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ARTICLE

Effect of Minimum Temperature on the Mechanical Properties and Reversed Austenite Content of 9%Ni Steel Subjected to Cryogenic Treatment

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Abstract: The effect of minimum temperature on the mechanical properties and reversed austenite content of 9%Ni steel subjected to cryogenic treatment was experimentally investigated. Cryogenic treatment with different temperatures and soaking time were conducted by combining with the newly developed quenching, lamellarizing and tempering (QLT) heat treatment of 9% Ni steel. The results show that the cryogenic treatment at −80 and −110 °C has no obvious influence on the reversed austenite content and mechanical properties of 9%Ni steel. However, the room temperature impact toughness is improved by cryogenic treatment at −140 °C for 24 h, which is attributed to the modification in the reversed austenite morphology from bulks into strips. The volume fraction of the reversed austenite decreases slightly due to the isothermal martensitic transformation at −140 °C. Cryogenic treatment at −196 °C for 24 h increases the volume fraction of reversed austenite and refines the secondary martensite lath, thereby improving both the room temperature impact toughness and cryogenic ductility. The observed results are mainly due to the precipitation of ultra-fine carbides and the increase of internal stress during cryogenic treatment, which provides more nucleation sites for the reversed austenite in the process of tempering.

Key words: 9%Ni steel; cryogenic treatment; reversed austenite; mechanical property; microstructure

Cryogenic treatment has been well recognized as an effective approach to improve the materials properties by promoting the microstructural modification. Studies have revealed that mechanical properties[1,2], wear resistance [3] and dimensional stability[4] of tool steels can be enhanced substantially by this treatment. The effect of this treatment on ferrous metals such as tool steels, carburized steels[5], structural alloy steel[6], cast iron[7] and stainless steel[8,9] has been studied extensively in recent years. What's more, studies related to the effect of cryogenic treatment on non-ferrous, composites[10] and polymer[11] have also been prevailed. It can improve the performance of aluminum alloy [12], magnesium alloys [12,13] and titanium alloy [14,15]. A large number of researches have reviewed the effects and mechanisms of cryogenic treatment on different materials[16,17]. It is confirmed that the main mechanisms of cryogenic treatment on tool steels are the transformation of retained austenite to martensite and the precipitation of ultra-fine carbide particles. However, improvement mechanisms for other kinds of steels as well as non-ferrous and metalloid have not been totally clarified.

The process technique of cryogenic treatment is one of the most key factors to determine the effect. Process parameters such as minimum temperature, soaking time, cooling rate, heating rate and the subsequent tempering all have different contributions to the effect of cryogenic treatment. What's more, as a complementary process to conventional heat treatment, cryogenic treatment must be integrated into the traditional process route. It is well known that cryogenic treatment should be executed after quenching and before tempering to transform the retained austenite as completely as possible[18]. Most of the previous

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studies on cryogenic treatment of steels have mainly focused on combining it with traditional quenching and tempering. However, different heat treatment schemes are needed to produce various microstructures of steels in order to obtain service performance. For example, bainite structure and reversed austenite can be obtained by isothermal quenching and intercritical quenching, respectively. Little study has been done on the combination of cryogenic treatment and these specific heat treatment schemes.

With the development of many industry branches involving cryogenic temperatures, the demands for cryogenic materials are continuously increased. The commercial 9%Ni steel is widely used around the world as a material of the inner walls for liquefied natural gas (LNG), liquid oxygen and liquid nitrogen storage tanks because of its excellent cryogenic fracture toughness at or below 111 K[19,20]. In order to obtain the superior cryogenic properties, a heat treatment scheme consisting of quenching, lamellarizing and tempering (QLT) is necessary. A mixed structure of lath martensite matrix and pro-eutectoid ferrite formed after the intercritical quenching, and a quantity of reversed austenite which can keep thermodynamically stability to 77 K formed after tempering [21,22]. The reversed austenite plays a very important role in the comprehensive mechanical properties, especially the cryogenic toughness of 9%Ni steel. Studies have been conducted to demonstrate the thermal stability of the reversed austenite, which reveals that just a little reduction occurs in the QLT sample after soaking in the liquid nitrogen [23]. However, the effect of cryogenic treatment on steels with this kind of microstructure is unknown. Zheng [24] studied the effect of deep cryogenic treatment on the formation of reversed austenite in the super martensitic stainless steel. The result revealed that the volume fraction of reversed austenite in the cryogenically treated steel is greater than that in the quenched and tempered steel. It can be seen that different effects between reversed austenite and retained austenite can be obtained in steels subjected to cryogenic treatment. Increasing the volume fraction of reversed austenite is beneficial to the impact toughness of steels.

Therefore, the present work is devoted to investigating the effect of minimum temperatures on the mechanical properties and reversed austenite of 9%Ni steel subjected to cryogenic treatment. Considering that lamellarizing is the most important process for the formation of reversed austenite, cryogenic treatment was conducted after lamellarizing and prior to tempering. Different minimum temperatures (–80, –110, –140 and –196 °C) and soaking time (2, 12 and 24 h) were adopted in the process of cryogenic treatment to optimize the process parameters.

1 Experiment

Commercially forged 9%Ni steel with a diameter of 150 mm was employed for this study. The chemical composition of the selected material is shown in Table 1. The raw material was conventionally normalized and tempered after forging. It was cut into round bars with 13 mm in diameter and 65 mm in length for the tensile tests, and small blocks with the sizes of 10.5 mm×10.5 mm× 55 mm for impact toughness tests by electrical discharge machining prior to heat treatment and cryogenic treatment.

The heat treatment of quenching, larmellarizing and tempering (QLT , Q: 790 °C for 90 min, water cooling, L: 670 °C for 90 min, water cooling, and T: 570 °C for 180 min, air cooling) was employed for 9%Ni steel. Cryogenic treatment was conducted after lamellarizing and prior to tempering in the present work. Considering that process parameters have different contribution to the final results, the minimum temperature and soaking time were adopted as two variables in the process of cryogenic treatment. The details of overall treatment group scheme are shown in Table 2. Temperatures of –80, –110, –140 and –196 °C were adopted for the cryogenic treatment with different soaking time of 2, 12 and 24 h at each temperature. In order to avoid thermal shock during the cooling, the samples were cooled slowly at a speed of 1 °C/min. The DC-B15/13 resistance furnace was employed for the heat treatment and the program controlled SLX-80 cryogenic system shown in Ref.[14] was adopted for the cryogenic treatment.

The standard tensile samples with a gage diameter of 5 mm and a gage length of 30 mm were used for tensile test by the MTS-SANS CMT500 universal tensile testing machine. The values of tensile strength, yield strength and elongation were obtained from the test. Impact tests were performed by the JBN-300B impact testing machine using the standard Charpy V-notch specimens (10 mm×10 mm×55 mm, standard EN10045). For each group, three samples were tested and then the values were averaged as the final result.

The scanning electron microscopy (SEM) of S-4300 made by Hitachi was used for the detection of fracture surface and microstructure of samples. The surface of samples used for the microstructure detection was ground in the sequence of 400#, 600#, 800#, 1000# and 1500# followed by mechanically polishing. After that, the surface was etched with a solution consisting of 4 vol% HNO_3 and 96 vol% CH_3CH_2OH for 10 s. The samples were also tested by the D8 Focus X-ray diffraction (XRD) made by Bruker.

2 Results and Discussion

2.1 Microstructure

Table 1 Chemical composition of 9%Ni steel (wt%)

Ni	Mn	Si	Cr	C	P	S	Fe
9.233	0.457	0.145	0.047	0.047	0.008	0.003	Bal.

Table 2 Process of 9%Ni steel subjected to cryogenic treatment

Group index	Temperature/°C	Soaking time/h
QLT	-	-
QLCT-1	−80	2, 12, 24
QLCT-2	−110	2, 12, 24
QLCT-3	−140	2, 12, 24
QLCT-4	−196	2, 12, 24

Previous studies have confirmed that the effect of deep cryogenic treatment on materials is greater than that of shallow cryogenic treatment, and the longer the soaking time, the greater the effect. Microstructural analyses were performed on the QLT, QLCT-3-24 and QLCT-4-24 specimens using SEM and XRD. The microstructure of samples treated by QLT and QLCT-3-24 is illustrated in Fig.1. In the QLT sample of 9%Ni steel, the microstructure consists of martensite laths, secondary martensite and reversed austenite. The secondary martensite is formed during intercritical quenching and reversed austenite is formed during tempering. The white regions represent the reserved austenite and secondary martensite, which disperse along the matrix of martensite lath in a granular shape and blocks, as shown in Fig.1a. Fig.1b shows the microstructure of QLCT-3-24 sample which has the same structural composition as the QLT sample. However, strip reversed austenite can be observed in the grain boundary of original austenite, within the grains, and between martensite laths in the microstructure of QLCT-3-24 sample. Most of the reversed austenite in the QLCT-3-24 sample is strip and film-like shaped. Simultaneously, a little reduction in the quantity of white block reversed austenite can be observed. It is well known that two different morphologies, the granular reversed austenite and the film-like reversed austenite, can be obtained by QLT treatment in 9%Ni steel[21]. The film-like and strip reversed austenite is more stable than the granular reversed austenite, which can improve the resistance to crack propagation. Comparison of the micrographs in Fig.1 reveals that the cryogenic treatment at –140 °C for 24 h (QLCT-3-24) changes the morphology of reversed austenite from block to strip.

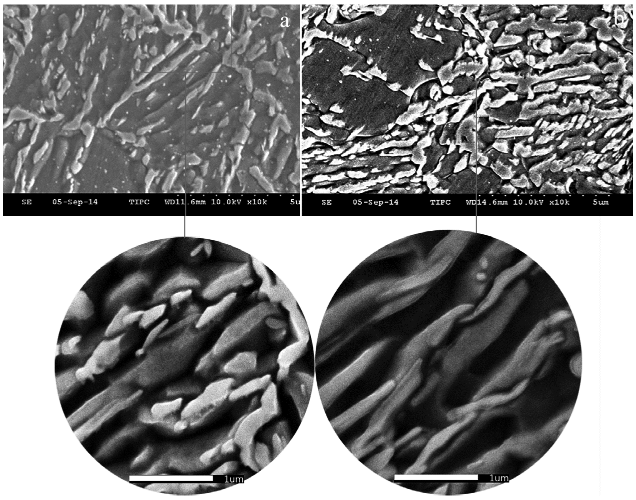

Fig.1 SEM micrographs of 9%Ni steel treated by QLT (a) and QLCT-3-24 (b)

Fig.2a and 2b show the microstructures of samples treated by QLT and QLCT-4-24. There is no obvious change

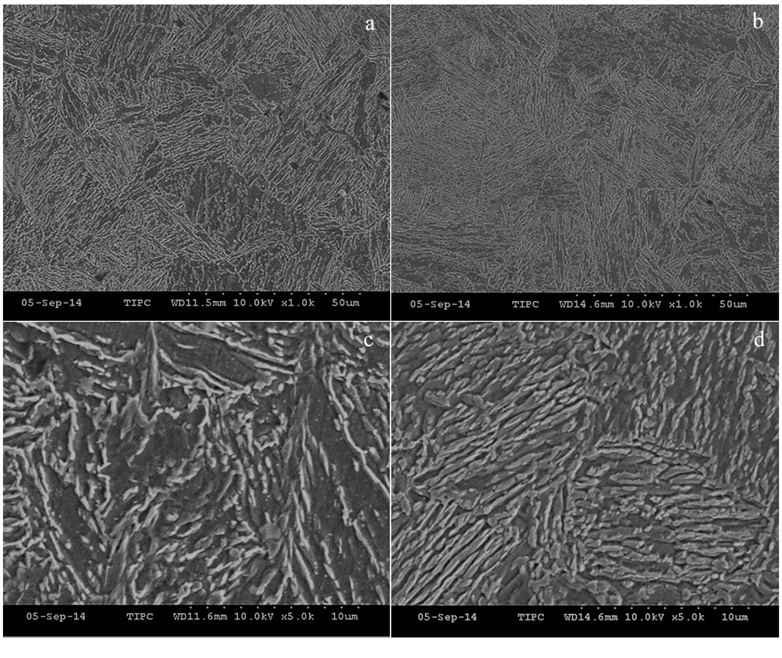

Fig.2 SEM images of 9%Ni steel treated by QLT (a, c) and QLCT-4-24 (b, d)

can be detected in the main structural constituents after QLCT-4-24 treatment. However, we can see in Fig.2b and 2d that, the martensite laths get more intensive and homogeneous and the white regions become more continuous. This comparison reveals that cryogenic treatment at –196 °C for 24 h refines the martensite lath and increases the volume fraction of reversed austenite of 9%Ni. Refinement of grain size can also be observed after cryogenic treatment of QLCT-4-24.

XRD patterns of samples subjected to QLT, QLCT-3-24 and QLCT-4-24 treatment are compared in Fig.3. In comparison to QLT treatment, QLCT-4-24 treatment markedly increases the intensity of characteristic diffraction peak of the austenite, while the QLCT-3-24 treatment has the opposite effect, as shown in Fig.3. The volume fractions in the QLT, QLCT-3-24 and QLCT-4-24 samples are 9.48%, 9.36% and 10.77%, respectively, which indicates that the volume fraction of reversed austenite for the samples cryogenic treated at –196 °C for 24 h is increased while that for the samples cryogenic treated at –140 °C for 24 h is reduced.

It is well acknowledged that the QLT treatment can increase the volume fraction and improve the distribution of reversed austenite which has significant influence on the toughness of 9%Ni steel. During the process of heating in the dual phase region, some of quenched martensite transforms into austenite and other keep reserved. Elements such as Ni and Mn in the remained quenched martensite diffuse into the austenite under the conditions of higher temperature, which make the austenite rich in solute atoms. After intercritical quenching, most of the austenite changes into secondary martensite with the enrichment of solute atoms while a little portion remains as retained austenite in the microstructure. In the subsequent tempering, the retained austenite grows up directly to be the bulk reversed austenite which is not so stable as the strip or film-like reversed austenite. Meanwhile, some positions with higher free energy become the nucleation points, which results in the formation of reversed austenite. The stability of reversed austenite is improved by the diffusion of solute elements in the secondary martensite. Therefore, the homogenous and thermostable reversed austenite is formed during continuous tempering.

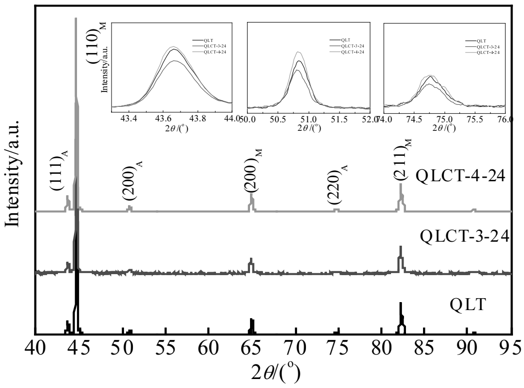

Fig.3 XRD patterns of 9%Ni steel treated by QLT, QCLT-3-24 and QCLT-4-24

Previous study have showed that the martensitic transformation occurs with isothermal kinetics within the temperature range of –100 to –170 °C, while no transformation is observed at –196 °C [25-29]. Cryogenic treatment at –140 °C after intercritical quenching promotes the isothermal martensitic transformation in 9%Ni steel, as a result of reducing formation of bulk reversed austenite during the process of tempering. Therefore, the volume fraction of reversed austenite is reduced slightly by cryogenic treatment. This transformation increases the internal stress between the martensite laths, which provides a higher driving force and greater internal energy for Ni diffusion, which has great contribution to the formation of reversed austenite. After cryogenic treatment, the microstructure gets more homogeneous, and the reversed austenite is distributed along the martensite laths uniformly in the shape of strip, as shown in the micrograph of QLCT-3-24 sample. These strip reversed austenite is beneficial to the room temperature impact toughness.

Cryogenic treatment at –196 °C cannot induce martensitic transformation. However, the participation of ultra-fine carbides occurs due to the lattice contraction of the supersaturated secondary martensite during the process of cryogenic treatment. These carbides are distributed along and between the martensite laths, which provides more nucleation points for the reversed austenite. The internal stress is increased due to the lattice contraction of martensite in the process of cryogenic temperature, which also provides more nucleation points for the reversed austenite in the subsequent tempering. As a result, both block and strip reversed austenite exist in the microstructure of 9%Ni steel. As the previous studies have shown, cryogenic treatment at –196 °C increases the volume fraction of reversed austenite and promotes a more uniform distribution of reversed austenite in super martensitic stainless steel [24]. This phenomenon can also be detected in the 9%Ni steel.

2.2 Mechanical properties

The mechanical properties at room temperature of samples treated by different processes were measured. As shown in Fig.4, the cryogenic treatment at different temperatures for different soaking time has little influence on the tensile strength and yield strength of 9%Ni steel. The elongation of 9%Ni steel increases slightly after cryogenic treatment at –140 and –196 °C, while there is no obvious change at other temperatures, as shown in Fig.5. In addition, the impact toughness is also improved after cryogenic treatment at –140 and –196 °C compared to the QLT

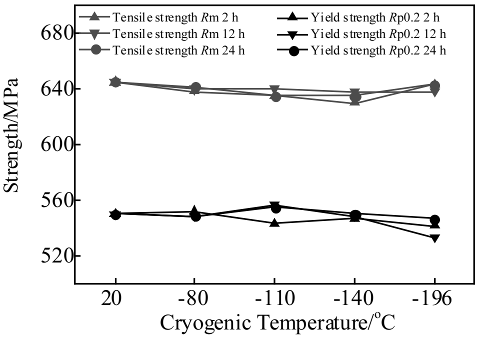

Fig.4 Tensile strength and yield strength of 9%Ni steel treated by different processes

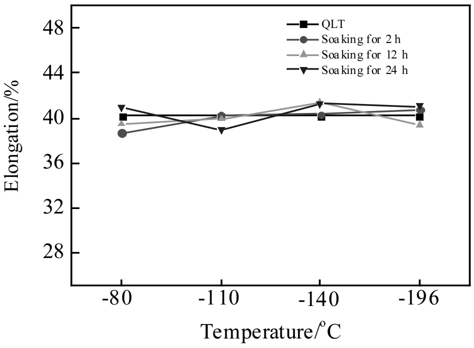

Fig.5 Elongation of 9%Ni steel treated by different cryogenic treatment processes

treatment, as shown in Fig. 6. As is observed, the improvement in impact toughness become greater as the soaking period is prolonged. The greatest improvement in impact toughness is obtained by the cryogenic treatment at −140 °C for 24 h (QLCT-3-24). This suggests that cryogenic treatment is favorable for improving the thermostability of reversed austenite that has great contribution to the impact toughness of 9%Ni steel, which increases by 23.3 J at room temperature.

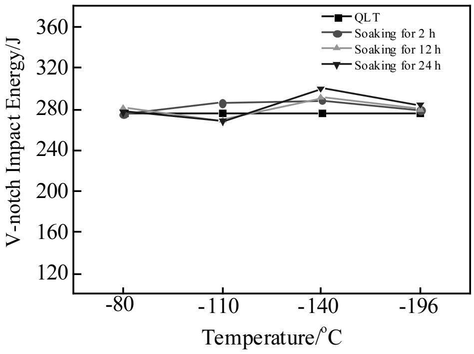

Fig.6 Room temperature impact toughness of 9%Ni steel treated by different processes

Previous researches show that deep cryogenic treatment (usually lower than −130 °C) is more beneficial than shallow cryogenic treatment, and cryogenic treatment at −80 and −110 °C has no obvious influence on the mechanical properties of 9%Ni steel. Considering the obvious improvement in impact toughness after cryogenic treatment, the impact fracture surfaces of QLT sample and QLCT-3-24 sample were detected by SEM. The fractography with two different magnified fracture surfaces are shown in Fig.7. As is observed, failure occurs by a mixed mode of microvoid coalescence and ductile tearing. It can be seen from the fracture surface of QLT sample that amount of micro-cracks and microvoids can be detected on the rough

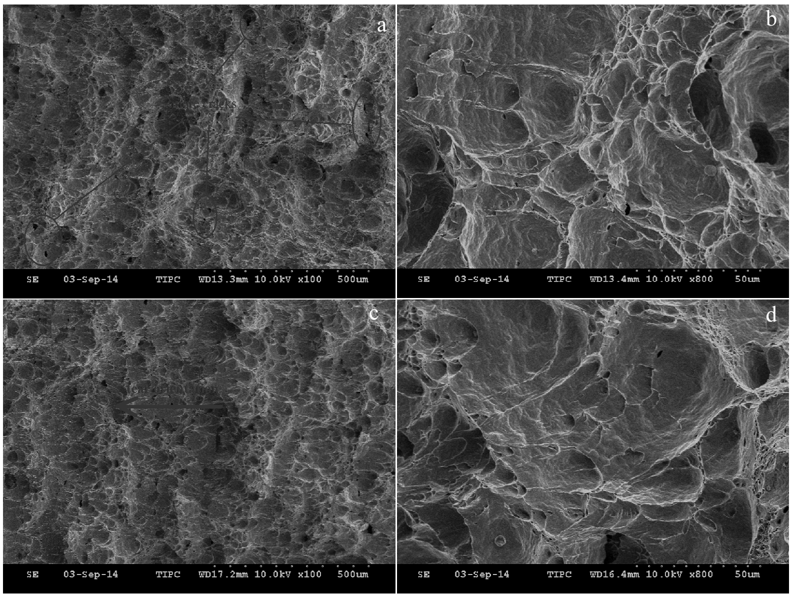

Fig.7 Fracture surfaces of 9%Ni steel treated by QLT (a, b) and QLCT-3-24 (c, d)

fracture surface. The fracture surface of QLCT-3-24 sample shows an obvious tear orientation, which is flatter and more uniform than that of the QLT one. As shown in Fig.7d, the tearing ridges get longer and the dimples get bigger after cryogenic treatment. It can be inferred that the formation of micro-cracks is hindered during the process of impacting. The QLCT-3-24 sample experiences more severe tear than the QLT sample before fracture. This change in fracture mode is consistent with the change in impact toughness.

Considering the wide application of 9%Ni steel in cryogenic environment, cryogenic tensile tests were conducted in samples treated by QLCT-3-24 at –140 °C and QLCT-4-24 at –196 °C. The engineering stress-strain curves are presented in Fig.8. It is acknowledged that the strength of most metals is increased with decreasing temperature.

The QLCT-3-24 sample exhibits a shortening in the strain hardening stage, while the QLCT-4-24 sample shows a obvious extension in the strain hardening stage. As a result, early fracture occurs in the QLCT-3-24 sample during the stretching process. It can be seen that the tensile characteristics of the QLCT-3-24 sample and the QLCT-4-24 sample at cryogenic temperatures are so different, which can be attributed to the distinguished changes in the microstructure during cryogenic treatment at different temperatures. A large number of studies have shown that the volume fraction and stability of reversed austenite has a great influence on the plasticity and ductility of 9%Ni steel [21-23]. The transformation of reversed austenite to martensite under tensile stress will relief the local stress concentration generated by the plastic deformation; as a result, the propagation of crack will be hindered. Therefore, the higher volume fraction of reversed austenite in the QLCT-4-24 sample is beneficial for delaying the initiation of microcrack and enhancing the ductility. On the contrary, the amount of reversed austenite gets smaller after the cryogenic treatment of QLCT-3-24, and as a result, the ductility is reduced.

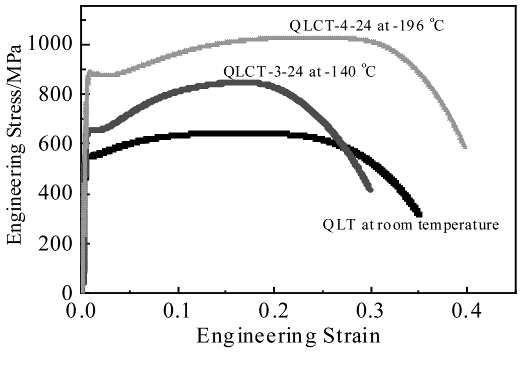

Fig.8 Engineering stress-strain curves of 9%Ni steel at cryogenic temperature

3 Conclusions

1) Cryogenic treatments at –80 and –110 °C have no obvious influence on the mechanical properties and microstructure of 9%Ni steel. However, the cryogenic treatment at –140 °C for 24 h (QLCT-3-24) reduces the volume fraction of reversed austenite while improving the thermally stability by changing the morphology to strips. As a result, the room temperature impact toughness of 9%Ni steel is increased by 23.3 J. The reduction in reversed austenite is mainly attributed to the isothermal martensitic transformation at –140 °C, which hinders the formation of bulk reversed austenite.

2) The volume fraction of the reversed austenite is increased from 9.48% to 10.77% by carrying out cryogenic treatment at –196 °C for 24 h (QLCT-4-24). There is no isothermal martensitic transformation at –196 °C, and the retained austenite grows directly into the bulk reversed austenite. Simultaneously, the participation of ultra-fine carbides and the increase of internal stress after cryogenic treatment provide more nucleation points for reversed austenite in the subsequent tempering. As a result, both the bulk and strip reversed austenite exist in the microstructure of 9%Ni steel. More importantly, the treatment of QLCT-4-24 refines the grain size and the secondary martensite laths.

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深冷处理最低温度对 9%Ni 钢力学性能及逆转奥氏体含量的影响

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摘 要：通过实验研究了深冷处理过程中的最低处理温度对 9%Ni 钢力学性能和逆转奥氏体含量的影响。采用了不同的深冷处理温度和保温时间，并与 9%Ni 钢新发展起来的热处理工艺淬火、亚稳淬火、回火（QLT）相结合。结果表明，−80 和−110 ℃的冷处理对 9%Ni 钢的力学性能和逆转奥氏体含量没有明显影响。然而，−140 ℃保温 24 h 的深冷处理能够提高 9%Ni 钢的冲击韧性，其机理主要在于深冷处理使得块状的逆转奥氏体转变为条状。此外，−140 ℃深冷处理通过等温马氏体转变使得逆转奥氏体的含量减少。−196 ℃保温 24 h 深冷处理增加了逆转奥氏体的含量，同时细化了二次马氏体板条组织， 从而使得 9%Ni 钢的室温和低温冲击韧性均得到提高。其机理主要是由于深冷−196 ℃深冷处理促使了超细碳化物的析出，同时增加了组织内应力，从而为逆转奥氏体在回火过程中的形核提供了更多了形核位置。

关键词：9%Ni钢；深冷处理；逆转奥氏体；机械性能；微观组织

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