Study on Microstructure Control of X80 Pipeline Steel and Precipitation of Nb Element

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Abstract. In this paper, X80 grade test steel was trial-produced in the laboratory, the mechanical properties, microstructure and precipitate morphology of the trial-produced test steel were analyzed and studied, and the precipitation law of Nb element in high-grade pipeline steel was studied by thermal simulation method. The results show that the X80 grade test steel has excellent mechanical properties, yield strength of 660 MPa, tensile strength of 720 MPa and yield ratio of 0.91. The impact energy is greater than 295 under -20 °C test conditions and the cross-section rate of the DWTT fiber reached 90% under -15 °C test conditions, and the test results completely meet the API 5L standard requirements. By the thermal simulation experiment, it is found that the precipitation process of Nb particles in the test steel is the nucleation growth process of controlled by diffusion. The tip temperature of the PTT curve is about 900 °C, and the Nb element in the test steel is found at 810 °C by solid solubility calculation can be completely precipitated.

1. Introduction
Pipeline transportation plays an irreplaceable role in transporting oil and natural gas over long distances, and has advantages such as economic rationality and transportation safety[1~2]. Therefore, it is particularly important to study the precipitation rules of high-grade pipeline steel. Pipeline steel of grade X70 and above is usually called high-grade pipeline steel. With the maturity of metallurgical components and processes, its internal structure and performance can be further improved. With the evolution and development of microstructure, the strength and toughness of pipeline steel are continuously improved[3~4].

Microalloying technology can effectively improve the comprehensive performance of pipeline steel, its basic principle is that microalloying elements are solid-dissolved in iron matrix and exist in the form of carbonitrides. Microalloying elements and their precipitates will affect the behavior of austenitic grain coarsening, austenitic recrystallization and phase transformation in steel to a large extent. In the production process of high-grade pipeline steel, the properties of the material are further improved through the precipitation strengthening of microalloying element precipitates[5]. Meanwhile, adjusting austenite and refining structure by using TMCP technology. The disadvantage is that various parameters of TMCP process, such as cooling system, temperature and deformation, will affect the precipitation behavior of microalloy elements to some extent. In this paper, the X80 pipeline steel produced by the laboratory is used as the object to study the microstructure performance control and isothermal precipitation of high-grade X80 pipeline steel, and provide theoretical and experimental basis for the industrial production of high-grade pipeline steel.
2. Composition design and microstructure control of test steel
This paper studies the high-grade X80 pipeline steel smelted and rolled in the laboratory. The chemical composition is shown in Table 1. It can be seen from Table 1 that the X80 pipeline steel produced in the laboratory is designed with low carbon content, strictly controlling the content of S and P elements, S ≤ 0.002%, P ≤ 0.01%; adding 0.08% Nb element to improve the test steel Recrystallization temperature, and the second phase particles were precipitated in the subsequent cooling process to produce precipitation enhancement; Adding 0.015% Ti element to increase the precipitation strengthening effect of the test steel, adding 0.25% Mo element to increase the hardenability of the test steel, so that the test steel can produce acicular ferrite and granular bainite structure in a wide range of cooling rate. At the same time, the test steel was added with 0.2% Cu element to enhance its corrosion resistance, and 0.2% Ni element was added to increase the fine grain strengthening effect of the test steel.

|        | C    | Si    | Mn    | S     | P     | Nb    | Ti    | Mo    | Cu    | Ni    | Pcm  |
|--------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|------|
| X80    | 0.055| 0.25  | 1.85  | ≤0.002| ≤0.01 | 0.08  | 0.015 | 0.25  | 0.20  | 0.2   | 0.21 |

The test steel was smelted in a 50kg vacuum induction furnace, then the ingot was heated and forged into a rectangular hot-rolled billet of 110 mm (length) × 100 mm (width) × 95 mm (height). The test steel was rolled into 11mm thick steel plate samples on a four-high hot rolling experimental mill. Rolling adopts two-stage controlled rolling process of recrystallization zone and non-recrystallization zone, the first stage is recrystallization zone rolling, the rolling temperature is set to 1130 ℃, the final rolling temperature is 1080 ℃, and the cumulative reduction ratio is >58%; The second stage was rolling in the non-recrystallization zone, the rolling temperature set at 930 ℃, the finishing temperature to 810 ℃, the compression ratio is 3.6, cooling temperature is 400 ℃. The specific rolling pass reduction control and temperature control are shown in table 2 and table 3.

| Rolling pass | Inlet thickness /mm | Outlet thickness /mm | Pass reduction /mm | Pass reduction rate /% | Cumulative reduction rate /% |
|--------------|---------------------|----------------------|--------------------|------------------------|-----------------------------|
| First stage rolling | 1 95               | 80                   | 15                 | 16                     | 16                          |
|               | 2 80               | 68                   | 14                 | 18                     | 31                          |
|               | 3 68               | 54                   | 14                 | 21                     | 45                          |
|               | 4 54               | 40                   | 14                 | 26                     | 58                          |
| Second stage rolling | 5 40               | 33                   | 7                  | 18                     | 18                          |
|               | 6 33               | 25                   | 8                  | 24                     | 38                          |
|               | 7 25               | 18                   | 7                  | 28                     | 55                          |
|               | 8 18               | 13                   | 5                  | 27                     | 68                          |
|               | 9 13               | 11                   | 2                  | 15                     | 73                          |

| First stage finishing temperature /℃ | Second stage rolling temperature /℃ | Second stage finishing temperature /℃ | Coiling temperature /℃ | Cooling speed /℃/s |
|--------------------------------------|--------------------------------------|--------------------------------------|------------------------|---------------------|
| 1130                                 | ≥1080                                 | 930                                  | 810                    | ≥35                 |

Figure 1 shows the microstructure of the X80 test steel produced in the laboratory. It can be seen from figure 1 that the microstructure of the X80 test steel produced in this trial is dominated by granular bainite (GB), with a small amount of acicular ferrite (AF) and polygonal ferrite (QF). There is no obvious difference between the rolling direction, the transverse direction and the 1/4 of the thickness of the sheet in the direction of 30°, the tissue is evenly distributed, and the A/M island is smaller in size and evenly distributed.
Figure 1. The microstructure of the X80 test steel plate at 1/4 thickness (A: rolling direction, B: transverse direction, C: 30° direction with rolling direction)

It can be seen from Fig.2 that there are dislocations and dislocation pile-up in the vicinity of the M/A island. At the same time, it can be seen that the grain boundary step emits dislocations into the intragranular, indicating that the yield of the adjacent two grains has a certain order, that is, the dislocation pile-up at the grain boundaries causes work hardening of the grains and stress concentration at the grain boundaries. The grain boundary strength is higher than the intragranular strength at normal temperature, but when the stress concentrates to a certain extent and reaches the yield strength of the adjacent grains, the grain boundary will emit dislocations in the adjacent grains, causing the adjacent grains to yield and reduce or eliminate the stress concentration of the grain boundary. In addition, the pinning effect of the precipitated particles on dislocations is very significant.

Figure 2. TEM morphology of X80 test steel

Figure 3 shows the morphology of precipitated particles in the prototype X80 test steel. It can be seen from Fig.3 that the precipitated particles of the test steel are mostly large in size, and the typical particles are mostly around 50nm, the precipitation type is mostly composite precipitation of Ti and Nb carbonitrides, the square particles and the circular particles overlap in the photograph. By energy
spectrum analysis, it can be known that the Nb content in the circular particles is high, the Ti content in the square particles is high, and the Nb/Ti atomic ratio is 7.1.

Table 4 shows the mechanical properties of the X80 test steel. It can be seen from Table 4 that the yield strength of the prototype X80 test steel is 660 MPa, the tensile strength is 720 MPa, the elongation A50 is 40%, and the yield ratio is 0.91. The DWTT performance was measured at -15°C with a fiber cross-section of 90%. Three parallel specimens were taken on the test steel plate and the impact properties were measured at -20°C and averaged. The impact energy was between 295J and 335J, and the fiber cross-section ratio was greater than 95%. From this, it can be seen that the prototype X80 test steel meets the requirements of API 5L standard.

Table 4. X80 test steel mechanical properties

| Steel grade | thickness | $R_0$/MPa | $R_e$/MPa | $\Delta\delta$/% | $R_0/R_e$ | DWTT (-15°C) | CVN (-20°C) | $\Delta\alpha$ | $\Delta A$ | SA% |
|-------------|-----------|------------|------------|----------------|------------|---------------|--------------|-------------|----------|-----|
| Measured value | 11mm | 660 | 720 | 40 | 0.91 | 90 | 335/295/297 | 100/95/95 |
| API 5L | 555~705 | 625~825 | $\geq 16$ | $\leq 0.93$ | 80~90 | $\geq 54$ | $\geq 70$ |

3. Experimental scheme for precipitation of Nb element in test steel

The laboratory-tested X80 test steel was processed into a cylinder of φ8×12 mm and placed on a Gleeble-3500 thermal simulation test machine for thermal simulation experiments. First, Heating of the sample with 10°C/s speed up to 1200°C, Second, the sample is kept for 30 min, then cool to 1.5°C/s cold speed to the deformation temperature, and then kept for 1 min, subsequent deformation, the deformation amount is 20%, the deformation rate is 5s⁻¹, and then the isothermal constant strain is maintained for 1000s, at the same time stress variation in the measurement. The deformation temperature is 800°C, 850°C, 900°C, 950°C, 1000°C, 1050°C and 1100°C. The logt-stress curve was made using the experimental data, and the starting position and the ending position of the platform were determined on the stress relaxation curve as the start time and end time of the precipitation. The experimental process route is shown in Figure 4.
4. Study on the kinetics of Nb element precipitation in test steel
According to the relationship between stress and precipitation during stress relaxation, the starting point and the ending point of precipitation can be determined on the stress relaxation curve. PTT curves (i.e., precipitation-temperature-time curves) were plotted by using experimental data, as shown in figure 5.

The PTT curve shown in figure 5 is “C-shaped”. The reason for this curve is mainly divided into the following two points. First, the diffusion rate of solute atoms in austenite and its super-saturation in austenite affect the precipitation rate, second, the nucleation growth process controlled by diffusion affects the precipitation process of Nb and Ti particles. The diffusion rate of solute atoms increases with increasing temperature, and the super-saturation of solute atoms in austenite decreases with the increase of temperature, so the precipitation process is slowed down; In contrast, if the temperature is lowered, although the super-saturation of the solute atoms in the austenite increases, the slower diffusion rate becomes the main controlling factor, and thus the precipitation process will be slow. According to the squeeze theorem, there must be a maximum precipitation process at a certain temperature in the middle, so that it has the best super-saturation and atomic diffusion velocity, and this temperature is defined as the tip temperature of PTT curve. According to the graph curve, it can be seen that the temperature of the tip of the nose is about 900°C, and the start time of the precipitation is not much different in the range of 800°C to 900°C, all around 5s.

4.1. Basic theory of precipitation of microalloy carbonitride
(1) Kinetics of microalloy carbonitride precipitation
The precipitation kinetics is mainly used to describe the relationship between the precipitation time and temperature of the precipitated particles of microalloy carbonitride and the degree of precipitation. The two most important factors influencing the precipitation kinetics are the nucleation rate and growth rate of the new phase. In the actual precipitation process, both of these factors are related to time. Therefore, this paper adopts Avrami equation to intuitively describe the phase change kinetics of microalloy carbonitride precipitation[6].

\[ X=1-\exp(-Bt) \] (1)

In formula (1), B and n are coefficients mainly related to factors such as nucleation rate and diffusion coefficient of control elements[7], whose size depends on phase change free energy, interface energy, phase change temperature, etc[8].

When the precipitation ratio of the start of precipitation and the completion of precipitation is set to 5% and 95%, respectively, the time required for the start of precipitation and the completion of precipitation can be separately calculated by the formula (1). Therefore, we can find that the order of magnitude of \( t_{0.95}/t_{0.05} \) required from the start of precipitation (X=5%) to the completion of precipitation (X= 95%) is only related to the index n, i.e:

\[ \lg \frac{t_{0.95}}{t_{0.05}} = \frac{15\pi t_1 \rho^2 \lambda^2}{8D_0} \frac{1}{2} \frac{[2(Co-C_M)]}{(C_N-C_M)}^{3/2} - 2\lg d^* d + \frac{1}{\ln 10} \frac{(1+\beta)^{3/2} \Delta G^* + \frac{5\sigma}{3}}{kT} \] (2)

Combined equations (1) and (2) can calculate and plot the precipitation start curve and the precipitation completion time curve can also be obtained by shifting the precipitation start curve to the right by an order of magnitude of 1.7664/n time[9].

(2) Dislocation linear nucleus

It is mainly for the case where the precipitated particles of the second phase are nucleated on the dislocation line and the nucleation rate is rapidly attenuated to zero[10], where n=1, and B can be calculated by the formula (3).

\[ B=\pi l_0 \tau_1 \lambda^2 \] (3)

This can be obtained

\[ \lg t_{0.05} = -1028994 - \lg c - \frac{15\pi t_1 \rho^2 \lambda^2}{8D_0} \frac{1}{2} \frac{[2(Co-C_M)]}{(C_N-C_M)}^{3/2} - 2\lg d^* d + \frac{1}{\ln 10} \frac{(1+\beta)^{3/2} \Delta G^* + \frac{5\sigma}{3}}{kT} \] (4)

The meaning of each parameter in formula (4) is as follows:

\( \tau_1 \): The effective nucleation time of the precipitated particles cannot be accurately calculated at present;

l: Dislocation line length;

D: Diffusion coefficient;

\[ c = \frac{8\pi}{15} K D_0 \frac{3}{2} \left[ \frac{2(Co-C_M)}{C_N-C_M} \right]^{3/2}, \text{基本上与温度无关} \]

Therefore, make \( \lg t_0 = - (\lg c + \frac{15\pi t_1 \rho^2 \lambda^2}{8D_0} \frac{1}{2} \frac{[2(Co-C_M)]}{(C_N-C_M)}^{3/2}) \), Can be obtained:

\[ \lg \frac{t_{0.05}}{t_0} = 1.28994 - 2\lg d^* d + \frac{1}{\ln 10} \frac{(1+\beta)^{3/2} \Delta G^* + \frac{5\sigma}{3}}{kT} \] (5)

4.2. Nb (C,N) Kinetic calculation of particle precipitation process

The test steel of this trial has a C content of 0.055% and a Nb content of 0.08%, whereby the solid solubility of the Nb element is calculated as follows:

\[ \frac{\lg [Nb]_x}{x} = 2.96-7510/1223 \] (6)

\[ \frac{\lg [Nb]_{1-x}}{1-x} = 2.96-10800/1223 \] (7)
The simultaneous (6)~(9) solution can be obtained: \[ [\text{Nb}] = 0.0034937\%, [\text{C}] = 0.052262\%, [\text{N}] = 0.0015319\%, x = 0.27677, \]
that is, the precipitated niobium carbonitride The chemical formula is NbC0.27677N0.72323. According to the above method, the solid solubility of Nb calculated from the corresponding element solid solubility is 950~810°C. As shown in Fig.6: as the temperature decreases, the solid solubility value of Nb in steel decreases exponentially. The solid solubility value of Nb at 810°C is 0.0003711\%, from which it can be seen that when the time is sufficiently long, the Nb element is almost completely precipitated at 810°C.

![Figure 6. Nb solid solubility during the second stage rolling process](image)

5. Conclusion
The yield strength of the prototype X80 test steel is 660MPa, the tensile strength is 720MPa, the elongation A50 is 40\%, and the yield ratio is 0.91. The DWTT performance was measured at -15°C with a fiber cross-section of 90\%. Takeing three parallel samples on the steel plate under the condition of -20°C to measure and average impact performance, the impact energy was between 295J and 335J, and the fiber cross-section ratio was greater than 95\%. Therefore, it can be seen that the prototype X80 test steel fully meets the requirements of API.5L;

Through the stress relaxation test, it is found that the PTT curve of X80 grade test steel has a typical C shape, indicating that the precipitation process of Nb particles in the test steel is the process of nucleation growth controlled by diffusion, and the precipitation speed not only affected by the degree of super-saturation in austenite, also will be solute atom diffusion velocity in the austenite. The precipitation temperature is preferably around 900°C according to the PTT curve;

As the rolling temperature decreases, the solid solubility value of Nb in the test steel decreases exponentially. The solid solubility value of Nb at 810°C is 0.0003711\%, from which it can be seen that when the time is sufficiently long, the Nb element is almost completely precipitated at 810°C.

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