Precipitates in Nb and Nb–V Microalloyed X80 Pipeline Steel

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Abstract: Precipitates in two X80 pipeline steels were studied by transmission electron microscopy equipped with an energy filtering system. The steels are microalloyed with niobium and niobium–vanadium (Nb–V), respectively, and produced by continuous hot rolling. Besides the precipitates TiN and (Ti, Nb) (C, N), which were 10–100 nm in size, a large number of precipitates smaller than 10 nm distributed in the two steels have been observed. In the Nb–V microalloyed steel, only a few titanium nitrides covered by vanadium compounds on the surface have been observed. It is inferred that the vanadium exists mainly in the matrix as a solid solution element. The fact has been accepted that there was no contribution to the precipitation strengthening of the X80 steel by adding 0.04–0.06% vanadium under the present production process. By contrast, the toughness of the Nb–V steel is deteriorated. Therefore, a better toughness property of the Nb microalloyed X80 results from the optimum microalloying composition design and the suitable accelerating cooling after hot rolling.

Key words: X80 pipeline steel, precipitate, electron energy filtering microscopy, microalloyed steel, Nb carbonitride, Ti nitride, TEM

INTRODUCTION

The niobium (Nb) and niobium–vanadium (Nb–V) microalloying method has been used for the development of 18.4-mm thickness specification X80 pipeline steel in the Maanshan iron and steel Co. A similar chemical composition and the same rolling schedule and cooling process were selected for the two microalloyed X80 pipeline steels, which were denoted as Nb steel and Nb–V steel, respectively, in the context. The two steels present similar strength properties but different Charpy impact toughness performance at low temperature. The strength of the pipeline steel is a cumulative contribution of grain refinement, Bainite, M/A constituent, solid solution strengthening, and precipitation hardening. Grain refinement may improve both strength and toughness simultaneously. However, precipitation hardening may deteriorate toughness. The two X80 steels with different microalloying design were selected for investigation in order to understand the different behavior of toughness for the two kinds of pipeline steels.

EXPERIMENTAL PROCEDURES

Samples were taken from the X80 pipeline steels produced by a 2,250-mm hot strip mill (Shi et al., 2008). The main composition of the steels denoted as Nb steel is as follows (in wt%): C ≤ 0.08; Si, 0.15–0.30; Mn, 1.5–2.0; Nb, 0.05–0.09; Ti ≤ 0.020; S ≤ 0.0020; and N ≤ 0.0050. Another steel denoted as Nb–V steel is added by 0.04–0.06% vanadium.

Standard tensile tests were carried out at room temperature according to ASTM E8 specification using a computerized tensile testing system. Impact toughness was measured using the standard Charpy V-notch impact test (ASTM 23) at –20°C. After cutting, grinding, polishing, and etching by 2% nital, the microstructure of the steels was observed first by optical microscopy. Thin foil specimens were prepared by electropolishing using a solution of 10% perchloric acid in acetic acid electrolyte. Specimens were examined by JEOL 2010F type transmission electron microscopy (TEM), X-ray energy-dispersive spectroscopy (EDX), and electron energy filtering microscopy.

RESULTS

Microstructures and Properties

Under almost the same industrial production conditions, the microstructures of the Nb steel and Nb–V steel are very similar, and the microstructures consist of quasi-acicular ferrite and polygonal ferrite. It is difficult to distinguish the microstructure between these two kinds of X80 steels by optical microscopy. By using TEM observation, it was made clear that the microstructure morphology comprises parallel needle-like or lamellar ferrite with residual austenite between the ferrite laths.

The tensile experiment results for measuring the mechanical properties of the Nb steel and Nb–V steel are listed in Table 1. It is clear that the two steels show similar mechanical properties obtained by tensile experiment (Shi et al., 2008; Zhu et al., 2009). However, the Nb steel has a higher impact toughness property than that of Nb–V steel

Table 1. Mechanical Properties of the Experimental Steels.

Steel	YS, $R_{t0.5}$ (MPa)	TS, R_m (MPa)	YS/TS Ratio	El, A_{50} (%)	Impact Toughness (-20°C) (J)		
Nb–V steel	580	660	0.879	28.5	323	343	344
Nb steel	585	660	0.886	26.5	473	475	457

Nb, niobium; V, vanadium.

at a temperature of -20°C . The Charpy V-notch impact energy value of the Nb steel at -20°C is up to 450 J, which is higher than the value of Nb–V steel obtained between 300 and 350 J. It is clear that the addition of 0.04–0.06% vanadium in the steel cannot further increase the strength, but it can decrease the toughness of the pipeline steels.

Precipitates in Nb and Nb–V X80 Steels

Precipitates in Nb–V microalloyed X80 steel were observed by TEM on extraction replica specimens (Zhu et al., 2009; Wang & Gu, 2010). One category of the precipitates is titanium nitride, which is of rectangular shape and is covered with round niobium carbonitride precipitate. The side length is about 50–100 nm. The element ratio of Nb and Ti in the particles is about 0.25. The second category of precipitate is niobium titanium carbonitride of size 20–40 nm, and the morphology shows spherical-shaped or irregular particles. The element ratio of Nb and Ti in the particles is variable between 7 and 1. In this study, the EDX analysis results also indicated the existence of the precipitates of niobium titanium carbonitride with a size of 30 nm (see Fig. 1). Electron energy loss spectroscopy analysis was also used to investigate the distribution of C, N, Nb, V, and Ti elements in precipitates in the Nb–V steel, which were about 20–40 nm in size. Energy-selected images of the element N, Ti, Nb, and V, respectively, of a particle are given in Figure 2. The results showed that the rectangular shaped TiN or (Ti, Nb) N particles precipitated first, and then VN, Nb(C, N), and/or Nb carbides grew from the surface of these nitride particles. The precipitates in Nb steel and Nb–V steel have the similar feature in morphology. Spherical or irregular-shaped Nb(C, N) precipitates grow from the surface of the rectangular TiN or (Ti, Nb) N particles. From the results of EDX and EELS analysis for the Nb–V steel, it is clear that the vanadium content is much lower than the Nb content in the precipitates that were 20–40 nm in size. However, no carbides or carbonitrides comprised by only vanadium and C or C and N have been observed.

In addition to the two categories of the precipitates mentioned above, the existence of a third category of precipitates is confirmed. A large number of precipitates that were about 10 nm in size were observed in Nb steel and Nb–V steel by TEM, as shown in Figure 3. A high-resolution TEM image of a plate-like particle is shown in Figure 4 with its Fourier transform. The observation results showed that the crystal structure of the precipitates are of fcc-based structure. It is clear that the existence of Moire fringe in the

Figure 1. Transmission electron microscopy images and energy-dispersive spectroscopy of the precipitates pointed by the arrow in X80 steels: (a) Nb steel and (b) Nb–V steel.

Figure 2. Energy-selected image of the elements N, Ti, Nb, and V, respectively, of a particle in Nb–V steel. Scale bar is 20 nm.

Figure 3. Fine precipitates in the X80 steel: (a) Nb steel and (b) Nb–V steel. Scale bar is 100 nm.

Figure 4. a: High-resolution image of a plate-like precipitate in ferrite matrix. b: Fourier transform of the high-resolution image of the particle and ferrite matrix (bcc [012] pattern). c: Fourier transform of the particle (fcc [114] pattern).

high-resolution TEM image on the particle indicates that this particle is superposed over ferrite matrix.

DISCUSSIONS

Precipitation Behavior

The first category of precipitates of larger size are mainly TiN or (Ti, Nb) (C, N) compounds. They usually precipitated at higher temperature. These nitrides and carbonitrides of Nb and Ti exist as the core of heterogeneous nucleation for Nb carbonitride precipitate to form complex compounds. The second category of precipitates, the Nb and Ti carbonitride, 20–40 nm in size, mainly form during the hot rolling. The fact can be understood by the solubility product of the carbides and nitrides in austenite. It increases in the sequence of TiN, NbN, VN, Nb(C, N), TiC, NbC, VC (Turkdogan, 1989). Therefore, nitrides precipitate at higher temperature; carbonitride and carbide precipitate later and may grow directly from the surface of the particle previously formed. The same sequence of the solubility product also exists in ferrite. The third category is Nb precipitates, which are smaller than 10 nm. They precipitate during coiling or/and the latter several rolling passes. As pointed out by Yong Qilong, the size of Nb(C, N) precipitates can be 2–5 nm in a low-carbon steel containing 0.06% Nb (Yong, 2006a).

Because the nitrogen content in the steel is as low as 0.005%, vanadium carbonitride will not precipitate in the austenite owing to its low content in the steel (Yong, 2006a). Once the rolling temperature decreased below 900°C, the rolling process was completed quickly. Diffusion and precipitation of vanadium would be hindered owing to the high cooling rate ($>20^{\circ}\text{C/s}$) and low coiling temperature ($<500^{\circ}\text{C}$). Some of the vanadium and/or Nb will be in solid solution state (Guo et al., 2009).

As all of the above compounds with elements Ti, Nb, and V possess the same FCC structure with approximating lattice parameters, it is very difficult to distinguish between them by HREM and electron diffraction on TEM. Because the nitrogen content is $<0.005\%$ in the steels, and it will give priority to form TiN, the very fine and dispersive particles with several nanometer scale in the X80 steels detected here more likely are niobium carbides (Perez, 2007).

Precipitation Hardening of the Fine Particles

Dislocations usually cut through or bypass the second phase during plastic deformation in crystal. The cutting-through mechanism takes a main role when the particle size is smaller than the critical size; otherwise, bypass mechanism will work. For Nb and V carbonitride, the critical size is 1.6 and 5.4 nm, respectively (Yong, 2006b). The strengthening mechanism of the precipitates in scale under 10 nm observed in this study is the Orowan bypass mechanism. The closer the particle size is to the critical size, the stronger the strengthening effect. The precipitation hardening effect of the fine dispersive particles is much stronger than the large complex particles. A comparison between the two steels showed that there is no contribution to the strengthening of the X80 steel by adding 0.04–0.06% vanadium. The experimental results suggest that the precipitation strengthening of the X80 steels should mainly be attributed to the dispersive precipitates of niobium carbides that are of several nanometers in size. By contrast, compounds of vanadium form and grow from other particles, which precipitated previously. This will increase the size of the precipitates in the steel and hence may deteriorate mechanical properties of the steel. In addition, compared with dissolved vanadium, grain boundary energy is decreased stronger by dissolved Nb (Shang et al., 2003; Shu et al., 2005). It makes the grain boundary cohesive force and the toughness of Nb steel become higher.

SUMMARY

1. In addition to the TiN and Nb(C, N) complex precipitates, a large number of spherical or plate-like precipi-

tates of size under 10 nm exist in the Nb microalloyed and the Nb–V microalloyed X80 pipeline steels. The precipitation strengthening of the X80 steels should mainly be attributed to the dispersive precipitates of Nb carbides that are of several nanometers in size.

2. The experimental results and theoretical analysis suggest that the precipitation of vanadium carbides and carbonitrides would be hindered owing to its low content and the high cooling rate after rolling and the low coiling temperature. The majority of vanadium is maintained in the solid solution state. It is the main reason that the two kinds of pipeline steels present different toughness performances.

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