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Precipitation behaviors of X80 acicular ferrite pipeline steel

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Abstract: The precipitation behaviors of X80 acicular ferrite pipeline steel were investigated by using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). The results show that dendritic precipitates in the as-cast steel slabs precipitate mainly in grain boundaries, and these dendritic precipitates dissolve and re-precipitate to two kinds of carbonitrides: Ti- and Nb-rich (Ti, Nb)(C, N) carbonitrides during reheating. Four types of precipitates mainly exist in the hot rolled plate: Ti-rich carbonitrides resulted from the dendritic carbonitrides undissolved during the reheating process; Ti-rich carbonitrides re-precipitated along austenite grain boundaries during the reheating process; NbC carbides mainly heterogeneously nucleated on the small pre-existing Nb-rich carbonitrides in the hot rolling process; and NbC carbides precipitated on dislocations during hot rolling.

Keywords: pipeline steel; precipitation; ferrite; carbonitride; dissolution

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1. Introduction

It is well established that the precipitation of carbonitrides in microalloyed steels such as Nb, V and Ti, plays a significant role in determining the microstructure and properties of X80 acicular ferrite pipeline steel [1]. Many researchers have studied the precipitation behaviors of these microalloying elements and their effect on the microstructure [2-7]. Titanium is usually added to X80 pipeline steel because TiN precipitates with a suitable size can suppress austenite grain coarsening at high temperature. The presence of Nb(C, N) can effectively retard recovery and recrystallization during hot rolling, facilitating austenite, and ferrite grain refinement. It also contributes to dispersion hardening as fine precipitates because of the high dislocation induced by deformation during hot rolling in the austenite region. However, few articles have carried out systematic research on the precipitation behaviors of X80 pipeline steel in as-cast slabs during the soaking and hot rolling process. The purpose of the present study is to identify the evolution of precipitates in X80 pipeline steel including the three stages mentioned above, based on transmission electron microscopy (TEM), thermodynamics and chemical composition analysis of carbonitrides.

2. Experimental procedure

The experimental X80 pipeline steel was prepared in a 50-kg vacuum induction furnace. The molten steel was poured into a mould and solidified to form slabs in dimensions of 90 mm×100 mm×110 mm (thickness×width×length). The base composition (wt%) of the investigated steel is C 0.054, Si 0.2, Mn 1.9, Nb 0.095, V 0.03, Ti 0.014, and N 0.004.

Two as-cast steel slabs were cooled down to room temperature in the air cooling condition at the same cooling velocity, marked A and B. The first batch specimens were ob-

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tained from the as-cast steel slab A. The as-cast steel slab A was reheated in the furnace holding for 1 h at a soaking temperature of 1200°C and then water-quenched. The second batch specimens were cut from this reheated and quenched slab. The rolling schedule of the as-cast steel slab B was designed as a two-stage thermomechanical process. After holding for 1 h at a soaking temperature of 1200°C, the first stage rolling was in the recrystallized austenite region at a higher temperature, the second stage rolling was in the non-recrystallized austenite region completed at a lower temperature of 830°C. As a result, a final plate of 11 mm thick was obtained. After hot rolling, the rolled plate was immediately cooled down to 360°C at a cooling rate of approximately of 30°C/s. The third batch specimens were obtained from the hot rolled plate. The study on the microstructure and precipitates was carried out using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS).

3. Results and discussion

3.1. Analysis of carbonitrides observed in as-cast steel slabs

The morphology of precipitates forming in the as-cast steel slabs in air cooling conditions is complicated. Fig. 1(a) shows three different types of precipitates: dendritic, near-spherical, and lathlike shapes. Compositions of these precipitates were investigated by using nano-beam EDS analysis and were identified as (Ti, Nb)(C, N) carbonitrides. Dendritic precipitates in the as-cast steel slabs were the highest. Compositions of both the center (marked 1) and wing parts (marked 2) in these dendritic carbonitrides are shown in Figs. 1(c) and 1(d). These dendritic carbonitrides are Ti-rich in the center and Nb-rich in the wing parts. The precipitates mainly precipitate along grain boundaries (Fig. 1(b)), and the sizes of the precipitates are quite small, ranging from 60 to 200 nm.

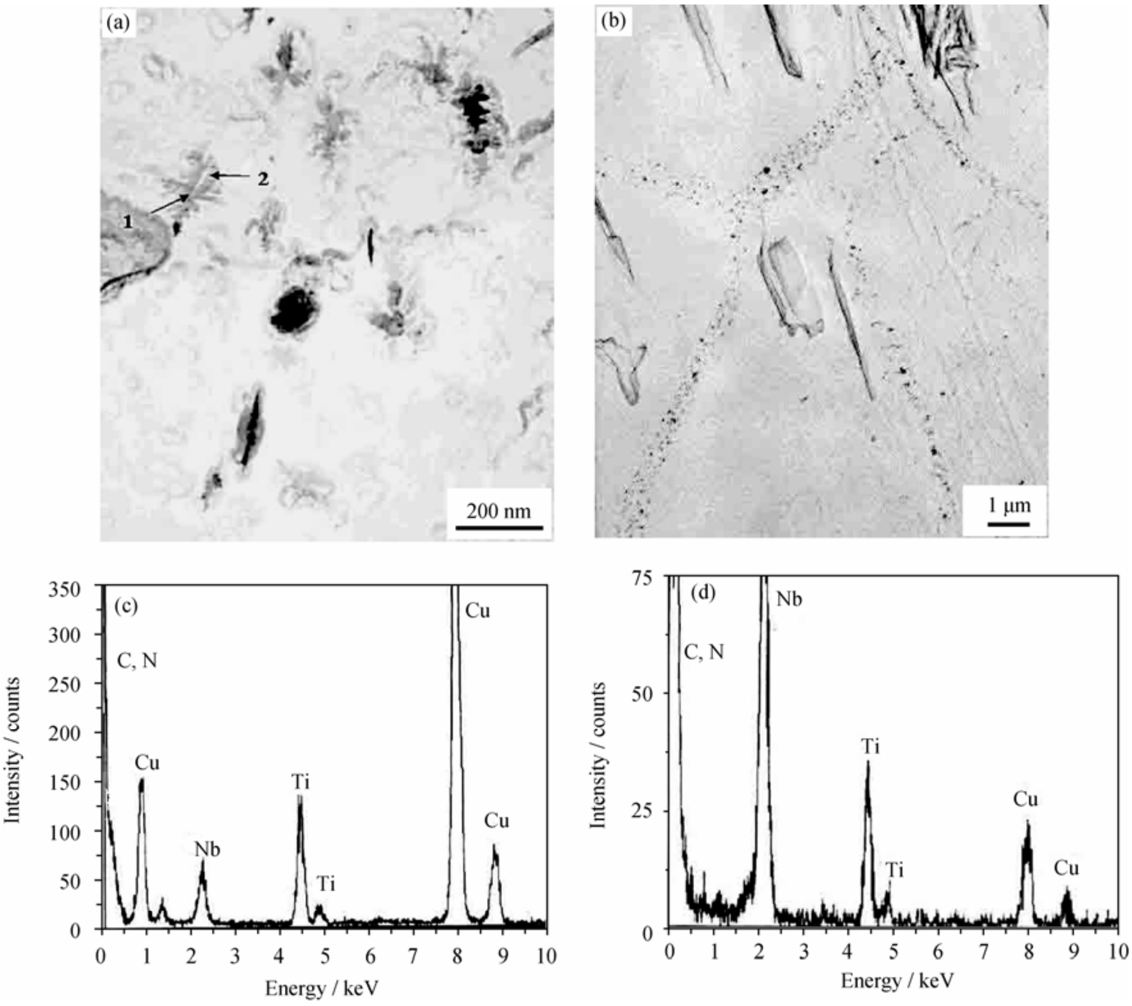

Fig. 1. Typical precipitates in the as-cast steel slabs (a), precipitates along grain boundaries (b), and compositions of region 1 (c) and region 2 (d).

The solubility product of carbide or nitride in austenite is given as [8]:

$$[\mathrm{M}][\mathrm{X}] = 10^{(A-B/T)} \tag{1}$$

where [M] is the content of the microalloying element, [X] the content of carbon or nitrogen in the solution at temperature T, and A and B are experimentally determined constants.

According to Eq. (1), TiN precipitates will form at a higher temperature in the austenite region. It is clear that the critical nucleation energy of precipitates at grain boundaries is much smaller than that in the grain matrix, and the grain boundaries are the main nucleation place. These precipitates with a spheroid morphology maintain the shape and composition at low temperature, while Nb(C, N) precipitates forming at relatively lower temperatures will form on the pre-existing TiN as the heterogeneous nucleation site due to the low nucleation driving force of chemical free energy arising from the chemical supersaturation of the solutes [9]. It is reported that these dendritic (Ti, Nb)(C, N) carbonitrides can precipitate in the lower temperature range of austenite during non-equilibrium cooling of the as-cast steel slabs [10]. In addition, the precipitates containing V were rarely observed in as-cast steel slabs.

3.2. Analysis of carbonitrides during reheating

In order to investigate the dissolution and reprecipitation behaviors of these carbonitrides during the reheating process, the distribution, composition, and morphology of the precipitates were examined after reheating at 1200°C for 1 h. Three types of precipitates were observed: large cubic and triangle shaped precipitates within austenite grains (Fig. 2(a)), new fine cubic precipitates formed within austenite grains (Fig. 2(b)), and new cubic precipitates formed along and near austenite grain boundaries (Fig. 2(c)).

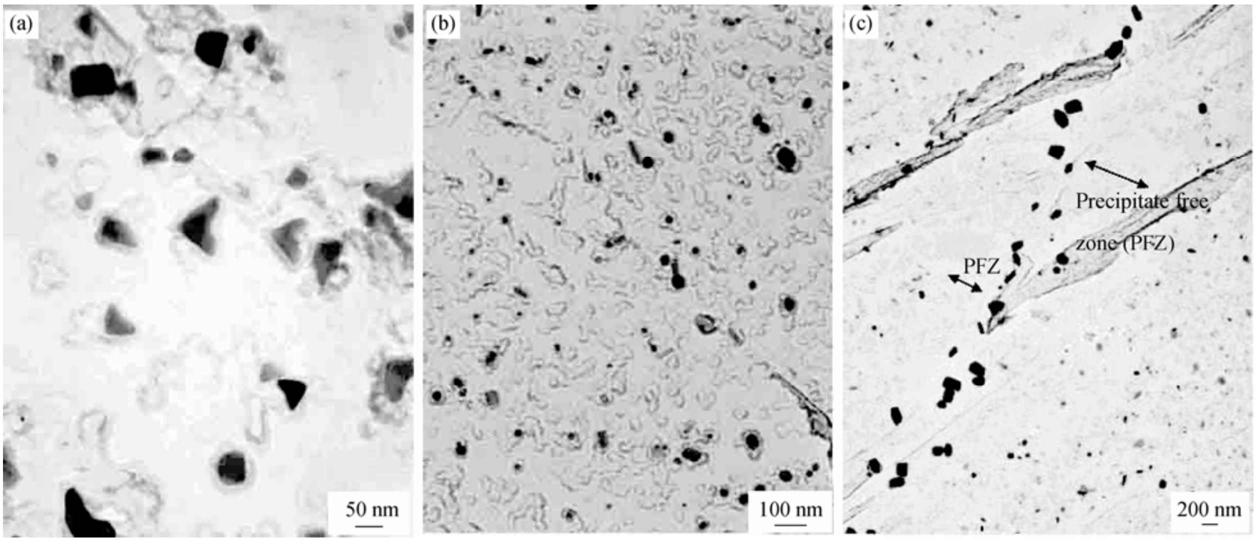

Fig. 2. Morphology and distribution of precipitates in the as-cast steel slabs reheated at 1200°C for 1 h.

The dendritic (Ti, Nb)(C, N) carbonitrides resulting from the non-equilibrium cooling disappeared. The composition of precipitates in Fig. 2(a) was Ti-rich carbonitrides. It is believed that the precipitates in Fig. 2(a) are undissolved carbonitrides during the reheating process.

The composition of precipitates observed both in the austenite matrix and along austenite grain boundaries (Figs. 2(b)) and 2(c)) was investigated by using nano-EDS analysis. The large carbonitrides along austenite grain boundaries were identified as Ti-rich (Ti, Nb)(C, N) carbonitrides, and the fine carbonitrides within austenite grains and near the austenite grain boundaries were identified as Nb-rich (Ti, Nb)(C, N) carbonitrides. As shown in Fig. 2(c), there is a precipitate free zone (PFZ) between large Ti-rich carbonitrides and Nb-rich carbonitrides. The PFZ is assumed to arise purely from the nucleation and growth of grain boundary precipitates causing solute depletion around the grain boundary and, hence, creating a PFZ [11]. Jun *et al.* reported that the dendritic carbonitrides mainly began to precipitate from 900 to 1000°C during non-equilibrium cooling [12]. During the reheating process, dendritic carbonitrides dissolved and Ti and Nb solutes near austenite grain boundaries diffused primarily to austenite grain boundaries. In addition, N and C solutes diffused from the austenite matrix to austenite grain boundaries, and formed stable Ti-rich (Ti, Nb)(C, N) carbonitrides. N solute had a higher diffusion coefficient in the austenite matrix, and primarily diffused to austenite grain boundaries during the reheating process, and formed large Ti-rich (Ti, Nb)(C, N) carbonitrides. For lower

N contents in the austenite matrix fine Nb-rich (Ti, Nb)(C, N) particles will precipitate in the austenite grain and near the austenite grain boundaries [10].

3.3. Analysis of carbonitrides in the hot rolled plate

The high magnification TEM micrograph clearly shows that the features of acicular ferrite involve an assemblage of interwoven nonparallel ferrite laths, and there is a high dislocation density in some laths near the sub-boundaries of acicular ferrite (Fig. 3(a)). Numerous fine precipitates heterogeneously distributed on dislocation lines in the acicular ferrite matrix are shown in Fig. 3(b). Fig. 3(c) shows precipitates in the hot rolled plate. The size of these precipitates is not uniform, ranging from 20 to 200 nm, and mainly distributes (visible) between 20 and 70 nm. Fig. 3(d) shows a heterogeneous precipitate which heterogeneously nucleates on the pre-existing precipitate.

From the experimental results, it is predicted that four types of precipitates mainly exist in the hot rolled plate: (1) Ti-rich carbonitrides resulted from the dendritic carbonitrides undissolved during the reheating process; (2) Ti-rich carbonitrides re-precipitated along austenite grain boundaries during the reheating process; (3) NbC carbides mainly heterogeneously nucleated on the small pre-existing Nb-rich carbonitrides in the hot rolling process, and the fine pre-existing Nb-rich carbonitrides precipitated within austenite grains and near the austenite grain boundaries during the reheating process; (4) NbC carbide particles precipitated on dislocations during hot rolling.

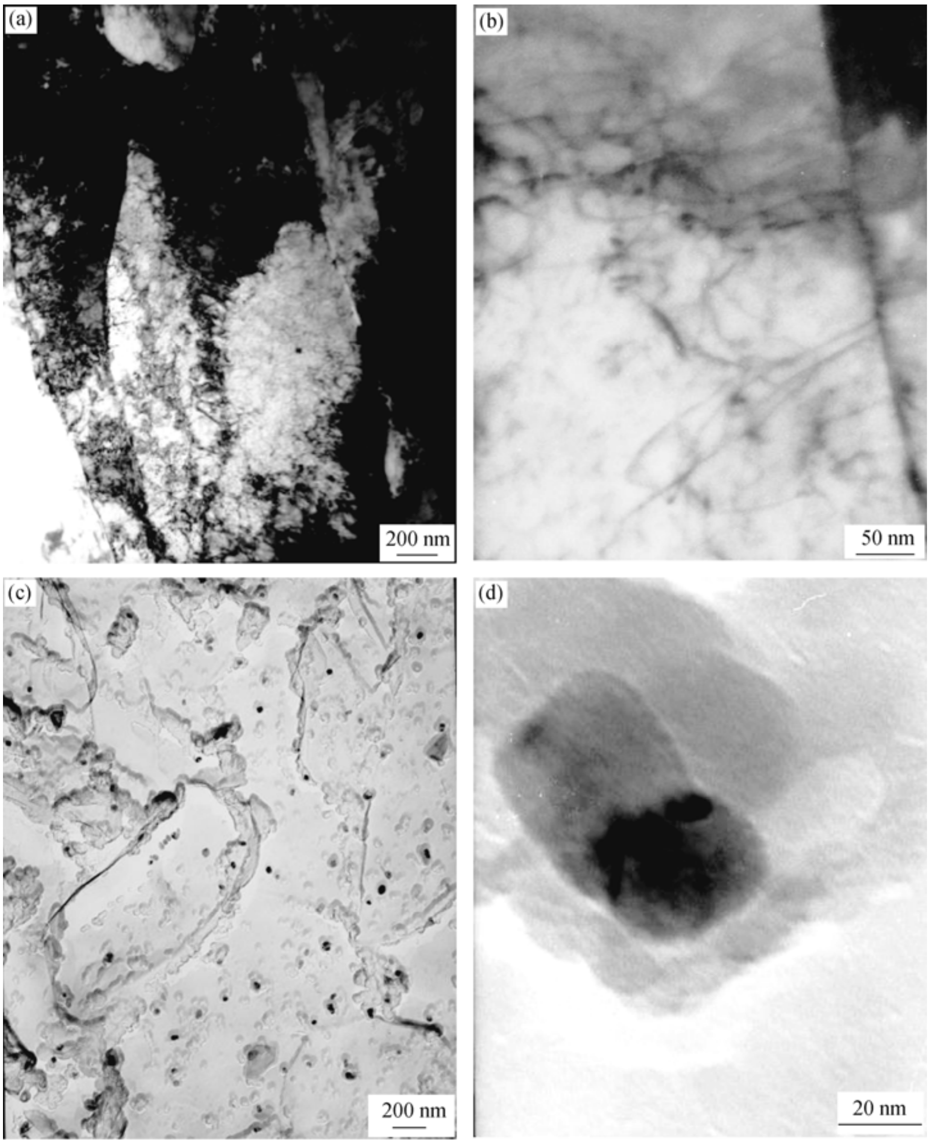

Fig. 3. Ferrite laths with a high dislocation density observed by TEM (a), fine precipitates heterogeneously distributed on dislocations (b), precipitates in the hot rolled plate (c), and heterogeneous precipitate (d).

These undissolved precipitates within austenite grains will be not effective in precipitation strengthening in the hot rolled plate. Ti-rich carbonitrides, which re-precipitated along austenite grain boundaries during the reheating process, may act as a barrier to austenite growth. The effectiveness of pinning particles mainly depends on their ability to resist particle coarsening, particularly at higher temperatures [13]. These fine Nb-rich carbonitrides observed near austenite grain boundaries will not be effective in restricting the grain growth of austenite during reheating.

These fine Nb-rich carbonitrides observed within austenite grains and near austenite grain boundaries acted as preferred nucleation sites for NbC carbides during hot deformation. It is well known that the precipitation kinetics of NbC will have direct influences on the recrystallization behavior of austenite during hot deformation. These precipitates formed during the reheating process can play harmful roles in the precipitation kinetics of NbC during hot rolling [12].

The most effective method of improving precipitation strengthening is strain-induced precipitation on dislocations during hot deformation. The presence of dislocations causes a significant acceleration in the nucleation of precipitates, and the precipitates of NbC nucleation on dislocations are fine, uniform, and dispersive [14]. The precipitation strengthening model is usually given as [15]:

$$\sigma = 8.9952 \times 10^{3} \times \frac{f^{1/2}}{d} \ln\left(2.417d\right) \qquad (2)$$

where σ is the precipitation strengthening increment, MPa; f the precipitate volume fraction; and d the particle diameter, nm. It can be seen that the precipitation strengthening level depends upon the precipitate volume fraction and particle sizes, and the precipitation strengthening increases with the decrease of particle sizes.

4. Conclusion

Based on TEM and EDS analysis used for detecting precipitates, the dendritic carbonitrides observed in as-cast steel slabs were dissolved and then re-precipitated to two kinds of carbonitrides during the reheating process: Ti-rich carbonitrides along austenite grain boundaries and Nb-rich carbonitrides within austenite grains and near austenite grain boundaries. Four types of precipitates mainly exist in the hot rolled plate: Ti-rich carbonitrides resulted from the dendritic carbonitrides undissolved and re-precipitated along austenite grain boundaries during the reheating process; NbC heterogeneously nucleated on fine pre-existing Nb-rich carbonitrides and NbC particles deposited on dislocations during the hot rolling process. Precipitates formed during the reheating process can play harmful roles in the precipitation kinetics of NbC during hot rolling.

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