$, and a scanning rate of 1°/min. The volume fraction of retained austenite was calculated using the following equation[^15]:

$$V_\gamma = \frac{1 - V_c}{1 + (R_\gamma / R_\alpha) \times (I_\gamma / I_\alpha)} \tag{1}$$

where I_γ and I_α are the integrated intensities of the austenite and martensite diffraction peaks, respectively, and R_γ and R_α are the structural factors of austenite and martensite, respectively. V_c is the volume fraction of carbides. Because the carbide volume fraction is small, it was neglected in the calculation.

An MH-3 Vickers hardness tester was used to make microhardness indentations on the specimens. A Supra 40 field-emission scanning electron microscope equipped with energy-dispersive spectroscopy (EDS) was used for in situ observation of the microstructure before and after DCT. A LEAP 4000X HR 3DAP was used to analyze the spatial distribution of elements in the quenched, cryogenically treated, and tempered specimens. The three heat-treated specimens were cut by wire electrical discharge machining into needle-shaped samples of 0.5 mm × 0.5 mm × 55 mm, and the needle-tip specimens required for the experiment were obtained by a two-step electrolytic polishing method[^16]. The data collected by 3DAP were post-processed using Posap software. JMat Pro® thermodynamic software was used to calculate the types and amounts of carbides in the equilibrium state.

2 Experimental Results and Analysis

2.1 Hardness and Phase Composition

The hardness values of high-carbon high-alloy steel SDC99 after quenching at 1030 °C, holding at −196 °C for 8 h, and tempering at 210 °C for 2 h are shown in Table 1. It can be seen from the table that the hardness of SDC99 in the quenched state is 62 HRC; after cryogenic treatment, the hardness is 64 HRC, an increase of 2 HRC compared with the quenched state, which is due to the transformation of retained austenite into martensite. After tempering at 210 °C, the specimen hardness decreased slightly to 63 HRC, 1 HRC lower than that after cryogenic treatment. During low-temperature tempering, carbides precipitate from martensite, reducing the carbon content of the matrix; therefore, the specimen hardness is slightly lower than that in the cryogenically treated state.

Figure 1 shows the XRD spectra of the quenched, cryogenically treated, and tempered specimens. The diffraction lines of martensite $(200)_{\mathrm{M}}$ and $(211)_{\mathrm{M}}$, as well as those of austenite $(200)_{\mathrm{A}}$, $(220)_{\mathrm{A}}$, and $(311)_{\mathrm{A}}$, were selected to calculate the volume fraction of retained austenite[^17]. The calculation results are shown in Table 1. The microstructure of SDC99 in the quenched state is mainly composed of cryptocrystalline martensite, retained austenite, and undissolved carbides; the volume fraction of retained austenite is 21.1%. After cryogenic treatment, the volume fraction of retained austenite decreases to 7.4%, a decrease of 13.7% compared with the quenched state; therefore, the hardness of SDC99 increases after cryogenic treatment. The retained austenite content of the tempered specimen is 5.4%, with only a small decrease compared with the cryogenically treated state. This is because the retained austenite that has not transformed after cryogenic treatment is very stable and is in a state of equiaxial compressive stress, making it difficult for it to continue transforming during subsequent tempering. An excessively high content of retained austenite in high-alloy steel reduces the strength of the material; however, retaining a certain amount of retained austenite can improve the toughness and wear resistance of the material[^18,^19]. Therefore, the properties of SDC99 steel after cryogenic treatment and tempering are superior to those obtained by conventional heat treatment[^20].

In Fig. 1, the diffraction-line intensities of the $(200)_{\mathrm{A}}$, $(220)_{\mathrm{A}}$, and $(311)_{\mathrm{A}}$ crystal planes decrease markedly after cryogenic treatment and decrease further after tempering, whereas the diffraction-line intensities of the $(200)_{\mathrm{M}}$ and $(211)_{\mathrm{M}}$ crystal planes increase continuously. After cryogenic treatment and tempering, the martensite diffraction peaks gradually become broader and their peak positions shift, indicating that the carbon content in martensite changes after cryogenic treatment[^21].

To further analyze carbon segregation and carbide precipitation behavior, the axial ratio (c/a) of martensite and the carbon content in martensite were calculated using empirical formulae[^22]. The structure of martensite is body-centered tetragonal, and its interplanar spacing is:

Fig. 1 XRD spectra of SDC99 steel after different heat treatment processes

Figure 1: Fig. 1 XRD spectra of SDC99 steel after different heat treatment processes

$$d_{(hkl)} = \frac{1}{\sqrt{\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}}} \tag{2}$$

Selecting $(200)_{\mathrm{M}}$ and $(112)_{\mathrm{M}}$ for calculation gives:

$$a = 2d_{(200)} \tag{3}$$

$$c = \frac{2}{\sqrt{\frac{1}{d^2_{(112)}} - \frac{1}{2d^2_{(200)}}}} \tag{4}$$

$$\frac{c}{a} = \sqrt{\frac{1}{d^2_{(200)}/d^2_{(112)} - 1}} \tag{5}$$

Also, $c = a_0 + 0.116p$ and $a = a_0 - 0.013p$[^22]; therefore:

$$p = \frac{c-a}{0.129} \tag{6}$$

where h, k, and l are crystal-plane indices; $d_{(hkl)}$ is the interplanar spacing of the (hkl) crystal plane; a and c are the lattice constants of martensite; a_0 is the lattice constant of α-Fe; and p is the carbon content in martensite.

Calculations show that the axial ratios (c/a) of martensite after the three heat-treatment processes—quenching, cryogenic treatment, and tempering—are 1.0289, 1.0278, and 1.0267, respectively, and the mass fractions of carbon in martensite are 0.64%, 0.61%, and 0.59%, respectively. It can be seen that, after cryogenic treatment, the tetragonality of martensite in the matrix decreases, and the crystal–

Fig. 1 XRD spectra of SDC99 steel after different heat treatment processes (The subscripts M and A denote martensite and austenite, respectively)

the lattice distortion is reduced, and the C content is lower than that in the quenched state. During the deep cryogenic process, the martensite lattice contracts, and the supersaturated C atoms in martensite experience a large stress within the lattice, placing them in a thermodynamically unstable state; thus their tendency to diffuse toward defects or form carbide precipitates increases. However, because the holding temperature for deep cryogenic treatment is extremely low (−196 ℃), and C atoms are difficult to diffuse below −100 ℃,

Fig. 3

Figure 2: Fig. 3

the plastic deformation caused by the martensitic transformation at low temperature increases the dislocation density; during dislocation slip, C atoms are captured and carried along with the dislocation motion[^23]. The further decrease in the C content of the matrix after tempering indicates that, during low-temperature tempering, C atoms may continue to segregate toward defects such as dislocations and twin boundaries, or form carbide precipitates.

2.2 Microstructure

Fig. 2 shows SEM images of SDC99 steel after quenching and deep cryogenic treatment. To investigate whether carbides precipitated during the deep cryogenic process, SEM images were taken in situ at the positions shown in Fig. 2a and c after deep cryogenic treatment, as shown in Fig. 2b and d. It can be seen from Fig. 2a and c that carbides of approximately 0.2–1.0 μm are distributed on the quenched martensitic matrix of SDC99. From Fig. 2b and d, after deep cryogenic treatment, some fine carbides have already desquamated, but no newly formed nanoscale carbide particles are observed, confirming that no significant carbide precipitation occurs during deep cryogenic treatment; carbide precipitation after deep cryogenic treatment should occur during tempering[^24].

2.3 3DAP Analysis

The spatial distributions of the principal alloying elements C, Cr, Mo, and V atoms in quenched SDC99 steel obtained by 3DAP are shown in Fig. 3. The atomic fractions of C, Cr, Mo, V, Si, and Mn in the sample are 1.63%, 5.04%, 0.69%, 0.13%, 1.13%, and 0.29%, respectively. Therefore, the intercepted region is mainly the quenched martensite phase containing supersaturated C. It can be seen from Fig. 3 that the principal alloying elements Cr, Mo, and V in the steel are uniformly distributed, whereas C exhibits local segregation. This is because SDC99 steel has a high alloying-element content, and the martensite start temperature M_s is 220 ℃[^25], higher than room temperature; after quenching, the specimen undergoes autotempering[^26], during which C atoms undergo short-range diffusion and segregate to defects such as dislocations, while Cr cannot precipitate in the form of alloy carbides. Therefore, the alloying elements in the quenched specimen are uniformly distributed, and only weak segregation of C atoms occurs.

To further study the distribution of C atoms in the intercepted region,

Fig. 3 Spatial distributions of C (a), Cr (b), Mo (c) and V (d) in quenched SDC99 steel (The box size is 38 nm$×38$nm$×$250 nm)

Fig. 2 SEM images of SDC99 steel after quenching (a, c) and DCT (b, d) at

Fig. 2

Figure 3: Fig. 2

Fig. 4

Figure 4: Fig. 4

low (a, b) and high (c, d) magnification.

precipitation and concentration changes. The C atoms in Fig. 3 were subjected to three-dimensional atom reconstruction, yielding spatial distribution maps of C isoconcentration surfaces with C atomic fractions of 4.0%, 4.5%, and 5.0%, respectively, as shown in Fig. 4. The distribution of C atoms in the selected region is relatively uniform; only some regions have a C content greater than 4.0%. This is because the holding process before quenching allows alloying elements such as C to be fully dissolved in the matrix. During quenching, in order to obtain a martensitic structure, the cooling rate is relatively high, so alloying elements such as C still retain the supersaturated state present at high temperature. However, when high-carbon high-alloy steel is quenched to room temperature, part of the retained austenite remains; therefore, the regions with relatively high C-atom concentration may be retained austenite.

Fig. 5 shows the atomic spatial distribution maps of different elements in SDC99 steel after quenching and deep cryogenic treatment at −196 °C for 8 h. It can be seen from the figure that, after deep cryogenic treatment, C exhibits obvious segregation, and a trace amount of V segregates in regions with relatively high C-atom concentration, whereas elements such as Cr and Mo do not form obvious segregation regions. V is a strong carbide-forming element and has an extremely strong affinity with C; therefore, it readily co-segregates with C. Cr and Mo, by contrast, are medium-to-strong carbide-forming elements, and their bonding ability with C is inferior to that of V.

Fig. 4 3DAP carbon atom maps in quenched SDC99 steel with C isoconcentrations of 4.0% (a), 4.5% (b) and 5.0% (c) (The box size is 38 nm$\times$38$nm\times$$250 nm)

During deep cryogenic treatment, retained austenite transforms into martensite under the action of temperature and stress. The segregation of C atoms may have two causes: (1) the martensitic transformation during deep cryogenic treatment induces plastic deformation, increasing the number of dislocations in the system[^27], and dislocation glide drives the migration of C atoms[^23]; (2) under the action of strong stress, retained austenite transforms into twinned martensite[^15,^28], and during heating to room temperature C atoms segregate at the twin/matrix interface. To further study the C-enriched region here, a region 40 nm in length was selected to analyze its C content; the result is shown in Fig. 6. It can be seen that the average C content of the selected region is close to 4%, far lower than that in cementite (25%) or ϵ-carbide (25%-

Fig. 5

Figure 5: Fig. 5

33%). Moreover, the C distribution does not form a typical carbide morphology; therefore, the possible phase or microstructure in this region is retained austenite and twinned martensite, or merely segregation of C atoms at interfaces or defects.

The selected region was subjected to three-dimensional atom reconstruction, and its isoconcentration surfaces with C atomic fractions of 4.0%, 4.5%, and 5.0% were analyzed; the results are shown in Fig. 7. It can be seen that the C atoms exhibit parallel lamellar segregation, and the spacing between these segregation regions of different concentrations is about 5–10 nm. In general, the C content of bulk retained austenite is 2.5%–5.6%. The volume fraction of this segregation region accounts for about 40%–50% of the entire microstructure. For SDC99 steel after deep cryogenic treatment, the microstructure contains only 7.4% retained austenite, indicating that this region cannot be retained austenite. Gavriljuk et al.[^23], through Mössbauer spectroscopy, suggested that the plastic deformation produced by low-temperature martensitic transformation during deep cryogenic treatment induces C atoms to–

Fig. 5 Spatial distributions of C (a), Cr (b), Mo (c) and V (d) in SDC99 steel after quenching and DCT (The box size is 76 nm$\times 73 nm \times$185 nm)

toward dislocations; however, in Fig. 7 the C atoms show lamellar, parallel segregation, which is inconsistent with the segregation morphology at dislocations.

Considering that, during cryogenic treatment, retained austenite transforms to martensite, the newly formed martensite has a high C content, and diffusion of C atoms at low temperature is difficult; therefore, its substructure is twins, which provide a large number of interfaces for C-atom segregation. At the same time, at low temperature the martensite lattice contracts, and the supersaturated C atoms in martensite experience a large compressive stress within the lattice. Under long-term stress, they readily segregate at twin interfaces. Such C-rich atomic segregation regions can be understood as pre-precipitation condensates before carbide-phase precipitation, similar to the solute-atom clusters, Guinier–Preston (G.P.) zones, formed in Al–Cu alloys during aging.

Fig. 8a shows the spatial distribution of C atoms in SDC99 steel after cryogenic treatment and tempering at 210 °C for 2 h. It can be seen that there are two forms of C segregation regions in the specimen: one consists of multiple lamellar C-rich regions in the lower part of the specimen (Area I). Atomic concentration analysis of this region (Fig. 8b) shows that the C concentration in this region reaches a maximum of 14%. This is a C-segregation region formed by further segregation during tempering from the C-segregation region produced during cryogenic treatment; its thickness is 10 nm. However, the Cr content in the C-rich region is close to that of the matrix, and the Cr concentration at the C-rich

Fig. 6

Figure 6: Fig. 6

region/matrix interface reaches a maximum of 14%. The non-carbide-forming element Si segregates at the interface between this region and the matrix, impeding the growth of the C-rich phase in this region. The other is a region at the tip of approximately 60 nm × 60 nm × 20 nm (Area II), where alloy carbides have formed. Fig. 8c shows the concentration distribution of alloying elements in this region. This carbide is rich in Cr and Mo. From calculation of the atomic ratio, the carbide type is $M_{23}C_6$, which is consistent with the result obtained by Jmat Pro® calculations that $M_{23}C_6$-type carbides are readily precipitated during tempering at low temperature, as shown in Fig. 9.

Fig. 6 Carbon content curve of SDC99 steel after quenching and DCT

3 Analysis and discussion

The martensitic transformation finish temperature M_f of high-carbon high-alloy SDC99 steel is below room temperature, approximately −30 °C

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. Therefore, its quenched microstructure consists of quenched martensite, retained austenite, and a small amount of eutectic carbides. Quenched martensite is a supersaturated solid solution of C and alloying elements in α-Fe. 3DAP observations show that the distribution of C in the quenched microstructure is relatively uniform (average C content 1.6%, atomic fraction), with only some regions having relatively high C-atom concentrations (>4.0%, atomic fraction). It is inferred that these regions may be retained austenite (17.6%, volume fraction). Retained austenite is a metastable phase with relatively low hardness; when the stress increases and the temperature decreases, it readily transforms into martensite with higher hardness.

When the quenched SDC99 specimen is cryogenically treated in liquid nitrogen at −196 °C, owing to the decrease in temperature and the increase in stress

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, approximately 9.9% of the retained austenite transforms into martensite, increasing the hardness of the specimen. However, cryogenic treatment cannot completely eliminate the retained austenite; 7.7% retained austenite still remains untransformed. Retained austenite has an fcc structure, and its stacking-fault energy

Fig. 7 3DAP carbon atom maps of SDC99 steel after quenching and DCT with C isoconcentrations of 4.0% (a), 4.5% (b) and 5.0% (c) (The box size is 76 nm$×75$nm×$243 nm)

Fig. 7

Figure 7: Fig. 7

Fig. 8

Figure 8: Fig. 8

Fig. 8 Spatial distribution of C atoms (a) and the content curves of alloying elements at areas I (b) and II (c) in SDC99 steel after DCT and tempering at 210 °C for 2 h (The box size of Fig. 8a is 76 nm × 75 nm × 243 nm)

Fig. 9 Type and quantity of carbides in SDC99 steel calculated by JMat Pro®

The equilibrium carbide content in SDC99 steel calculated by JMat Pro® is shown in Fig. 9. At low temperature, during the deep cryogenic treatment process, the macroscopic contraction caused by rapid cooling makes the piled-up planes in the crystal lattice slip. Therefore, the substructure of the newly formed martensite is fine twins [28], and the newly formed twinned martensite provides sites for the segregation of supersaturated C atoms. It should be pointed out that the diffusion ability of C atoms decreases exponentially with decreasing temperature, and at low temperature C atoms cannot be thermally activated to diffuse. However, the plastic deformation introduced during the martensitic transformation produces a large number of dislocations [23]. During the slipping process, the dislocations can capture C atoms, and the C atoms "frozen" at low temperature move through the motion of the dislocations. During the process in which the temperature recovers from the deep cryogenic temperature to room temperature, when the temperature is higher than −50 °C, C atoms can obtain sufficient thermal activation and diffuse outward along grain boundaries. However, at this temperature the diffusion of C atoms is still relatively difficult, the diffusion distance is extremely short, and C atoms readily segregate at "short-range channels" for diffusion, such as twin interfaces or dislocations, providing effective nucleation cores for carbide precipitation and growth during tempering. The 3DAP results show that the segregation region is about 5–10 nm, and the carbon concentration in the segregation region is close to 4% (atomic fraction). At the deep cryogenic temperature or at room temperature, alloying atoms such as Fe, Cr, Mo, and V cannot diffuse; therefore, carbides cannot form.

During tempering at 210 °C, as the temperature rises, the mobility of C atoms increases, and alloying atoms such as Cr and Mo can also obtain sufficient thermal activation and diffuse. This is because, during the deep cryogenic treatment process, a large amount of retained austenite transforms into twinned martensite [15]. However, at low temperature, diffusion of alloying elements is difficult,

Fig. 9

Figure 9: Fig. 9

and only C atoms can diffuse upon recovery to room temperature; therefore, alloy carbides cannot precipitate. Nevertheless, the twins and dislocation substructures formed during deep cryogenic treatment provide effective nucleation sites for the nucleation of carbides. During tempering at 210 °C, on the one hand, the C-enriched regions formed during deep cryogenic treatment continue to be enriched, forming plate-like C-rich phases of about 10 nm, in which the C concentration is as high as 14% (atomic fraction), while the Cr element already has a certain diffusion capability. On the other hand, C and alloying atoms such as Fe, Cr, Mo, and V form $M_{23}C_6$-type carbides with a certain stoichiometric ratio. The size of the alloy carbides precipitated at this temperature is ···

extremely small and, being dispersed in the matrix, can improve the wear resistance of high-carbon high-alloy steel[30]. In addition, after low-temperature tempering, 5.2% retained austenite still remains in the matrix. This retained austenite, which has not transformed even after deep cryogenic treatment and tempering, is a rather stable phase; it is usually distributed as films around martensite, where it can relieve stress and improve material toughness, thereby helping to improve the wear resistance of the steel.

4 Conclusions

(1) After high-carbon high-alloy steel SDC99 was quenched from 1030 °C to room temperature, the volume fraction of retained austenite was 21.1%. Because self-tempering occurred, C atoms showed slight segregation.

(2) After quenching followed by deep cryogenic treatment at −196 °C for 8 h, part of the retained austenite transformed into martensite, and its volume fraction decreased to 7.4%. C atoms segregated at newly formed martensite grain boundaries. During the recovery from the deep cryogenic temperature to room temperature, C atoms further segregated, forming parallel plate-like segregation zones 5–10 nm thick, but did not precipitate in the form of carbides.

(3) After quenching, deep cryogenic treatment at −196 °C for 8 h, and tempering at 210 °C for 2 h, the volume fraction of retained austenite was 5.4%. During deep cryogenic treatment, C atoms segregated at newly formed twin martensite grain boundaries, or further enriched to form C-rich phases about 10 nm thick, or formed $M_{23}C_6$ carbides together with alloying elements such as Cr and Mo. These nanoscale carbides are dispersed in the matrix and are the key reason for the significant improvement in the wear resistance of high-carbon high-alloy steel after deep cryogenic treatment.

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References

[1] Baldissera P, Delprete C. *Open Mech Eng J*, 2008; 2(8): 1

[2] Huang J Y, Zhu Y T, Liao X Z, Beyerlein I J, Bourke M A, Mitchell T E. *Mater Sci Eng*, 2003; A339: 241

[3] Das D, Dutta A K, Toppo V, Ray K K. *Mater Manuf Processes*, 2007; 22: 47

[4] Meng F, Tagashira K, Azuma R, Sohma H. *ISIJ Int*, 1994; 34: 205

[5] Li S H, Deng L H, Wu X C, Wang H B, Min Y A. *Mater Sci Eng*, 2010; A527: 6899

[6] Li S H, Deng L H, Wu X C, Wang H B, Min Y A, Min N. *Mater Sci Eng*, 2010; A527: 7950

[7] Li S H, Min N, Deng L H, Wu X C, Min Y A, Wang H B. *Mater Sci Eng*, 2011; A528: 1247

[8] Li S H, Min N, Li J W, Wu X C, Li C H, Tang L L. *Mater Sci Eng*, 2013; A575: 51

[9] Tyshchenko A I, Theisen W, Oppenkowski A, Siebert S, Razumov O N, Skoblik A P. *Mater Sci Eng*, 2010; A527: 7027

[10] Zhu C, Cerezo A, Smith G D W. *Ultramicroscopy*, 2009; 109: 545

[11] Wilde J, Cerezo A, Smith G D W. *Scr Mater*, 2000; 43: 39

[12] Liu Q D, Liu W Q, Wang Z M, Zhou B X. *Acta Metall Sin*, 2009; 45: 1281
(刘庆冬, 刘文庆, 王泽民, 周邦新. 金属学报, 2009; 45: 1281)

[13] Liu Q D, Peng J C, Liu W Q, Zhou B X. *Acta Metall Sin*, 2009; 45: 1288
(刘庆冬, 彭剑超, 刘文庆, 周邦新. 金属学报, 2009; 45: 1288)

[14] Liu Q D, Chu Y L, Peng J C, Liu W Q, Zhou B X. *Acta Metall Sin*, 2009; 45: 1297
(刘庆冬, 褚于良, 彭剑超, 刘文庆, 周邦新. 金属学报, 2009; 45: 1297)

[15] Matteo V, Karen P, Marcel A J S. *Acta Mater*, 2014; 65: 383

[16] Liu Q D, Liu W Q, Wang Z M, Zhou B X. *Acta Metall Sin*, 2008; 44: 786
(刘庆冬, 刘文庆, 王泽民, 周邦新. 金属学报, 2008; 44: 786)

[17] Xie Z J, Ren Y Q, Zhou W H, Yang J R, Shang C J, Misra R D K. *Mater Sci Eng*, 2014; A603: 69

[18] Clarke A J, Speer J G, Miller M K, Hackenberg R E, Edmonds D V, Matlock D K, Rizzo F C, Clarke K D, Moor E De. *Acta Mater*, 2008; 56: 16

[19] Gao G H, Zhang H, Gui X L, Luo P, Tan Z L, Bai B Z. *Acta Mater*, 2014; 76: 425

[20] Li S H, Xie Y Z, Wu X C. *Cryogenics*, 2010; 50: 89

[21] Duan C Z, Wang M J. *J Iron Steel Res*, 2008; 20(8): 38
(段春争, 王敏杰. 钢铁研究学报, 2008; 20(8): 38)

[22] Kurdjumov G V. *Metall Trans*, 1976; 7A: 999

[23] Gavriljuk V G, Theisen W, Sirosh V V, Polshin E V, Kortmann A K, Mogilny G S, Petrov Y N, Tarusin Y V. *Acta Mater*, 2013; 61: 1705

[24] Tyshchenko A I, Theisen W, Oppenkowski A, Siebert S, Razumov O N, Skoblik A P, Sirosh V A, Petrov Y N, Gavriljuk V G. *Mater Sci Eng*, 2010; A527: 7027

[25] Li J W, Tang L L, Li S H, Wu X C. *Mater Des*, 2013; 47: 653

[26] Liu Q D, Chu Y L, Wang Z M, Liu W Q, Zhou B X. *Acta Metall Sin*, 2008; 44: 1281
(刘庆冬, 褚于良, 王泽民, 刘文庆, 周邦新. 金属学报, 2008; 44: 1281)

[27] Li S H, Deng L H, Wu X C, Min Y A, Wang H B. *Cryogenics*, 2010; 50: 754

[28] Li S Y, Liu T Z, Li G. *Mater Rev*, 2003; 17(8): 80
(李士燕, 刘天佐, 李钢. 材料导报, 2003; 17(8): 80)

[29] Li J W, Feng Y, Tang L L, Wu X C. *Mater Lett*, 2013; 100: 274

[30] Li S H. *PhD Dissertation*, Shanghai University, 2011
(李绍宏. 上海大学博士学位论文, 2011)

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