STUDY OF CHEMICAL COMPOSITION AND THERMAL STABILITY OF REVERTED AUSTENITE IN QLT-TREATED 9% Ni STEEL

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Abstract

Utilizing high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD), chemical composition characteristics and thermal stability of reverted Austenite (RA) in 9%Ni steel processed by quench-lamellarize-temper (QLT) heat-treatment has been investigated. The results showed that Austenite-stabilizing elements, such as Ni, Mn, are inclined to concentrate in reverted Austenite and distribute unevenly in it, higher near the boundary as high as 21% and lower in the centre. It was also found that RA has good heat and mechanical stability in 9%Ni steel but likely loses its stability and transform to Martensite undergoing both ultra low temperature and mechanical loading, accordingly inducing plasticity unceasingly.

Introduction

Continuously increasing demand for clear energy sources has actively stimulated the development of liquefied natural gas (LNG) industry over the past decade in the world [1]. 9%Ni steel is one of rather significant cryogenic materials in LNG tanks, which is directly subject to dramatically frozen LNG (-165℃) and required for excellent cryogenic toughness due to engineering safety. Traditional commercial 9%Ni steel is delivered by quench-temper (QT) heat-treatment with excellent cryogenic toughness under modern metallurgic condition [2, 3]. Cryogenic toughness of 9%Ni steel is closely associated with the content of reverted austenite (RA) and its stability [4, 5]. Thus high content of thermally stable reverted austenite usually represents good toughness of 9%Ni steel. Quench-lamellarize-temper (QLT) process has been often utilized in the research of BCC-structured Ni-containing steels (for example 5.5%Ni steel and 9%Ni steel) in recent decades [6]. The intercritical quenching (L step) shall be added at the temperature between Ac1 and Ac3 prior to tempering of QT heat-treatment for the purpose of enhancing notch toughness and improving cryogenic embrittlement resistance. 5.5%Ni cryogenic steels has been studied to reach a similar toughness level to 9%Ni steel. However, QLT treatment has not been carefully researched for the purpose of excavating cryogenic toughness of 9%Ni steel. This work tried to investigate the alloy enrichment and thermal stability of RA in 9%Ni steel treated by QLT.

Experimental

Commercial 9%Ni steel for Chinese LNG tanks was used to this study with the chemical composition of 9%Ni-0.64%Mn-0.3%Si-0.06%C (mass fraction). The Ac1 and Ac3 points of the steel are 610℃ and 705℃ respectively. Heat treatment is 800℃ soaking for 1 hr and quenching, then different L step (600-720℃) and quenching, finalized by 560℃ tempering. And the typical QLT in this study is 800℃ (Q) +660℃ (L)+560℃ (T).

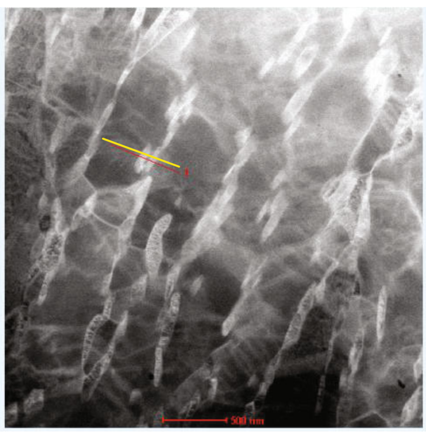
Charpy V-notched impact tests were carried out at -196℃ (77K) on JB50 impact tester. The impact specimens were put into liquefied nitrogen for at least 10 min and finished the test within 3 seconds after being taken out. Standard tensile specimens were machined with working part of Φ10mm×50mm and tested on MTS810 tester at room temperature (RM, 20℃), -120℃,-165℃ and -196℃, respectively. Extra tensile tests were started and stopped at retained strain of 0.05, 0.10 and 0.15 respectively.

Fine microstructure of experimental materials was observed through FEI Tecnai G2.0 high resolution transmission electron microscopy (HRTEM) and micro-zone alloy composition of RA were tested by EDAX energy-spectrum within a resolution of 5-10 nm. Tensile and impact specimens were taken to measure the volume fraction of RA by XRD combined with Rietveld whole-spectrum over-fitting analysis. Utilizing commercial materials calculation software Thermo-Calc/DICTRA, dynamic simulation of QLT heat-treatment of 9%Ni steel according to PAN's work [7] was made and compared with observation results.

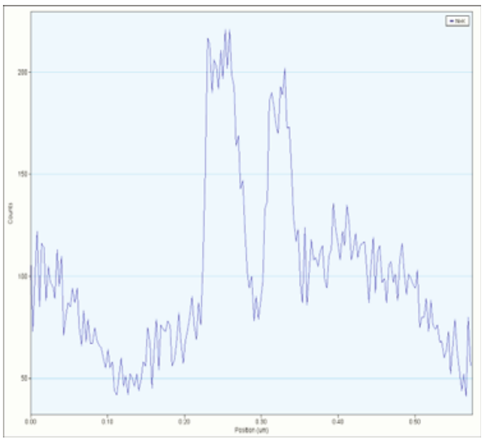
Results

<u>Micro-zone chemical composition of RA</u>

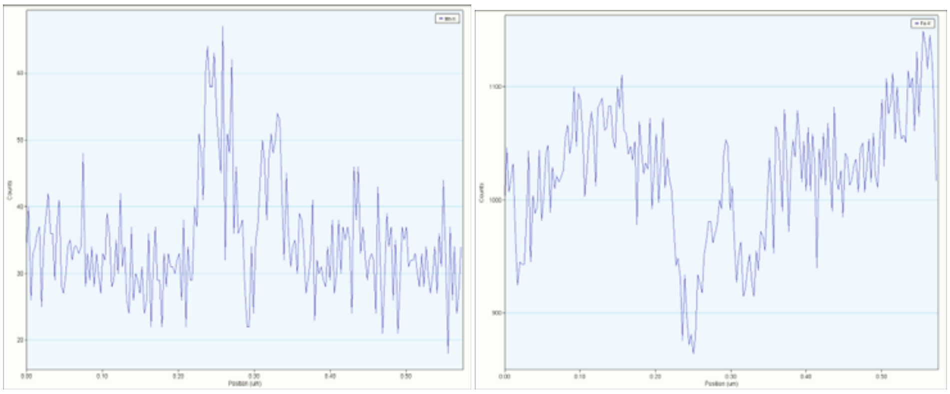
Composition scanning results of RA through HDTEM were shown in fig.1. There existed Ni, Mn peaks and Fe troughs at the RA positions, revealing notable concentration enrichment of austenite-stabilizing elements, such as Ni, Mn, in RA. Further analysis on energy spectrum showed that chemical composition distributed unevenly within a single RA, higher near the boundary and lower in the centre, which was invariably found in the experimental materials.



(a) Morphology of RA



(b) Ni K



(c) Mn K (d) Fe K

Fig.1 micro-zone line scanning over RA and matrix

Quantified composition measurement of Ni, Mn elements was made in RA and matrix, and positioning scheme was shown in fig.2, where point 3, 5 and 7 denoted RA near the α/γ boundary, point 4 the middle of RA, point 2 and point 6 denoted matrix near α/γ boundary and point 1 matrix far from RA. From the measurement results, highest concentration (mass fraction) of Ni element reached as high as 21% on the boundary of RA while 18% on the opposite boundary of the same RA. However, Ni concentration at the middle of designated RA dropped to 13.6%, reduced by 20-30% compared to that of the boundary position but still higher than balanced composition (9%Ni) of the materials. Ni concentration of the matrix close to RA dropped dramatically to some 4.0% and that far from RA recovered to balance concentration (about 9%) of the materials. The distribution of Mn concentration was revealed similar to Ni element. Highest Mn concentration reached about 2.1% with enrichment coefficient of over 3.0 (ratio of local and balanced concentration of alloy elements).

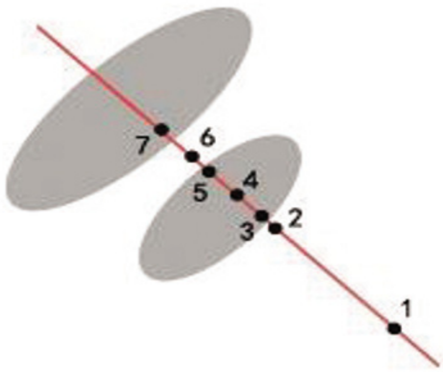


Fig.2 positioning scheme of chemical composition measurement in fig.1(a)

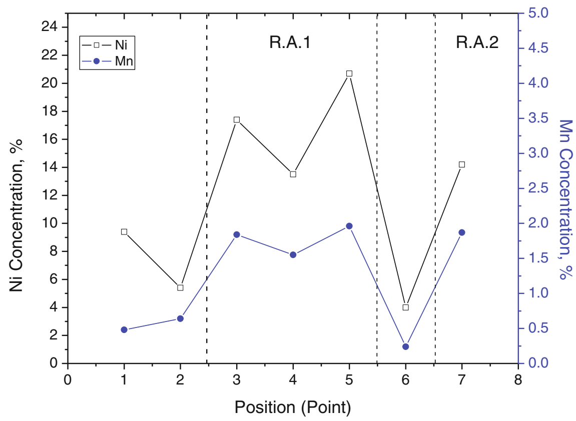


Fig.3 alloy element distribution in RA and matrix of experimental materials

Stability

Heat stability of RA was studied by volume fraction variation of RA in the specimens before and after soaking at 77K (liquefied nitrogen) for 10 hr. The result was shown in fig.4. The result indicated that volume fraction of RA almost remained unchanged after 77K soaking whatever L temperature was selected (600, 640, 660 and 700 ℃). That implied that RA in 9%Ni steel by QLT process enjoys good heat stability.

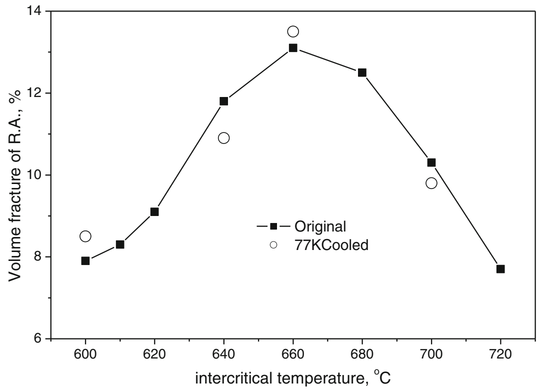


Fig.4 Effect of super-cooling on volume fraction of RA (cooling at 77K)

Volume fraction variation of RA with plastic strain at different temperatures was shown in fig.5. The results revealed that RA would keep stable under mechanical loading at RM. However, mechanical loading at different low temperatures would drive RA reduced, and the lower temperature, bigger reduction in RA. As an example, 15% strain at -196 ℃ made RA reduced by relatively 77%, remaining 3.1% in volume fraction. It was inferred that RA possessed excellent mechanical stability at TM but would transform more or less if strained at the temperature below -120℃. When deformed by 15% at -196℃, RA would lose its thermal stability and mostly transform to martensite. XRD specimens were taken for volume fraction measurement of RA closely along fracture surface of 77K impact specimens and the results were shown in fig.6. Impact loading drove RA of 9%Ni steel reduced to below 1%, even much lower than that after low temperature tensile deformation.

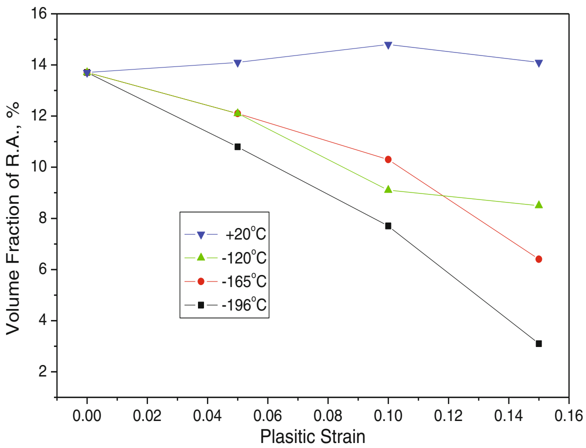


Fig.5 volume fraction Variation of RA with plastic strain at different temperatures

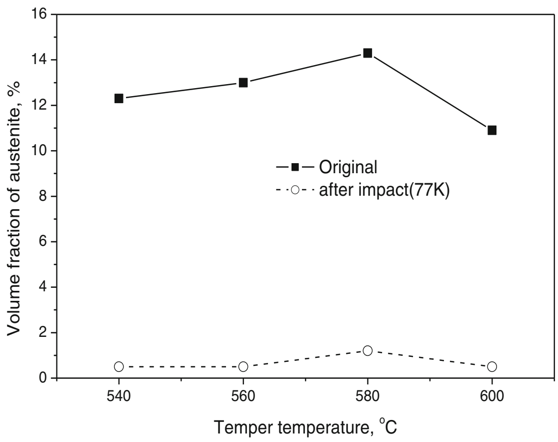
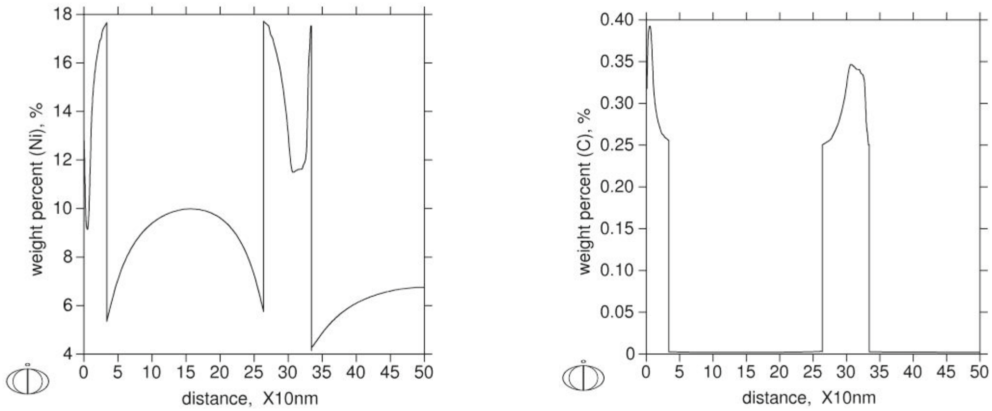


Fig.6 variation of RA under 77K impact loading

Discussion

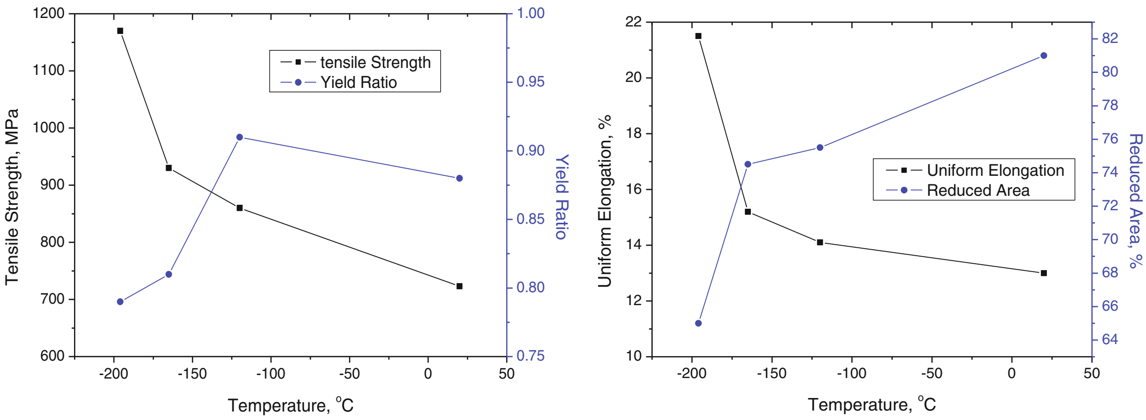
L step, inserted between normal quenching (Q) and tempering (T), has a significant influence on fine microstrucuture of 9%Ni steel. Final composition profiles simulated with a single lath by DICTRA software, treated by typical QLT process, was shown in fig.7. The calculation results revealed that, there occurred marked concentration fluctuation at several positions within a single lath after QLT treatment, with peak C concentration as high as about 0.4% or seven times as balance one, and with peak Ni concentration as high as about 18% or twice as balance one. The effectiveness of chemical composition congregation is in favor of thermal stable austenite remained till room temperature. The simulation results has inferred that, Ni element distribute unevenly within a single RA, higher in the α/γ boundary and lower inside the austenite, which was in a good accord with experimental results in fig.1 and fig.3.



（a）Element Ni （b）Element C

Fig.7 composition profile for typical QLT treatment (DICTRA simulation)

Tensile properties of experimental materials at different temperatures were shown in fig.8. With decreasing testing temperature, tensile strength rose up. This conforms to general mechanical behavior of BCC-structured materials. Inevitable interstitial impurity atoms generate non-spherical distortion of BCC lattice, resulting in both helical and edge dislocations pinned up. Dropped temperature lifts critical resolved shear stress which unpins dislocations. As a result, fracture mode transits from shear to cleavage fracture and the material becomes embrittled accompanied with the decreased plasticity. However, with tensile temperatures decreasing, uniform elongation increased though reduced area percentage decreased. Uniform elongation At -196℃ was enhanced to as large as 21.5%, much larger than that at RM. Yield ratio also tends to decline unexpectedly, exhibiting some toughening performance.



(a) Strength (b) plasticity

Fig.8 variation of strength and plasticity properties with testing temperature

The above "toughening" behavior with dropped temperatures can be explained by RA transition during tensile process. It is found from fig.7 that tensile loading at low temperature will drive RA to lose its stability and transform gradually. It is implied overwhelmingly evidently that unceasing transformation of RA will provide tensile specimens with continuous work hardening and prolong uniform elongating process. Continuous work hardening enlarges the gap between yield strength (YS) and ultimate tensile strength (UTS) and thus decreases the yield ratio. The prolonged elongating process enhances uniform elongation. The performance of RA after low-temperature loading is so-called TRIP (transformation induced plasticity) effect, which was proposed to interpret high cryogenic toughness produced by BCC-structured Ni-containing steels, such as 5.5%Ni steel and 9%Ni steel [5,8]. Since the amount of transformed RA at -196 ℃ is much larger than that at other temperatures, it is reasonable to exhibit more "toughening" data concerning yield ratio and uniform elongation. It shall be noticed that the yield ratio of QLT-treated 9%Ni steel is no more than 0.81 at -165 ℃, which is service temperature for LNG tanks. In this sense, 9%Ni steel processed by QLT heat-treatment enjoys high allowance for safe running.

Conclusions

1) Alloy elements in reverted austenite structure of 9% Ni steel distributes unevenly. Highest concentrations of Ni, Mn elements in reverted austenite are inclined to occur near the boundary between reverted austenite and matrix while the matrix near the boundary possesses lowest ones.

2) Reverted austenite in 9%Ni steel has excellent heat and mechanical stability. However, it is potential to lose its stability and transit to martensite undergoing both ultra low temperature and mechanical loading.

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