Effects of Q&T parameters on phase transformation, microstructure, precipitation and mechanical properties in a PS-30Cr2Nb pipeline steel

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Abstract
The heat treatments with different quenching and tempering temperatures were conducted to clarify the effects of Q&T (quenching and tempering) parameters on phase transformation, microstructure, precipitation, mechanical properties in a PS-30Cr2Nb pipeline steel. Results indicate that the optimum property of tensile strength of 892 MPa and elongation of 19.17% was obtained at a low quenching (950 °C) and low tempering temperature (570 °C). Finer prior austenite grains and carbides contributed to the higher strength. Besides, the content of coarsening carbides increased with tempering temperature and quenching temperature. The increased content of coarsening carbides is responsible for the deteriorative comprehensive performance. In addition, Fe3C particle was gradually substituted by the alloy carbides with the proceeding of tempering by the dynamic assignment of elements.

1. Introduction

Pipeline steels are used for the transportation of oil and gas, and are high technology, high value products [1–3]. A well-developed system of oil and gas exploitation consists of a series of pipeline steels which joints each other by welding [4, 5]. Pipeline steels have an enormous application market in China due to the vast land resources and abundant petroleum resources in China. The annual consumption of pipeline steel is very large, motivating the development of the advanced pipeline steels [6–10]. The service life of pipeline steels should be long enough to reduce the replacement cost. Therefore, more and higher quality requirements for pipeline steels are successively put forward to satisfy the complex topography and extreme weather conditions. For all this, customers put a high requirement to the strength, toughness and welding performance of pipeline steels. Furthermore, the resistance ability of hydrogen-induced cracking (HIC) and sulfide stress corrosion cracking (SSCC) in pipe-line steels should not be neglected either [11–15].

Pipeline steels are commonly treated by quenching and tempering process (Q&T) to obtain a good toughness phase such as tempered martensite or bainite. Quenching process provides a high strength microstructure and appropriate tempering process ensures the superior toughness in the steels. Quenching and tempering process are widely used in many special steels such as the cryogenic pressure vessel steel, the automotive steel and spring steel etc. For instance, Chen et al [16] investigated the influences of soaking and tempering temperatures on the microstructure and mechanical properties of 65Si2MnWE spring steel. Guo et al [17] discussed the effects of combined addition of copper (Cu) and niobium (Nb) on the microstructure, hardness and precipitation behavior during tempering in ultra-low carbon steels. In the research of Nagao et al [18], the influence of nanosized (Ti, Mo)C precipitates on hydrogen embrittlement of tempered lath martensitic
steel was analyzed and it was found that the introduction of nanosized (Ti, Mo)C precipitates improves the HIC of a high-strength tempered lath martensitic steel by providing a high density of hydrogen traps. Ju et al [19] investigated the carbide precipitation in low-carbon low alloy quench and tempered steels and revealed that auto-tempering occurred in the tested steels during water quenching, and cementite and ε'-carbide were both observed in microstructure.

Steel PS-30Cr2Nb, a newly developed pipeline steel, is normally heat-treated by Q&T process. However, the mechanical properties of PS-30Cr2Nb steel are unstable and easily affected by the quenching and tempering temperatures. Therefore, in the present study, the heat treatments with different quenching and tempering temperatures were conducted to clarify the effects of Q&T parameters on phase transformation, microstructure, precipitation, mechanical properties in a PS-30Cr2Nb pipeline steel. Results provide a useful guidance for the accurate control of Q&T parameters and ensuring the performance stability of PS-30Cr2Nb pipeline steel.

2. Experimental procedures

The investigated steel was taken from the commercially produced PS-30Cr2Nb pipeline steel with chemical compositions of Fe-0.08C-0.33Si-1.50Mn-0.054Cu-0.208Ni-0.30Cr-0.206Mo-0.014Ti-0.02Nb-0.021Al. In order to obtain the accurate Ac1 and Ac3 temperatures signifying the starting and the finishing temperatures of austenite transformation, a thermal simulation experiment with a heating rate of 3 °C min⁻¹ was conducted with the tested steel on a Gleeble 3500 thermo-mechanical simulator. According to the record dilatation and temperature in figure 1, the Ac1 and Ac3 temperatures were determined to be about 754 and 912 °C, respectively. Tangent method was applied to determine the critical temperature [20–22].

Figure 2 illustrates the thermal simulation experiment procedures with various quenching and tempering processes. Figure 3(a) gives the corresponding dimension of cylindrical specimens for the thermal-simulator experiments. Thermocouple was spot welded in the heating zone of Φ6 cylinder specimens. Specimens were heated to 950 and 1100 °C (both larger than 912 °C) at a heating rate of 20 °C s⁻¹ and held for 10 min followed

![Figure 1. Dilatation-temperature result of the tested steel.](image1)

![Figure 2. Thermal simulation experiment procedures.](image2)
by 50% deformation at a strain rate of 0.1 s$^{-1}$. Then the specimens were quenched to room temperature at a cooling rate of 100 °C s$^{-1}$. After that, specimens were reheated to tempering temperature of 570 and 620 °C at 10 °C s$^{-1}$ and isothermally held for 30 min before subsequent cooling to room temperature at 5 °C s$^{-1}$.

According to the quenching and tempering parameters, specimens were labeled as 950–570, 950–620 and 1100–620, respectively. During the thermal simulation experiments, the dilatation-temperature-time data was synchronously recorded.

Microstructure observations were conducted on a Zeiss optical microscope (OM), Nova400 Nano field emission scanning electron microscope (FE-SEM) and JEM–2100F transmission electron microscope (TEM) equipped with energy disperse spectroscopy (INCA–EDS). In addition, the precipitations were captured and analyzed by TEM and EDS. Specimens for precipitations observation by TEM were prepared by carbon replica. Related methods for laboratory sample preparation were given in author’s previous studies [23–25]. Besides, Adobe Photoshop 2013 was used to characterize the grains in the obtained microstructures. Tensile tests were performed on the Instron–3599 universal tensile testing machine at room temperature. Nonstandard specimens were machined according to figure 3(b). Duplicate tests were carried out to ensure the accuracy of the experiments. As the deformation and heat treatment were conducted on a thermo-mechanical simulator, the sample dimension was limited to a small size and larger specimens could not be tested on this equipment to characterize the material performance. Therefore, small specimens were used in the present study. Small specimens were often used by other researchers [26, 27].

3. Results and discussion

3.1. Phase transformation

Figure 4 gives the dilatation-temperature curves of specimens at different quenching and tempering temperatures, indicating the change of specimen diameters after deformation. It is evident that a few bainite formed in the specimens quenched at 950 °C, while no bainite transformation was observed in the specimens quenched at 1100 °C during cooling. After bainite transformation, apparent martensite transformations happened in all specimens. The starting phase transition temperatures of martensite (PTs) in the three specimens were 480, 479 and 497 °C, respectively. There was little change of PTs in specimens quenched at the same temperature, whereas the PTs increased apparently at high quenching temperature, which is consistent with results reported by Bhadeshia et al [28]. Firstly, the bainite transformation hindered the martensite transformation due to the carbon emission during bainite transformation. The carbon content in the untransformed austenite was higher, enhancing the chemical stability of untransformed austenite. In addition, with the decrease of quenching temperature, the prior austenite grain (PAG) size was supposed to decrease,
increasing the strength of austenite. Consequently, the martensite transformation was postponed with the decrease of quenching temperature.

During the quenching process, martensite transformations happened, and the transformation amount can be calculated and expressed by the absolute value of dilatation change. Figure 5 exhibits the quantitative transformation amount of martensite during quenching process, where martensite transformation started at point PT\(_s\) and finished at PT\(_f\). The dilatation curve went up from point PT\(_s\) to point PT\(_f\) during martensite transformation. Assuming that no transformation happened during the cooling process, the dilatation would decrease from point PT\(_s\) to point PT\(_f\). Thus, the absolute value of the height of PT\(_f\)-PT\(_f\) represents the amount of martensite transformation. It is discernible from figure 5(d) that the transformation amount had little change at the same quenching temperature (950 °C), while it increased obviously at higher quenching temperature of 1100 °C. At the same quenching temperature, the PAG and the precipitation state were almost the same and the martensite transformation was supposed to be same. But, the amount of martensite transformation in the specimen quenched at 1100 °C was apparent more than that in the specimens quenched at 950 °C, which could be explained by the increased PT\(_s\) point (figure 4(c)) and easier growth of martensite laths in larger austenite grains at high temperature.

### 3.2. Microstructure

Figure 6 shows the microstructures of quenching martensite in specimen quenched at 950 °C and specimens quenched and tempered at different temperatures. It is clear that the quenched martensite phase is pretty pure without visible precipitations. Moreover, some retained austenite (RA) would form as well between the lathy martensite. In addition, it is reasonable to infer that a lot of dislocations aggregate in the quenched martensite lath. The initiation and aggregation of dislocations in the martensite are related to the crystal texture and transformation mechanism of lath martensite. Observation from the tempered microstructures, it is noticeable that lots of carbides precipitated in the tempered martensite. Secondly, in the specimen 1100–620, relative fewer amount carbides were observed. This is caused by larger prior austenite grains. To characterize the PAG boundaries, contour lines were drawn by Adobe Photoshop and presented in figure 7. It is discernible that the dimensions of PAGs have little change in the specimens quenched at the same temperature despite of different tempering temperature. However, the PAGs apparently become larger, resulting in the longer martensitic
microstructure at higher quenching temperature of 1100 °C. With the increased PAG in the specimen quenched at 1100 °C, the grain boundary area decreases, thus providing less nucleation sites for carbides during tempering. Besides, a lot of deformed dislocations are generated in deformed specimens after quenching, which act as the fast track for the elements diffusion during tempering. At a higher quenching temperature, the amount of deformed dislocations decreases, which was unfavorable for the precipitations. Thirdly, in the specimen 1100–620, carbides distributed on the grain boundaries of prior austenite were much more visible. The dimension of carbides obviously increased with the increase of quenching temperature at the same tempering temperature. This is because the heterogeneous nucleation sites (grain boundaries and defects) for carbides in specimen 1100–620 is limited and gradually attenuate to zero with the tempering. Besides, the precipitation and growth of carbides results in the decrease of supersaturation in its surrounding metal matrix, and causing a drastically decrease in the phase transformation free energy. Therefore, the alloying elements continually migrate from small-size carbides to the relative large-size carbides by long-range diffusion, which prompts the dissolution and coarsening of carbides in specimen 1100–620.

Figure 8 shows the coarsening particles in the specimen 1100–620 and its corresponding schematic diagram. It is evident that the grain boundaries become the main sites for the coarsening carbides, especially the intersections of grain boundaries such as the trigeminal grain boundary. The grain boundaries are the conclusive parclose for the elements diffusion which are easy to generate and accumulate multifarious defects and alloy elements. Moreover, the free energy at grain boundaries is relatively higher than that within the grains, which is beneficial for the growth of carbides. In specimen 1100–620, the grain boundary area is the smallest while the elements diffusion is the most prosperous due to the relatively less dislocations and martensitic laths. It is much easier for the diffusion elements such as Fe, Mn and Cr ions to be aggregated at the limited grain boundaries. Therefore, the coarsening particles are clearly more prone to appear in the specimen 1100–620. The coarsening particles at the grain boundaries often become the origin of the cracks and lead to the final material failure. Besides, the precipitation strengthening effect by the precipitations decreases.
3.3. Precipitation

TEM morphologies of precipitations and the corresponding EDS results of carbon replica patterns are depicted in figures 9–11. These precipitates are mainly identified as a composite precipitation of carbon and alloy elements according to the corresponding energy spectrum. Composite precipitation is preferential because mutual dissolution occurs easily in these particles. In specimen 950–570, the dimension of carbides is small and these carbides mainly distribute as round granule. Some particles are determined to be $(\text{Nb, Ti})\text{C}$ particles while some others are orthorhombic $(\text{Fe, Mn, Cr})_3\text{C}$ particles. Less Mn and Cr elements are detected in the $(\text{Fe, Mn, Cr})_3\text{C}$ particle, while the total weight ratio of Fe and C is 87.74, indicating that these carbides are mainly cementite particles $(\text{Fe}_3\text{C})$ containing a few amount of element Mn and Cr.

The precipitations in the specimen 950–620 are shown in figure 10. It is clear that coarsening phenomenon occurs in some carbides. These coarsening carbides mainly present in the shape of long bar. According to the spectrum results, the granular carbides are $(\text{Nb, Ti})\text{C}$. However, for the coarsening carbides, the total weight ratio of Fe and C is 51.18 which is obviously reduced compared to that in the specimen 950–570. The total weight ratio of other alloying elements increases to 48.82, in which the effects of Nb and Ti are prominent. In addition, it seems that the amount of precipitations in specimen 950–620 is decreased compared to that in specimen 950–570. It is possible caused by the increasing coarsening carbides. In order to compare the content of precipitates quantitatively, the average total numbers of precipitates per unit area of $\mu\text{m}^2$ in several TEM images for each specimen were determined. The content of precipitates decreased from $240\ \mu\text{m}^{-2}$ in specimen 950–570 to $189\ \mu\text{m}^{-2}$ in specimen 950–620.

In the specimen 1100–620, large amounts of coarsening carbides are observed (figure 11). These coarsening carbides distribute in ellipsoidal or spherical patterns. According to the spectrum result, the total weight ratio of Fe and C is 36.22, while the total weight ratio of other alloying elements increases to 63.78. The total weight ratio of Nb, Ti and C increases to 89.13. It manifests that the coarsening carbides are the composited precipitate of $(\text{Nb, Ti})\text{C}$ and $(\text{Fe}_3\text{C})$, in which the $(\text{Nb, Ti})\text{C}$ particles are dominating. Furthermore, the content of carbides in specimen 1100–620 obviously decreased $(52\ \mu\text{m}^{-2})$. It is well known that the formation of carbides includes nucleation and growth, in which the nucleation process mainly depends on the temperature and nucleation sites and the growth relies on the temperature. With the increasing tempering temperature, the atom diffusion and combination between alloy elements and carbon atoms are prosperous. Hence, the content of carbides should
increase with the tempering temperature. However, in specimens 950–620 and 1100–620, due to the dissolution of small carbides, the content of carbides decreases in the end. In addition, with the increasing quenching temperature in specimen 1100–620, the PAGs grow larger and dislocation density decreases, thus providing less nucleation sites for carbides during tempering. Therefore, the content of carbides in the specimen quenched at 1100 °C is the smallest.

**Figure 7.** Contour lines of tempered martensite in specimens: (a) 950–570, (b) 950–620 and (c) 1100–620.

**Figure 8.** (a) Coarsening particles in the specimen 1100–620 and (b) Its schematic diagram.
According to Gibbs-Thomson theory, the concentration of carbon atoms in small carbides is higher than that in larger carbides. Thus the smaller carbides are unstable at a higher tempering temperature, which facilitates the migration of carbon atoms and the coarsening of carbides. Figure 12 exhibits the schematic diagram of the formation mechanism for coarsening carbides. The increased amount of other alloying elements in the Fe₃C particles is caused by the dynamic assignment of elements at higher tempering temperature. Normally, the Mn, Cr, Nb, Ti atoms aggregate in the Fe₃C particle, while the Si and Al atoms diffuse towards the metal matrix. This behavior can be explained by the in situ nucleation of alloy carbide relying on Fe₃C particle. At higher tempering temperature, the diffusion of alloy elements with large diffusion activation energy is sufficient. The Fe₃C particles are the most unstable in chemical stability, thus the strong carbide forming elements such as...
Nb, Ti, Mn etc increasingly supersede the weak carbide forming elements. Finally, the Fe₃C particles are gradually substituted by the alloy carbide. In addition, the lattice misfit between the particles macroaxis and matrix is large. And it is easy for the alloy elements to diffuse into the carbides from the direction with a large lattice misfit. Thus, the carbides turn to grow along macroaxis at a high tempering temperature. With the proceeding of tempering, the concentration difference of alloy elements along the axial direction of carbides decreases, weakening the diffusibility of elements and accelerating the enrichment of alloy elements at the interface between the carbides and metal matrix. Finally, the carbides further grow up and turn to be an ellipsoidal or spherical morphology. For the specimen 1100–620, the tempering temperature is high enough for the coarsening of carbides. Besides, due to the relative larger PAGs, the dynamic allocation of alloy elements is limited in the fewer content of carbides. As a consequence, coarsening carbides are more likely to appear at high quenching and tempering temperatures.

3.4. Mechanical properties
Figure 13 presents the engineering stress-strain curves of specimens quenched and tempered at different temperatures. Specimen 950–570 exhibits the maximum tensile strength of 892 MPa and total elongation of 19.17%. The tensile strength decreased to 850 MPa in specimen tempered at 620 °C and 815 MPa in specimen quenched at 1100 °C. It is clear that apparent yield points occurred in the specimens, and the yield strength also decreased in sequence. The largest strength of specimen 950–570 is attributed to the more fine carbides and dislocation in microstructure, while the decrease of strength and elongation in specimen 950–620 may be ascribed to coarse carbides and less dislocations. The further decrease of strength and better elongation in specimen 1100–620 are caused by larger PAGs, less dislocations, large carbides in the microstructure. Results
reveal that the optimum quenching and tempering temperatures are 950 and 570 °C, respectively, for the best mechanical properties.

Various investigations have been carried out to study the effect of tempering temperature on the mechanical properties of different steel grades [30, 31]. In general, the tensile strength is deteriorated with the increasing tempering temperature due to the recovery of martensitic laths and the coarsening carbides, which is in accordance with the results in current work. The coarsening of carbides not only weakens the precipitation strengthening effect, but also impairs the solution strengthening effect. However, the effect of quenching temperature on the microstructure and precipitations has not been fully clarified. In the present study, with the increase of quenching temperature, the strength obviously decreased. According to Hall-Petch equation [23], which explains the relationship between strength and grain size, the strength increases with the refined grains. Therefore, in the specimen quenched at 1100 °C, the decrease in strength is mainly originated from the larger PAGs, the decrease and coarsening of carbides. Thus, the effects of both grain refinement and precipitation strengthening were weakened.

Therefore, for the PS-30Cr2Nb pipeline steel in the present study, the optimum property of tensile strength of 892 MPa and elongation of 19.17% was obtained at a low quenching temperature (950 °C) and tempering temperature (570 °C). Finer PAGs and carbides contribute to the higher strength. The coarse carbides in specimen treated at high quenching and tempering temperatures are responsible for the deteriorative performance.

4. Conclusions

The current work focused on the relationships between Q&T parameters and phase transformation, microstructure, precipitation and mechanical properties in the PS-30Cr2Nb pipeline steel. Microstructure observation and precipitation analysis were carried out in the quenched and tempered specimens. Following conclusions can be obtained:

(1) The optimum property of tensile strength of 892 MPa and elongation of 19.17% was obtained at a low quenching (950 °C) and tempering temperature (570 °C). Finer PAGs and carbides contribute to the higher strength.

(2) The content of coarse carbides increased with tempering temperature and quenching temperature. The coarse carbides are responsible for the deteriorative performance.

(3) Fe₃C particles were gradually substituted by the alloy carbides with the proceeding of tempering by the dynamic assignment of elements.

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