Effect of double quenching process and tempering temperature on the microstructure and mechanical properties of a High Strength Low Alloy Steel

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Abstract. Effect of double quenching process and tempering temperature on the microstructure and mechanical properties of a High Strength Low Alloy Steel was investigated by OM, SEM, TEM methods and so on. The results demonstrated that double quenching process could refine prior austenite grains (PAG) effectively and the average diameter of PAG was refined by 5.4μm compared with single quenching process. Yield strength and tensile strength of double quenching and tempered specimens (QQT) and single quenching and tempering specimens (QT) exhibited similar variation trend with tempering temperature. Yield strength increased monotonously with increasing tempering temperatures. However, tensile strength descended at first and then recovered with rising tempering temperature. QQT specimens displayed greatly improved impact absorbing energy at -80°C but a little improved yield strength compared with QT specimens owing to the refined microstructure caused by double quenching process. Considerable austenite formed during holding process of tempering (670°C) in which elements of nickel, manganese and copper aggregated. And some of the aforementioned austenite transformed to hard phases (secondary Martensite and M-A islands) and some are retained as islands of austenite after water cooling. The presence of hard phases is the main reason for recovering tensile strength and deteriorating impact absorbing energy at -80°C.

1. Introduction
Low-carbon, copper-strengthened high strength low alloy steel 100 (HSLA100) is broadly applied in hull structure, pipeline and equipment of mining and dredging [1-5]. The low carbon content (≤ 0.07wt.%) is adopted in HSLA100 to avoid pre-heating process before welding, greatly curtailing the processing cost. The strength loss caused by lower carbon content is offset by strengthening of Cu-rich precipitates during the aging process. Low temperature toughness is also another important mechanical property in this steel owing to the wicked service circumstance and loading conditions. Generally, Niobium (Nb) was added as a kind of micro-alloying element in HSLA100 to refine the microstructure by the pinning effect of Nb(C, N) precipitating during hot-rolling process on grain boundaries of austenite. Quenched-tempered process is normally applied in HSLA100 after hot-rolling and the typical applied microstructure of this steel consists of tempered Martensite (M) and (or) Bainite (B) matrix and Cu-rich precipitates of diameters ranging from 2nm to 25nm precipitating in the matrix [1].
Steel with higher strength under the condition of superior low temperature toughness can reduce the manufacturing cost, lose weight of constructions and lower the carbon emission, generating great benefits [6]. It is a well-known fact that refined grains of prior austenite could improve both yield strength and low temperature toughness due to the increased areas of grain boundaries [7, 8]. And process of heat treatments is greatly valued in producing medium and heavy plate because of the advantages for adjusting microstructure without complex operations. Double quenching process, a relatively novel heat treatment, is extensively studied due to the refining effect on the size of prior austenite grains (PAG) and thus refining the size of packet and block of M[9-11]. Consequently, we present here the effect of double quenching process on microstructure and mechanical properties of HSIA100 steel. Furthermore, evolution of microstructure and mechanical properties with increased tempering temperature under heat treatments of double-quenching and tempering was also investigated.

2. Materials and methods
The tested steel plates were commercially hot-rolling of 20 mm thickness and the composition was C0.02–0.07, Si0.39, Mn0.5–0.8, (Ni+Cr+Mo)>4.0, Cu1.50, Nb0.03, Al0.02, Fe balance (mass %). As-rolled plates were firstly heated to 900 °C, holding for 1 h and then water quenched to room temperature (Q). The single quenched plates were again heated to 880 °C, holding for 10 min and water quenched to room temperature (QQ). Q and QQ specimens were then tempered at 620 °C–670 °C for 2h and then water cooled to room temperature respectively, termed as QT and QQT process.

Mechanical properties of both QT and QQT specimens were tested. The tensile properties were evaluated with rod specimens of 5 mm diameter according to GB/228.1-2010. The axial direction of rod tensile specimens was perpendicular to rolling direction. Charpy impacting tests were conducted using standard transverse impacting specimens of 10*10*55mm at -80 °C according to GB/T 229-2007, and the V notch was on the plane of transverse direction and normal direction. Double tensile specimens and three impacting specimens were tested for each tempered condition and the average values were applied.

Grain boundaries of prior austenite were etched using supersaturated solution of picric acid mixed with some detergent and the average intercept of PAG was obtained by intercepting method according to GBT 6394-2002. The macro microstructures were observed with Optical Microscope (OM), Scanning Electron Microscope (SEM). Transmission Electron Microscope (TEM) was applied to observe the refined microstructure and Cu-rich precipitates of tempered specimens.

3. Results and discussion
3.1. Mechanical properties
Fig. 1 shows the average values of yield strength (RP0.2), tensile strength (Rm) and impact absorbing energy for QT and QQT specimens. Variations of RP0.2 and Rm of both QT and QQT specimens show similar trend with increasing temperature. Taking as QQT specimens for example, RP0.2 declines with increasing tempering temperature and the lowest and highest RP0.2 were 690 MPa, 870.5 MPa respectively. Variation of Rm with tempering temperature, however, exhibits two stages. During tempering temperature of 620~650 °C, Rm of QQT specimens show similar variation trend with RP0.2. During tempering temperature of 660~670 °C, Rm of QQT specimens recover with increasing tempering temperature. QT specimens all obtain impact absorbing energy more than 200J at -80 °C and exhibit more excellent low temperature toughness during the whole range of tempering temperature compared with QT specimens, shown as Fig. 1b. And the best toughness is obtained in QQT specimens tempered at 640 °C. It is also seen from Fig.1 that QQT specimens show a little improvement on RP0.2 but obvious enhancement for low temperature toughness.
3.2. Microstructure

3.2.1. Quenched microstructure. SEM images of Q and QQ specimens are illustrated in Fig. 2ab. Microstructures of both Q and QQ specimens consist of M matrix and minor B, and M packet boundaries are readily visible within prior austenite grain boundaries (PAGB). Vickers hardness of Q and QQ specimens is HV367, HV361 with 5 Kg loading respectively. Fig. 2cd shows PAGB of Q and QQ specimens, and PAG of QQ specimen are evidently refined compared with Q specimen. The average intercept of PAG for Q and QQ specimen is 11.95 μm, 7.64 μm respectively, and the average diameter of PAG for Q and QQ specimens is 13.3 μm, 7.9μm respectively.

![Microstructure images](image1)

**Figure 1.** Mechanical properties of tested steel as a function of tempering temperature: (a) strength, (b) impact absorbing energy at -80 °C.

![Microstructure images](image2)

**Figure 2.** Microstructure and prior austenite grain boundaries for Q and QQ specimens: (a) and (c) for Q specimens, (b) and (d) for QQ specimens.

3.2.2. Tempered microstructural evolution. Fig. 3 shows SEM images for microstructural evolution with increasing tempering temperatures ranging from 620~670 °C for QQT specimens. Certain laths of M seem to be merged and recovery after tempering [12], and white-bright phases with rod and chain-like shape exist within tempered M/B matrix. It is also found that those white-bright phases exhibit parallel arrangement indicated by broken circle (Fig 3d) and evidently coarsen at high tempering temperatures (Fig 3d). Those white-bright phases may be the mixture of cementite and transformation product of austenite formed in holding process of tempering after water cooling at low tempering temperature (620 °C). And the above white-bright phases are mainly the transformation product of...
austenite at high tempering temperature (660, 670 °C). Because cementite gradually resolves and transformation product of austenite gradually augments with increasing tempering temperature.

Fig. 4 shows the results of EDS analysis of white-bright phase and tempered M matrix labeled as A and B respectively in Fig. 3d. White-bright phases formed at 670 °C occur segregation of Ni, Cu and Mn alloy elements compared with tempered M matrix. The corresponding micro-hardness indentation of white-bright phase and tempered M matrix in specimens tempered at 670°C are displayed in Fig. 5 and the value of micro-hardness is HV414, HV319 with 10g loading respectively. It is reasonable to deem coarsened hard white-bright phases as secondary M or M/A islands transformed from austenite after water cooling. And this need to be further discussed in Section 3.3.1.

3.2.3. TEM analysis. Fig. 6 displays the refined microstructural evolution of QQT samples with increasing tempering temperature. Tempered LM and elliptical spherical Cu-rich precipitates

Figure 3. Microstructural evolution of double-quenched specimens at different tempering temperatures: (a) 620°C, (b) 640°C, (c) 660°C, (d) 670°C.

Figure 4. Elementa analysis of A and B spots selected from figure 3d by EDS.

Figure 5. Microstructure and micro-hardness indentation of double-quenched specimen tempered at 670°C: (a) original microstructure, (b) micro-hardness indentation.
precipitating in LM are easily observed in Fig.6a, and dislocations with un-fully recovery are readily visible within certain laths. Fig.6bc illustrates the film-like secondary M transformed from austenite between laths after water cooling and the corresponding selected area diffraction pattern. Film-like secondary M with length of about 0.43 μm and width of about 0.12 μm is consistent with the observation of white-bright phase in SEM (Fig. 6). Cell-like sub-grain forms and incises laths of M indicating the occurrence of recrystallization, and coarseness of Cu-rich precipitates within laths is also shown in Fig.6d. Average diameter of Cu-rich precipitates in specimens tempered at 620, 640, 670 ℃ is 17.05, 22.59, 28.86 nm respectively. Fig. 6def shows bright image, dark image and selected area diffraction pattern of a film-like M/A island transformed from austenite after water cooling. Retained austenite and M contained in M/A island conform to Kurdjumov-Sachs (K-S) relationship, i.e., (-1-11) γ // (01-1) α, [-110] γ // [1-1-1] α. Fig7abc shows bright image, dark image and selected area diffraction pattern of island shaped austenite locating at crystal corner transformed from austenite due to be of sufficient thermal stability. Fig7d shows bright image, selected area diffraction pattern of island shaped secondary M between laths.

Figure 6. TEM image and selected area diffraction pattern of double-quenched specimen tempered at different temperatures: bright images at 620 ℃(a), 640 ℃(b), diffraction pattern of secondary M(c) in (b), bright image of M/A island at 670 ℃(d), dark image of M/A island at 670 ℃(e), diffraction pattern of M/A island (f).
3.3. Discussion

3.3.1. Thermal calculation of equilibrium phases and transformation products of austenite. Thermal calculation of main equilibrium phases of tested steel was conducted by thermal-calculation software, and the relevant results are shown in Fig. 8. Fig. 8a shows austenite could exist during 500–760 °C, and the volume fraction increases with increasing temperature. The volume fraction of austenite is 8.8%, 13%, 24.8% when the temperature is 620, 640, 670 °C respectively. Volume fraction of Cu-rich precipitates declines with increasing temperature, and the dissolving temperature for Cu-rich precipitates is nearly 700 °C. The volume fraction of Ferrite is also reduce with increasing temperature during 500-760 °C. Fig. 8b exhibits variation of main alloying elements (C, Mn, Ni, Cu) contained in austenite with increasing temperature and the enriching extent for the above alloys contained in austenite increases with dropping temperatures. Taking austenite formed at 670 °C for instance, mass contents of C, Mn, Ni, and Cu contained in it are 0.136%, 2.27%, 6.27%, 2.32% respectively and are several fold than the contents of relevant alloys shown in nominal composition. The calculated results for enrichment of the above elements contained in austenite formed at 670 °C are consistent with the results of EDS analysis of white-bright phases.

Austenite formed during holding process of tempering transforms to different kind of products, which was determined by grain size and the content of alloying elements contained in austenite after water cooling. On the one hand, the higher contents of alloying elements such as C, Mn, Ni, and Cu contained in austenite, the lower the temperature of M starting transformation. And austenite with high
contentment of the above alloy elements is inclined to be retained at room temperature after quenching. On the other hand, the smaller the austenite grains, the easier it is supposed to be retained at room temperature after quenching, i.e., size stabilizing effect of austenite. Chen et al [13] shows that this effect is caused by lacking in effective nucleation positions in extremely fine austenite grains. The combination of observation made by SEM, TEM, micro-hardness and tensile tests could make a conclusion that partial austenite formed at 670 °C transformed to hard phase of secondary M and M/A island after water cooling, and partial austenite were still retained at room temperature. It is reasonable to make a hypothesis that austenite formed at temperature lower than 670 °C is inclined to be retained at room temperature, taking grain size and enriching extent of alloy elements contained in austenite into consideration. And coarsening of Cu-rich precipitates, recovery of dislocation and soften of M/B matrix also occurs with increasing tempering temperature [14].

3.3.2. Strengthening and toughening mechanism. Yielding phenomenon in steel is the outcome of slipping of massive dislocations [15]. In other words, yield strength of steels depends on how easily a large number of dislocations slip. The mechanism for yield strength of tested steel declined with increased tempering temperatures in QQT specimens is as follows. The average diameters of Cu-rich precipitates increased with increasing tempering temperature, however, the volume fraction of Cu-rich precipitates exhibited the opposite trend with increasing tempering temperature. The comprehensive changes of Cu-rich precipitates led to the reduce of precipitating strengthening effect according to the Orowan mechanism expressed by Eq.(1) [16]:

$$\Delta \sigma_{Orowan} = \frac{MGB}{\sqrt{\frac{4\pi}{3}}} f$$  \hspace{1cm} (1)

Where M is Taylor factor, G is the shear modulus of matrix taken as 80GPa, b is the burgers vector, r is the average radius of Cu-rich precipitates and f is the volume fraction of Cu-rich precipitates. Furthermore, strengthening effect caused by dislocation and solidification also reduce due to dislocation recovery and solidification atoms precipitating from M/B matrix during tempering.

Mechanism for Variation of tensile strength with tempering temperature ranging from 620~650 °C is similar to the one of yield strength. However, tensile strength of QQT specimens tempered at 670 °C recovers, which is caused by the formation of hard phases of secondary M and M/A island after tempering. Microstructure of QQT specimens tempering at 670 °C consists of soft tempered M/B matrix and hard phases. Model of tensile strength of dual-phase steel is expressed by Eq. (2) [17]:

$$R_m = \lambda_\alpha(1 - f_\beta)R_m^\alpha + \lambda_\beta f_\beta R_m^\beta$$  \hspace{1cm} (2)

Where Rm is the tensile strength of dual-phase steel, $\lambda_\alpha$ and $\lambda_\beta$ is the constant about uniform true strain respectively, $f_\beta$ is the volume fraction of $\beta$ phase and $R_m^\alpha$, $R_m^\beta$ is the tensile strength of $\alpha$, $\beta$ phase respectively. It could be seen from Eq. (2) that formation of hard phases is a key reason for recovering of tensile strength.

Fig. 9 shows the impact fracture surfaces for QT and QQT specimens. All fracture surfaces of QQT specimens consist of fibrous area and shear lip zone, and all ones of QT specimens consist of fibrous area, evident cleavage area and shear lip zone. The ratios of cleavage area accounting for the whole fracture surface for QT specimens tempered at 620, 670 °C are larger than others, indicating the relatively poor total absorbing energy. Detailed observation for central areas of QT and QQT specimens tempered at 660 °C were shown in Fig. 9bc. Central area of QQT specimen is characteristic of numerous dimples connecting (Fig. 9b), indicating ductile fracture mode. However, ones of QT specimens consist of flat cleavage facets connected by tear ridges (Fig. 9c), indicating quasi-cleavage fracture mode. It could make a conclusion that the refinement of PAG caused by double quenching process converts the fracture mode. Beneficial effect of lower P, S brittle elements contained in zones of grain boundaries caused by grain refinement is also attributed to this conversion.
Figure 9. Characteristics of impact fracture surfaces for QT and QQT specimens: (a) macro image of QT and QQT specimens tempered at 620, 640, 660, 670 °C, (b) detailed observation for central area in fracture surface of QQT specimen (b) and QT specimen (c) tempered at 660 °C.

Variation of low temperature toughness of QQT specimens with increasing temperature show similar trends with QT specimens. Taking QQT specimens for instance, toughness improved with increasing tempering temperature ranging from 620~640 °C, subsequently declined with increasing tempering temperature. The best toughness (258.3J) was obtained in specimens tempered at 640 °C. The toughening mechanisms for tempered specimens during tempering temperature of 620~670 °C are determined by integrated effects of following factors.

1. Coarsening of Cu-rich precipitates and elevating extent of dislocation recovery in M/B matrix with increasing tempering temperature improved the toughness; 2. Austenite formed at holding process of tempering absorbed P and S brittle element from matrix, purifying the matrix, and ‘TRIP effect’ of island shaped retained austenite in the course of impacting deformation process improved toughness[18]; 3. Hard phases of secondary M and M/A island formed after tempering at high temperatures deteriorated toughness, because hard phases are usually the initiation resource of crack nucleation and the interfaces between hard phases and matrix are usually the propagation path during crack propagation.

4. Conclusion
   1. Double quenching process effectively refined the prior austenite grains compared with traditional single quenching process, the average diameter of austenite grains for Q and QQ specimens were 13.3 μm, 7.9 μm respectively.
   2. Cu-rich precipitates coarsened with increasing tempering temperature, and the average diameter of Cu-rich precipitates at tempering temperature of 620, 640, 670 °C is 17.05, 22.59, 28.86 nm respectively. Film-like and island shaped austenite formed in holding process of tempering (670 °C) obtained complicated transforming products after water cooling, including secondary M, M/A island and island-shaped austenite depending on grain size and enriching extent of alloying elements.
   3. QQT specimens during the tempering temperature of 620~670 °C exhibited greatly improved low temperature toughness and a little higher yield strength caused by grain refinement compared with QT specimens. And the optimal combination of strength and low temperature toughness is \( R_{p0.2}=821\text{MPa}, R_m=842.5\text{MPa}, \) and total impact absorbing energy at -80 °C is 258.3J. Hard phases
such as secondary M and M/A island formed after tempering (670 °C) led to recovery of tensile strength and deterioration of toughness for QQT specimens.

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