Influence of Nb Content on Microstructure and Mechanical Properties of a 7%Ni Steel

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Abstract

The influence of Nb content on the microstructure and cryogenic mechanical properties of a 7%Ni steel was investigated within the Nb content range from 0 to 0.05%. The microstructure was characterized by optical microscope, scanning electron microscope, transmission electron microscopy and X-ray diffraction, and the low-temperature mechanical property tests were conducted. The Nb addition can effectively refine the prior austenite grains and microstructure of the steel. Fine niobium precipitates with a diameter of about 10–50 nm were observed. They tend to be spherical and locate mainly in the vicinity of grain boundaries. Although there are considerable amounts of reversed austenite forming at grain boundaries in the specimen containing the highest Nb content, no Nb element was detected in such reversed austenite, which implies that Nb element did not affect the formation of the reversed austenite directly. Mechanical test results suggest that the strength of the 7%Ni steel is not simply in relation to the prior austenite grain size, but also depends on the amount of reversed austenite. On the other hand, the grain refinement, enhanced with increasing Nb content, has a good effect on cryogenic toughness.

Keywords 7%Ni steel · Nb content · Niobium precipitate · Reversed austenite · Cryogenic mechanical properties

1 Introduction

As a clean and efficient energy source, liquefied natural gas (LNG) has become a new hotspot in the global energy market. Many huge LNG projects have been constructed in recent years, and more such projects will be needed in the future. The temperature for LNG storage and transportation is about $-162\text{ }^{\circ}\text{C}$; thus, the steel for LNG storage tanks need to have good cryogenic mechanical properties. At present, the large LNG storage facilities are built using mainly 9%Ni steel because of its excellent toughness and

moderate strength at liquid nitrogen temperature ($-196\text{ }^{\circ}\text{C}$). However, due to the huge demand and high price of nickel resource, it is better to reduce the Ni content in 9%Ni steel for saving nickel resource and lowering alloying cost. By appropriate alloying and processing, 7%Ni steel could be a good substitute for 9%Ni steel, which has nearly the same mechanical properties as 9%Ni steel [1]. However, as a new grade, there remains a distance for 7%Ni to become mature enough and further investigations are still necessary.

The critical importance of reversed austenite to cryogenic service of low-carbon high-nickel steels has been well recognized [2, 3]. The amount, morphology and distribution of reversed austenite significantly affect the cryogenic mechanical properties of Ni-containing cryogenic steels. Moreover, microstructure refinement is supposed to succeed in obtaining reversed austenite and improving cryogenic mechanical properties of Ni-containing cryogenic steels. Nb is regarded as an important microalloying element, which has an obvious influence on the grain refinement and moderate precipitation strengthening of steels [4, 5]. Although there have been a lot of researches about the influence of Nb addition on

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mechanical properties of Nb-microalloyed steels [6–8], only a few investigations have been performed on the effect of Nb content on the microstructure, especially the formation of reversed austenite, and the cryogenic mechanical properties of Ni-containing cryogenic steel. The pinning effect of Nb precipitates on grain boundaries can restrain the growth of grain, which may affect the formation of reversed austenite and be beneficial for cryogenic mechanical properties. Thus, in this study, an attempt was made to correlate the microstructure and cryogenic mechanical properties of a 7%Ni cryogenic steel with different amounts of Nb addition.

2 Experimental

Three groups of experiment steels, containing 0.04%C, 7.3%Ni, a few Mn and Si, are supplied as 15-mm-diameter rotary swaged bars. The addition of Nb in each group of steel is 0% (Steel A), 0.025% (Steel B) and 0.05% (Steel C), respectively.

Specimens with a size of $\phi 15 \text{ mm} \times 360 \text{ mm}$ were cut from the bars. As shown in Fig. 1, all specimens were quenched in water to room temperature after heating at 830 °C for 1 h, then intercritically quenched in water to room temperature after heating at 690 °C for 1 h and, finally, tempered at 580 °C for 1 h, followed by water cooling.

Tensile test specimens with gauge diameter of 5 mm and V-notch Charpy impact specimens with size of 10 mm $\times$ 10 mm $\times$ 55 mm were machined from the treated samples. The tensile test and impact test, with three specimens in each group, were conducted at $-196 \text{ }^{\circ}\text{C}$ in liquid nitrogen environment.

The specimens for microstructure and prior austenite grain observation were mechanically ground, polished, etched in 4% nital solution and saturated water solution of picric acid and then observed via a Zeiss optical microscope (OM) and JSM-6301F scanning electron microscope (SEM). The mean grain size was averaged from several hundreds of grains selected randomly from OM images.

Fig. 1 Scheme of heat treatment

The fractography and crack profile of selected impact specimens were observed using an SSX-550 SEM and a Zeiss FE-SEM (FE: field emission), respectively. The specimens, electrolytically polished with a solution of 10% perchloric acid and 90% ethanol, were analyzed by X-ray diffraction (XRD) to determine the phases after heat treatment. The pseudo-binary phase diagram of Nb-7%Ni steel was calculated using Thermo-Calc software.

The morphologies of reversed austenite, fine niobium precipitates and dislocations were observed using a Tecnai G2 F20 transmission electron microscope (TEM), and the chemical compositions of reversed austenite were analyzed using an energy-dispersive spectrometer (EDS). The TEM sample preparation procedure is as follows: Disks of 3 mm diameter were punched from the thin wafers after mechanically ground on SiC abrasive papers to 50 μm , and then they were chemically thinned to foils by twin-jet polishing at $-25 \text{ }^{\circ}\text{C}$, using a solution of 5% perchloric acid and 95% ethanol as electrolyte.

3 Results and Discussion

3.1 Influence of Nb Content on Microstructure

The OM and SEM micrographs of the specimens containing different Nb contents are shown in Fig. 2. The prior austenite grain boundaries and typical tempered martensite microstructure consisting of martensite laths are clearly revealed in the OM micrographs (Fig. 2a, c, e) and SEM micrographs (Fig. 2b, d, f), respectively. As shown in Fig. 2, the microstructures of the Nb-microalloyed specimens are much finer than that of the Nb-free specimen. The measured prior austenite grain sizes as a function of Nb content are shown in Fig. 3. It can be seen that the specimen containing 0.05%Nb has the finest grain of prior austenite and the specimen with zero Nb content has the coarsest grain of prior austenite. Compared with Nb-free specimen, the average grain size of the specimen microalloyed with 0.05%Nb is refined by 68.0%. Moreover, it can be found from the error bars in Fig. 3 that with increasing Nb content, the scattering range of grain size tends to become narrower, which suggests a higher homogeneity of grain size. Obviously, the grain size of the steel is significantly refined and the microstructure becomes more homogeneous by addition of trace Nb content, which is in good accordance with the previous studies [4, 5].

In order to reveal the detail of the grain refinement by addition of Nb in microalloyed specimens, further observation was carried out by applying TEM. As shown in Fig. 4, most of the fine precipitates are detected to distribute at grain boundaries or in the vicinity of grain

Fig. 2 OM **a, c, e** and SEM **b, d, f** images of specimens containing Nb contents of 0% **a, b**, 0.025% **c, d**, 0.05% **e, f**

boundaries. The fine precipitates tend to be spherical, and the sizes of them in Steels B and C are about 10–21 nm and 18–50 nm in diameter, respectively. EDS analysis in black-circled areas in Fig. 4a and b showed that Nb content in such regions are about 1.0 and 1.5%, respectively, which implies that such fine precipitates could be niobium-

bearing precipitate, such as NbC or NbCN. The Nb content is lower than expected values since the selected niobium precipitates are very tiny; both precipitates and matrix around them were covered by the EDS spot. It is known that Nb atoms are apt to segregate to grain boundaries during heat treatment to reduce lattice distortion.

Fig. 3 Effect of Nb content on grain size of prior austenite

Fig. 5 Pseudo-binary phase diagram of Nb-7%Ni steel

Fig. 4 Morphologies of fine precipitates in Nb-microalloyed specimens: **a** 0.025%Nb; **b** 0.05%Nb

Meanwhile, Nb atoms can strongly attract carbon and nitrogen atoms to form niobium carbides or carbonitrides [9, 10]. This may explain why the niobium precipitates tend to form at grain boundaries or in the vicinity of grain boundaries. By the use of Thermo-Calc software, the pseudo-binary phase diagram of Nb-7%Ni steel was calculated and is presented in Fig. 5. It can be seen that the initial temperature for niobium carbide precipitating dramatically increases when Nb content increases from 0 to 0.05%. In other words, the steel containing 0.05%Nb has stronger driving force for niobium to precipitate than the other two steels. As a result, the size and quantity of niobium carbide precipitation in Steel C would be larger and more.

Nb exists in steels mainly with two forms, i.e., dissolving in solid solution or precipitating in precipitate phases, such as NbC or NbCN. During cooling from the swaging temperature, the supersaturated Nb precipitated out from the matrix and produced niobium precipitates at lattice defects such as grain boundaries and dislocations,

which played an important role in restraining growth of austenite grains during subsequent heating processes, such as austenization. Meanwhile, there were still a part of Nb atoms staying in solid solution, which were apt to segregate to grain boundaries to reduce free energy [4]. During later process of heat treatment, Nb atoms in solid solution could contribute to solute drag of austenite grain boundaries; in other words, the grain boundaries have to drag Nb atoms to move together [11]. Based on the solute drag theory, more driving force for grain boundaries movement would be needed and the grain growth would be retarded due to the weak diffusion ability of Nb atoms. The inhibition of prior austenite grain growth would lead to the refinement of final martensite microstructure. This is what we have observed in this work, and the microstructures of Steels B and C were refined by microalloying with Nb.

3.2 Influence of Nb Content on Reversed Austenite

It is known that reversed austenite is fairly responsible for the high toughness, especially the low-temperature impact toughness, of Ni-containing steels [12, 13]. Figure 6 shows the XRD patterns of the specimens containing different Nb contents after heat treatment; the individual diffracting planes from the bcc-martensite to fcc-austenite (bcc: bulk-centered cubic; fcc: face-centered cubic) are clearly identified and labeled as well in the figure. It indicates that martensite is the main phase in the specimens and the amount of reversed austenite seems to be low. As shown in the figure, the $(220)_\gamma$ peaks of Steels A, B and C are weak or absent because of the seriously preferential orientation of grains, which was caused by the swaging process. It would severely affect the measurement accuracy of the volume fraction of reversed austenite. Thus, it may not be appropriate to determine the amount of reversed austenite here by XRD method. While it is no doubt that Nb-free and Nb-microalloyed specimens would be quite different in amount of reversed austenite, due to the finer microstructure in Nb-microalloyed specimens, there would be more nucleation sites, such as martensite lath boundaries and prior austenite grain boundaries, for reversed austenite [14]. Figure 7 shows the backscattered electron images of Steels A, B and C, and it can be seen that a certain amount of precipitates are distributed on the grain boundaries. By EDS analysis, the enrichment of Ni element was detected in these precipitates; particularly, the Ni content in these precipitates is about 8.1 to 9.5%. It is known that Ni element is always enriched in reversed austenite in Ni-containing steels [15, 16]; thus, it can be inferred that these precipitates are reversed austenite. As shown in Fig. 7, the reversed austenite mainly formed along grain boundaries

Fig. 6 XRD patterns of specimens after heat treatment: **a** 0%Nb; **b** 0.025%Nb; **c** 0.05%Nb

and more reversed austenite could be observed with increasing Nb content. In combination with Fig. 3, the evolution of the reversed austenite is in accordance with that of the grains, i.e., grains become finer and finer due to the increase in Nb content and refined microstructure promotes the nucleation of the reversed austenite by providing more nucleation sites and fast diffusion channels.

The detailed microstructure of the reversed austenite in Nb-free and Nb-microalloyed specimens was examined by TEM and is presented in Fig. 8. It can be found that some reversed austenite formed along the boundaries of martensite lath and prior austenite. In addition, there were no significant changes in the morphology of the reversed austenite as Nb content increased from 0 to 0.05%. Furthermore, chemical composition analysis by EDS of the reversed austenite in Steels A, B and C detected no Nb element. It seems that Nb element did not affect the formation of the reversed austenite directly.

3.3 Influence of Nb Content on Mechanical Properties

Figure 9 shows the low-temperature tensile properties of Steels A, B and C. It can be seen that with increasing Nb content, both tensile strength and yield strength increase at first, reaching a maximum at 0.025%Nb, and then slightly decrease at the highest Nb content. In contrast, the elongation has no significant changes when Nb content increases from 0 to 0.05%.

Compared with the Nb-free specimen, the tensile strength and yield strength of the Nb-microalloyed specimens have been improved obviously. For example, the tensile strength and yield strength were improved by about 7.0% and 11.3%, respectively, by adding 0.025%Nb. In combination with microstructure characterization, as shown in Figs. 2 and 4, the improvement in tensile strength and yield strength can be attributed to the grain refinement and the fine niobium precipitates. Grain refinement and precipitates strengthening are two of the main strengthening mechanisms of steels [17]. The quantitative relationship between strength and grain size can be described by the famous Hall–Petch equation. The smaller grains accompany with more grain boundaries, which can act as obstacles to dislocations, and the greater the proportion of grain boundaries, the stronger the effect of obstacles on dislocations, resulting in the improvement in strength. The fine niobium precipitates can also strengthen the steel by acting as dislocation obstacles. As a result, there is a remarkable enhancement of the strength of Nb-microalloyed specimens. The slight change in strength between Steels B and C may be related to the existence of reversed austenite. As shown in Fig. 6, more amount of reversed austenite was observed in Steel C. Reversed austenite is a

Fig. 7 Backscattered electron images of specimens containing different Nb contents: **a** 0%Nb; **b** 0.025%Nb; **c** 0.05% Nb

Fig. 8 Morphologies of reversed austenite in specimens containing different Nb contents: **a** 0%Nb; **b** 0.025%Nb; **c** 0.05%Nb

Fig. 9 Cryogenic tensile properties of specimens as a function of Nb content at -196°C

soft phase, whereas martensite is a hard phase. The strength of specimens, which depends on the hard one, would be reduced with higher amount of reversed austenite and

therefore lead to a lower strength of Steel C. The slight decrease (about 3.6% decrease) in elongation brought by Nb microalloying may be attributed to the precipitates in Nb-microalloyed specimens. But anyhow, all specimens show good ductility (with the elongations above 25%).

Figure 10 shows the low-temperature Charpy impact test result as a function of Nb content. The cryogenic toughness has a considerable increase as the Nb content increases from 0 to 0.05%, and Steel C shows the most excellent low-temperature toughness among the three steels. Such improvement in cryogenic toughness could be related to grain refinement and increasing amount of reversed austenite. Figure 11 shows the SEM fractographic images of the impact specimens containing different Nb contents. The insets show the details of crack propagation near the fracture surface. There are plenty of tear ridges and ductile dimples on the fracture surfaces of Steels A, B and C, which indicate excellent cryogenic toughness of such steels. With increasing Nb content, the amount of tear ridges becomes higher and the size of ductile dimples

becomes smaller, implying a better resistance to crack propagation which leads to a certain increase in toughness. Some reversed austenites were observed in the front zone of crack propagation, and the crack propagation was found to stop at grain boundaries, which may prove the inhibiting effect of reversed austenite and grain boundaries on crack propagation.

It is known that grain boundaries can impede crack propagation and grain refinement gives rise to more grain boundaries, which would increase crack propagation resistance. In addition, because the prior austenite grains were refined, martensite packets would become fine [18, 19] and more energy has to be consumed for cracks to propagate through them. Crack usually propagates along a certain crystallographic orientation in martensite packet, but when it attempts to run from one packet to another, it needs to largely change its direction at boundary of martensite packet, due to the change of crystallographic orientation [20]. So, more hard work has to be done to go through the boundaries, resulting in the improvement in

crack propagation resistance. Moreover, grain refinement can lower the microsegregation of impurity elements, such as P and S, at grain boundaries; as a result, interface cohesion would be enhanced. Besides grain refinement, the amount of reversed austenite is another important influence factor on cryogenic toughness [21, 22]. Reversed austenite is softer than matrix and can decrease the stress concentration in front zone of crack propagation. It can also absorb energy through plastic deformation and phase transformation, which is beneficial to restrain crack propagation and increase cryogenic toughness.

4 Conclusion

The influence of Nb content on the microstructure and the cryogenic mechanical properties of a 7%Ni steel was investigated within the Nb content range from 0 to 0.05%. The Nb addition can effectively refine the prior austenite grains and microstructure. The fine niobium precipitates with a diameter of about 10–50 nm formed in Nb-microalloyed specimens, and they tend to be spherical and locate mainly in the vicinity of grain boundaries. Although considerable amount of reversed austenite formed at grain boundaries of the specimen containing the highest Nb content, no Nb element was detected in such reversed austenite, which implies that Nb element did not affect the formation of the reversed austenite directly. Mechanical test results suggest that the strength of the 7%Ni steel is not simply in relation to the prior austenite grain size, but also depends on the amount of reversed austenite. On the other hand, grain refinement, enhanced with increasing Nb content, has a good effect on cryogenic toughness.

Fig. 10 Cryogenic toughness (A_{KV}) of specimens as a function of Nb content at $-192\text{ }^{\circ}\text{C}$

Fig. 11 Fracture morphologies of impact specimens containing different Nb contents: **a** 0%Nb; **b** 0.025%Nb; **c** 0.05%Nb

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