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Carbide and Nitride Precipitation in High Temperature Tensiled Specimens and Hot Ductility of Nb – and Ti – Containing Steel CC Slabs*

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Abstract: Hot ductility of the Nb- and Ti-containing line-pipe steel CC slab specimens were measured under the strain rate of 1×10^{-3}/s. Three types of precipitates were found in the fractured specimens. One was the block--shaped coarse TiN particles precipitated at high temperature. Another type was the fine dynamic precipitation products precipitated at 950~900 ℃ which caused remarkable ductility reduction of the steel. The third type was the co-existed precipitates formed by fine Nb precipitates nucleating and growing on TiN particles. Compared with Nb-containing steel which contains no Ti, there was no ductility drop for Nb- and Ti-containing steel at temperature between 850 ℃ and A_{r3} and, the $\gamma \to \alpha$ transformation inside the grain matrixes proceeded faster, which both improved the ductility of the steel in the low ductility temperature Region Ⅲ.

Key words: Nb-Ti micro alloying steel, CC slab, hot ductility, carbides, nitrides, precipitation

Niobium and titanium are both elements with strong affinities to react with nitrogen and carbon to form carbides and nitrides in steel. In continuous casting, slabs of steel containing Nb and Ti are susceptible to surface crack defects owing to nitride and carbide precipitation. Although researches [1~5] indicated that titanium could raise the ductility of the Nb-containing steel at high temperature, occurrences of surface cracks of the Nb- and Ti-containing steel CC slabs are still significantly higher than common steel slabs in continuous casting production. In order to understand ductility change of the Nb- and Ti-containing steel more clearly and consequently take measures to prevent slab surface defects, the hot ductility of the Nb- and Ti-containing line-pipe steel slabs and the precipitation of carbides and nitrides are investigated.

1 Experimental Method

Hot ductility measurement was carried out with the Gleeble-1500 hot tensile test machine. Specimens, 110 mm in length, 10 mm in diameter, were taken from X-52 line-pipe steel CC slabs produced by Baoshan Iron and Steel Co. The specimen in length is perpendicular to the slab casting direction and parallel to the dendrites. The chemical composition of the specimens is(%): $w_C = 0.092$, $w_{Si} = 0.276$, $w_{Mn} = 1.02$, $w_P = 0.010$, $w_S = 0.041$, $w_{Nb} = 0.022$, $w_{Al} = 0.033$, $w_{Ti} = 0.017$, $w_N = 0.0042$.

In the hot tensile test, after the specimen was placed, Ar flow with a flowrate of 1 L/min was conducted into the specimen chamber. The specimen was heated up with the heating rate of 10 ℃/s to 1 350 ℃, held at this temperature for 5 min, and then cooled to the tensile temperature with a cooling rate of 3 ℃/s. Some specimens were heated to 1 400 ℃ from 1 350 ℃ for the measurements above 1 350 ℃. After holding at the tensile temperature for 2 min, tensile test was performed with the strain rate of 1×10^{-3}/s. After the specimen was fractured it was immediately quenched with water. The reduction of area of the specimens were used as a characteristic value for the hot ductility of the

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tested steels.

The fractured specimens were examined with optical microscope and scanning electron microscope. Precipitates were extracted with carbon replicas from some specimens, observed with TEM and quantitatively analyzed by TEM-EDAX. Volume fraction of precipitates was determined with electrochemical extraction method[6], in which precipitates were extracted from the specimen by electrolysis in 10%KCl-0.5%citric acid water solution and filted with 0.2 μm filters.

2 Results

2.1 Precipitation fraction

Fig. 1 shows the amounts of the precipitates electro-chemically extracted from the specimens fractured at different temperatures. Precipitation of Ti occurs at high temperature. The mass fraction of precipitated titanium to total titanium in the steel surpasses 60% even at 1 300 ℃. Niobium precipaiton occurs mainly when the temperature decreases to lower than 1 050 ℃. According to the dynamic precipitation "C" curve[7], the nose temperature for Nb(C,N) is around 950 ℃. In the present study, the precipitation of niobium reaches the maximum when the temperature decreases to 925 ℃, which is in agreement with the Nb(C,N) dynamic precipitation curve.

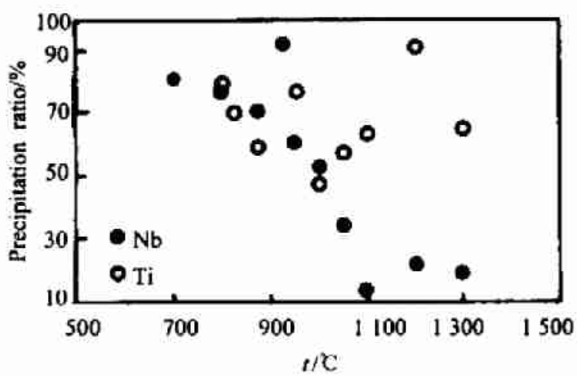

Fig.1 Variation of precipitation ratio with temperature

From Fig. 2, morphology of the precipitates in the fractured specimens can be classified into three types: (a) block-shaped precipitates, (b) fine precipitates and (c) co-existed precipitates.

(a) Block-shaped precipitates.

Fig. 2(a) shows the block-shaped precipitate observed on the specimen fractured at 1100 ℃. This type precipitates can form at higher temperature and their sizes are usually larger than 80 nm. It is known from EDAX analysis (Fig. 3) that titanium is the main constitutes of the particles. The precipitates usually contain 60% ~ 90% titanium and about 10% niobium. Electron diffraction pattern indicates that this type particles are TiN with B1 type lattice structure.

(b) Fine precipitates.

These fine precipitates only can be found on specimens fractured at temperatures around 900 ℃. They are either in spherical or in cubic shape formed along the grain boundaries and also inside the grain matrixes. As EDAX analysis can not be made on single particle because of fine size, electron diffraction is made on some gathered fine precipitates. From the obtained diffraction patterns, these fine precipitates are identified to be Nb(C,N). In the experiment, specimens with similar temperature history but without strain were examined and no fine precipitates as shown in Fig. 2(b) were observed. This fact revels that these fine precipitates are dynamic precipitation products.

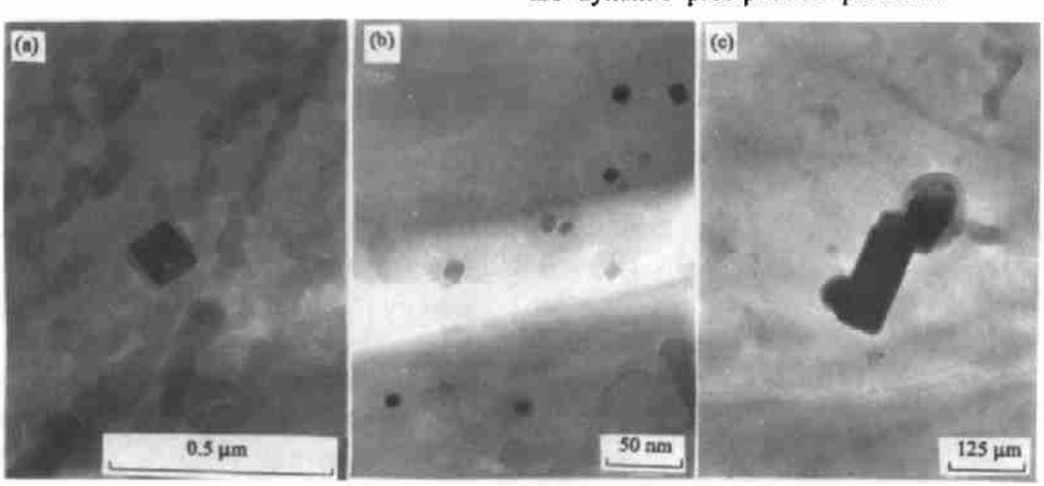

Fig.2 Typical precipitates observed in fractured specimens

(a) block-shaped precipitates (b) fine precipitates (c) co-existed precipitates

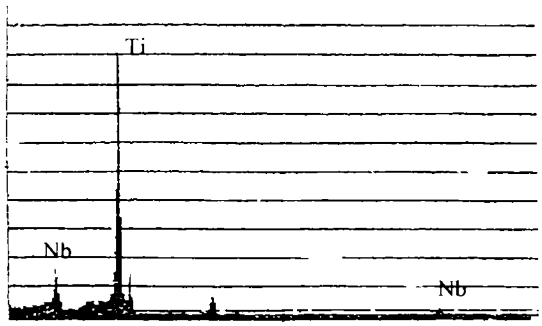

Fig.3 EDAX spectrum of the block-shaped precipitates

(c) Co-existed precipitates.

Fig. 2(c) shows the co-existed precipitate observed on specimen fractured at 825 ℃. It can be seen that a fine spherical particle formed on a block-shaped particle. EDAX analysis identifies that the block-shaped particle mainly contains Ti while the spherical one mainly contains Nb. This is because, at lower temperature, precipitation is retarded owing to decreased diffusion rate. Nb(C, N) is easier to nucleate and grow on existed TiN particles that were precipitated at higher temperature.

2.2 Hot ductility

Fig. 4 shows the RA values of the fractured specimens in temperature range from 1 400 ℃ to 600 ℃. Hot ductility of steel CC slab specimens (w_C: 0.177%, w_{Nb}: 0.024%) produced by Baoshan Iron and Steel Co. which contains no Ti is also illustrated in the figure for sake of comparison.

The Nb- and Ti-containing steel has high RA values at 1 350 ~ 975 ℃. When the temperature falls to below 975 ℃, entering the so called low ductility temperature Region Ⅲ, the hot ductility of the steel begins to decrease. When the temperature is further lowered to 900 ~ 850 ℃, the hot ductility is

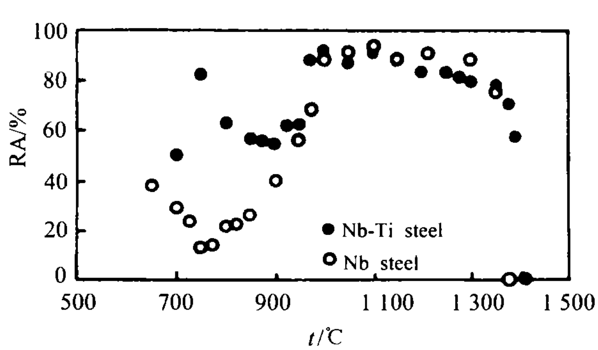

Fig.4 Comparison of hot ductility of Nb-Ti containing steel with Nb-steel

decreased to its minimum. RA values falls to 55.1% ~ 56.4%.

As the temperature is lowered to less than 850 ℃, the RA value of the Nb-containing steel continues to drop, while the ductility of Nb- and Ti-containing steel stops decreasing and begins to recover with decreasing temperature. It is observed on the fractured specimen of the Nb- and Ti-containing steel that, when temperature decreases to 800 ℃, proeutectoid ferrite films form along the γ grain boundaries. If 800 ℃ is considered to be the A_{r3} temperature of the Nb- and Ti-containing steel based on observation, unlike most carbon steels, there is no ductility drop for Nb- and Ti-containing steel in the temperature range between 850 ℃ and A_{r3}.

In the low ductility temperature Region Ⅲ the hot ductility of the Nb- and Ti-containing steel is better than Nb-containing steel, which can be attributed to the titanium contained in the steel. TiN and TiN-rich precipitates are formed at high temperatures (close to the solidius[8]) and so tend to be coarse and randomly distributed. These coarse and randomly distributed precipitates are not detrimental to the steel ductility.

When the temperature decreases to below 1 000 ℃, Nb(C, N) starts to precipitate from γ grains. At temperature ranging from 1 000 ℃ to 900 ℃, the ductility of the steel is not considerably reduced because Nb(C, N) precipitates are relatively coarse owing to the relatively high precipitating temperatures. As the temperature decreases to less than 950 ℃, Nb(C, N) precipitation reaches maximum. These fine precipitates result in a significant ductility decrease of the steel because (1) γ grain boundaries are pinned by the fine precipitates which retards the recrystallization of the steel and (2) the precipitates accelerate the steel grain boundary sliding and result in boundary cracks. It can be seen in Fig. 5 and Fig. 6 that cracks are formed along γ grain boundaries. The fracture facet is smooth indicating that the fracture mode is of intergranular. As shown in Fig.4, at 950 ~ 900 ℃, there is only a slight ductility difference between Nb- and Ti-containing steel and Nb-containing steel. This fact indicates that Ti-containing steel can also become brittle in this temperature range owing to the precipitation of the fine carbonitrides. To reduce slab surface cracks of Nb- and Ti-containing steel,

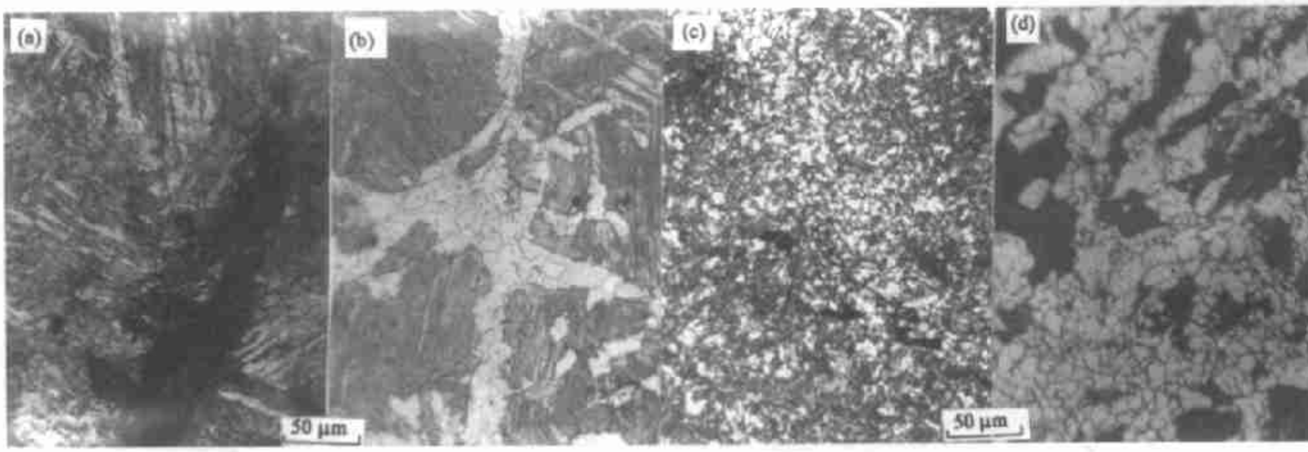

Fig.5 Microstructures of the specimens fractured at different temperatures
(a) 900 ℃ (b) 775 ℃ (c) 750 ℃ (d) 700 ℃

measures must be taken to prevent the formation of the fine Nb(C,N) precipitates in this temperature region.

When the temperature decreases to lower than 850 ℃, hot ductility of Nb-containing steel continuous to decline. This is because that AlN begins to precipitate in addition to Nb(C,N) precipitation. The "nose" temperature of the AlN precipitation "C" curve was found at 815 ℃ [9]. Different from Nb-containing steel, the ductility of Nb- and Ti-containing steel does not decrease with decreasing temperature when temperature is lower than 850 ℃. The reason is that Ti preferentially reacts with nitrogen at higher temperature and consequently reduces the amount of nitrogen available to react with Nb and Al to form more detrimental Nb(C,N) and AlN precipitates.

Usually, ductility of proeutectoid carbon steel decreases further when temperature decreases to $\gamma+\alpha$ two phase region because of the formation of the filmlike proeutectoid ferrite along the γ grain boundaries. In this temperature region, the flow stress level of the ferrite phase is about 1/4 of the austenite phase and the work hardening rate of the ferrite phase is exceedingly small. Thus, deformation will occur preferentially on the ferrite phase until intergranular fracture occurs.

In Nb- and Ti-containing steel, $\gamma \rightarrow \alpha$ transformation starts at 800 ℃. The ferrite film along the γ grain boundaries at 775 ℃ has increased to about 50 μm and also has grown into the grain interiors (Fig. 5b). This has considerably reduced the stress concentration at the grain boundaries. At 750 ℃ (Fig. 5c), $\gamma \rightarrow \alpha$ transformation takes place inside the grain matrixes and the previously existed α films at the grain boundaries are completely vanished. The RA value of Nb- and Ti-containing steel rises above 80% at 750 ℃ and the fracture mode is also changed from intergranular to transgranular (Fig. 6b).

Fig. 7 shows the structures of the Nb-containing steel specimens fractured at 750 ℃ and 650 ℃ respectively. Ferrite film and voids in the film can

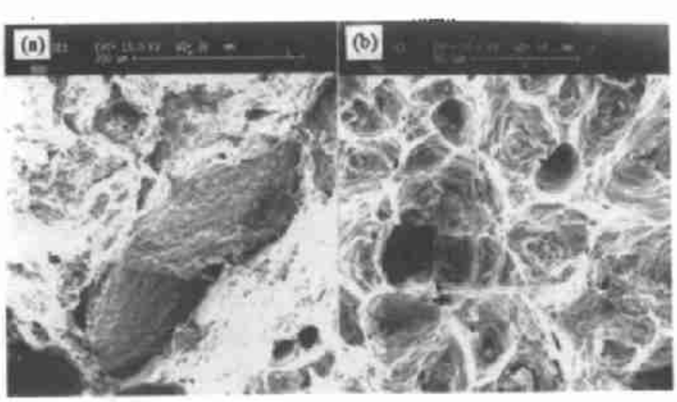

Fig.6 Fracture surface of the specimens fracture at 900℃ and 750℃ respectively
(a) 900℃ (b) 750℃

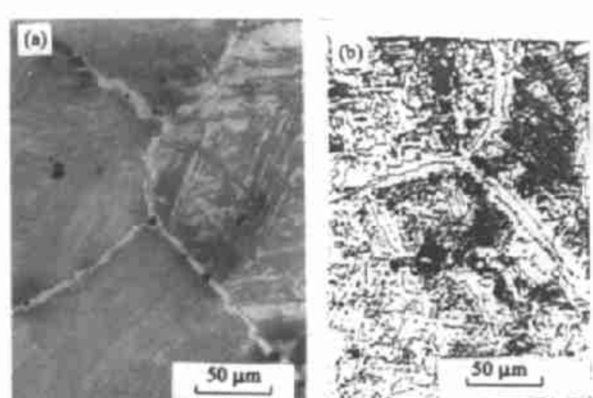

Fig.7 Microstructure of the specimens of Nb steel
(a) 750℃ (b) 650℃

be observed along the γ grain boundaries in the specimen fracture at 750 ℃. As the Nb-containing steel contains more carbon, its A_{r3} temperature is higher and the volume fraction of the α phase in $\gamma \rightarrow \alpha$ two-phase temperature region is larger than the Nb- and Ti-containing steel. When the temperature decreases to 650 ℃, in Nb-containing steel, α film is still existed at the grain boundaries though $\gamma \rightarrow \alpha$ transfer has already taken place inside the grains. However, at 750 ℃ in Nb- and Ti-containing steel, a larger portion of austenite has been transferred into ferrite (Fig. 5c). This is another reason that the ductility of Nb- and Ti-containing steel is better than Nb-containing steel.

3 Conclusions

(1) The ductility of Nb- and Ti-containing steel is better than Nb-containing steel in the low ductility temperature Region Ⅲ.

(2) In Nb- and Ti-containing steel, TiN precipitates at high temperatures while Niobium precipitation occurs mainly after the temperature decreases to lower than 1 050 ℃. At 925 ℃ niobium precipitation reaches the maximum.

(3) Three types of precipitates were found in Nb-Ti steel specimens. One was the block-shaped coarse TiN particles precipitated at high temperature. Another type was the fine dynamic precipitation products precipitated at 950~900 ℃ which caused a remarkable ductility reduction of the steel in this temperature region. The third type was the co-existed precipitates formed by fine Nb precipitates nucleating and growing on TiN particles.

(4) Compared to Nb-containing steel which contains no Ti, there was no ductility drop for Nb- and Ti-containing steel at temperature between 850 ℃ and A_{r3} and, the $\gamma \rightarrow \alpha$ transformation inside the grain matrixes proceeds faster, which both improved the ductility of the steel in the low ductility temperature Region Ⅲ.

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