DEVELOPMENT OF HIGH STRENGTH AND HIGH PERFORMANCE STEELS AT POSCO THROUGH HIPERS-21 PROJECT

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ABSTRACT

The purpose of HIPERS-21 project is the development of new concept steels having high strength and high performance. In this project, as well as new steels, the application technologies such as welding process and constructional design also have been developed. Various steels have been developed or are under development including high strength plates for construction and shipbuilding, fine-grained multi-phase hot strips for automobile and linepipe, rod steels for high strength bolt resistant against delayed fracture, etc.. The main metallurgical keyword for the new concept steels is GRAIN REFINEMENT for strengthening without extra alloy addition and off-line heat treatment even though other performances such as weldability, corrosion resistance, yield ratio, etc., are also important features of the developed steels. In this paper, the technological aspects of developed steels and the efforts for the application to industries are introduced.

KEYWORDS

fine grain; strain-induced dynamic transformation(SIDT); HAZ toughness; weathering steel; bolt steel

INTRODUCTION

This project was started in 1998 as a ten year term project. During the first five years, lab scale development of new technologies and intermediate commercial development of new steels have been carried out as shown in Table 1. The second five years are being devoted to develop commercial products on the base of fundamental technologies developed in the first stage. Followings are the key technologies developed in the first stage of the project.

(1) High strength fine-grained steel
- Investigation of refining mechanisms during heavy deformation
- Strain-Induced Dynamic Transformation(SIDT) as a tool for grain refinement
- Characteristics of SIDT ferrite
- Evaluation of mechanical properties of fine-grained multi-phase steel

(2) HAZ performance and welding process
- Improvement of HAZ toughness through thermal stabilization of TiN particles
- Oxide metallurgy for obtaining intragranular acicular ferrite in HAZ
- Development of high speed multi-electrode welding system

(3) Weathering steel for seaside environment
- Development of Ca-added weathering steel for seaside environment
- Development of coating solution for stabilization of α-FeOOH

(4) High strength bolt steel resistant to hydrogen attack

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- Improvement of resistance to delayed fracture through microstructural modification

(5) Design for construction using fine-grained steels
- Development of flexible-stiff mixed structure for application of high strength steel
- Design criteria for application of continuously yielding steel

Table 1. Developing target of HIPERS-21 project.

First Stage (National Project)	Second Stage (POSCO Project)
Fundamental Technologies (1998~2002)	Commercial Development (2003~2007)
- Grain refinement through Strain-Induced Dynamic Transformation(SIDT) - Improvement of HAZ toughness with thermally stabilized TiN precipitates - Weathering steel for seaside environment - High strength bolt steel resistant to hydrogen attack - Design for construction using fine-grained high strength steels	- Fine-grained multi-phase hot strip for automotive application - Fine-grained linepipe steel for sour environment - Fine-grained weathering steel plate - Thick gauge plate for high heat-input welding - High strength bolt steel for construction - Manufacturing ferrite + cementite steels by SIDT and its application

In the second stage of the project, various scale-up researches through pilot and field production have been carried out to check the feasibility and limit of commercial application of new technologies. Fine-grained hot strips having 2~3μm ferrite grains have been produced utilizing SIDT phenomena on mass production scale at the existing mill. The application of grain refinement to weathering steel can improve the strength level without deterioration of weathering performance. Plain carbon steels possessing ferrite + pearlite microstructure when normally produced can be produced as ferrite + cementite steels by SIDT rolling, which can be applied for improving the performance or overcoming the difficulties of manufacturing processes of existing products. Nitrogen-modification technology for thermal stabilization of TiN particles in HAZ was successfully applied to the commercial development of thick-gauge high heat-input shipbuilding plate which was originally aimed at preventing the HAZ degradation of fine-grained steels. High strength bolt steels having tensile strength over 1300MPa are also under development applying multi-phase microstructure for reducing the sensitivity to hydrogen attack.

FINE-GRAINED STEELS

Table 2 shows the results of heavy deformation(over 80%) experiments on plain low carbon steel at various deformation temperature regions. Heavy deformation results in fine ferrite, i.e., less than 2μm, regardless of deformation temperature where refining mechanism is changing from SIDT of austenite to dynamic recrystallization(DRX) of ferrite as the deformation temperature is lowered. It is not clear whether the refinement is enhanced by low temperature deformation, but if DRX of ferrite is involved the ferrite grain size can be refined below 1μm. It has been proven that about 2μm is the limit of refinement of ferrite by SIDT of supercooled austenite utilizing the existing rolling facilities. And further refining doesn’t seem to remarkably improve the mechanical properties as compared to the efforts to be made.

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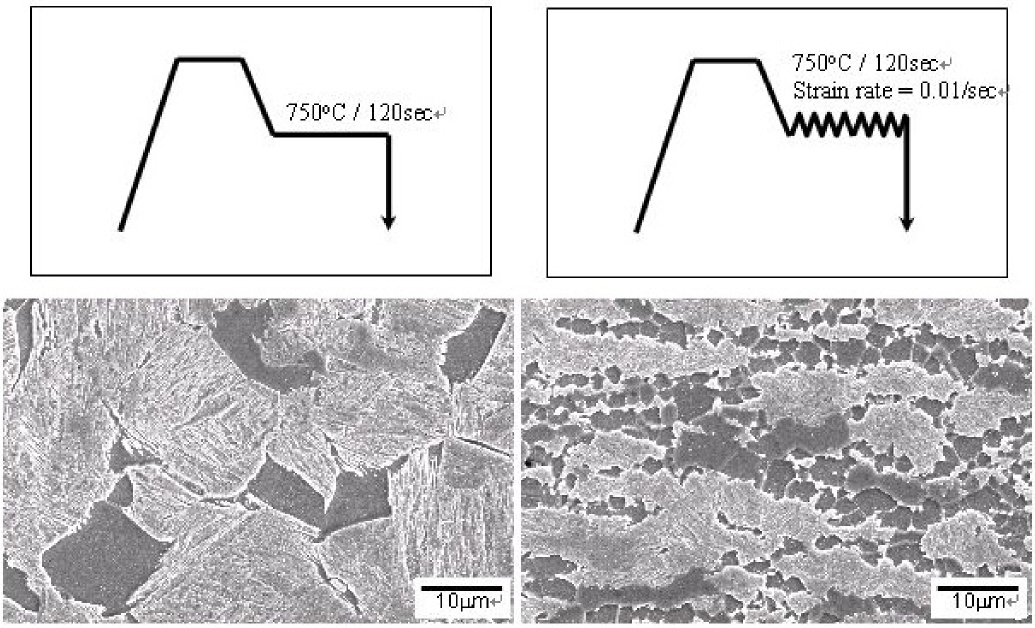
Table 2. Grain refinement by heavy deformation at various temperature regions.

Deformation Temperature	Refinement Mechanism	Ferrite Grain Size
Deformation of supercooled γ (Ae3 > T_d > Ar3)	SIDT	2μm
Deformation of duplex ($\alpha + \gamma$) (Ar3 > T_d > Ar1)	SIDT and DRX of α	1μm
Deformation of α (T_d < Ar1)	DRX of α	0.6μm

Fig. 1 shows the microstructures of low carbon steel(0.15C-0.4Si-1.5Mn) isothermally transformed at 750°C for 120 seconds just above Ar3 followed by ice-brine quenching[1)]. The difference between Figs. 1(a) and 1(b) is that the specimen for Fig. 1(a) was not deformed during isothermal transformation while deformation was continuously imposed on the specimen for Fig. 1(b) during isothermal transformation. Therefore, Fig. 1(b) is dynamic transformation since the transformation is being occurred during deformation. Ferrite grain size of dynamic transformation is much finer than that of statically transformed one and fraction transformed is almost doubled. Especially the number of ferrite grains increases remarkably when transformation is dynamic, about 16 times as many, from which one can deduce that the nucleation rate is much higher in dynamic transformation. The austenite supercooled to between Ae3 and Ar3 will start to transform when sufficient time passes over incubation period. It is generally known that deformation accelerates the transformation process. If the transformation starts under deformation, then the fraction transformed during deformation is called 'dynamic'. As can be seen from Fig. 1(b), dynamically transformed ferrite grain size is about 2~3μm which cannot be obtained by conventional thermo-mechanical control process(TMCP).

In order to manufacture fine-grained steels by using exiting rolling mills, SIDT should occur even under light



(a) (b)

Fig. 1. SEM micrographs of specimens transformed at 750°C for 120sec (a) without loading and (b) under compression at the strain rate of 0.01/sec and total stain of 1.2 (reheating temperature = 1050°C).

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successive rolling passes. Fortunately, the SIDT phenomenon has a threshold or critical level of strain under which no SIDT occurs just like DRX. Fig. 2 exhibits that strain over threshold level is necessary for the occurrence of SIDT and as the strain over threshold level increases the fraction of dynamically transformed ferrite fraction increases. This figure gives us two important messages: (1) heavy deformation in a single pass can give fine ferrite in the whole specimen and (2) light deformation can also result in fine ferrite if the strain exceeds a critical level even though the amount is small. Then the key issue becomes whether the fine ferrite are preserved and accumulated during multiple light passes with finite interpass times where the amount of strain at each pass exceeds the critical strain.

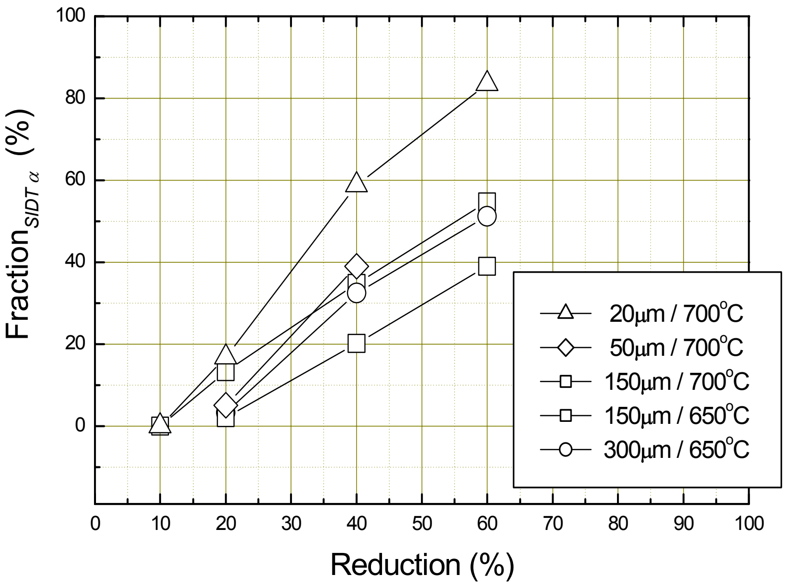

Fig. 2. Effects of austenite grain size and deformation temperature on the fraction of SIDT ferrite as a function of reduction in 0.15C-0.25Si-1.1Mn-0.01Ti steel.

Fig. 3(a) represents an example in which accumulated SIDT ferrite reaches the equilibrium fraction at the deformation temperature by 4-pass deformation of supercooled austenite with 20% reduction in each pass. The final microstructure in Fig. 3(b) shows that SIDT ferrite is kept fine during the successive passes and the whole specimen consists of uniform and fine ferrite with quenched microstructure.

Various SIDT rolling experiments have been carried out at plate and hot strip mills. Fig. 4 compares the typical microstructures of conventional rolling and SIDT rolling. Fig. 4(a) is obtained from conventional plate rolling finished at above Tnr and Fig. 4(b) is for conventional TMCP plate rolling. Figs. 4(c) and 4(d) are those from SIDT rolling in plate mill and hot strip mill, respectively. As expected, the final ferrite grain size was below 5μm for SIDT rolling. The relatively coarser ferrite in SIDT plate rolling(~5μm) is due to the longer interpass time than SIDT hot strip rolling(2~3μm). Interpass time is very important parameter for obtaining fine ferrite in multi-pass rolling because it causes release of deformation energy of austenite which in turn reduces the fraction of SIDT ferrite. Very fine SIDT ferrite is mixed with relatively coarser statically transformed ferrite in multi-pass light deformation rolling process. As a conclusion, it can be said that the shorter the interpass time, the finer the final microstructure at a given total amount of deformation. Fine ferrite hot strip was evaluated in various aspects to examine the applicability to automobile and linepipe, etc.. It was observed that SIDT of plain carbon steels have distinguishing features and could be applied to various processes or products with some modifications. And fine

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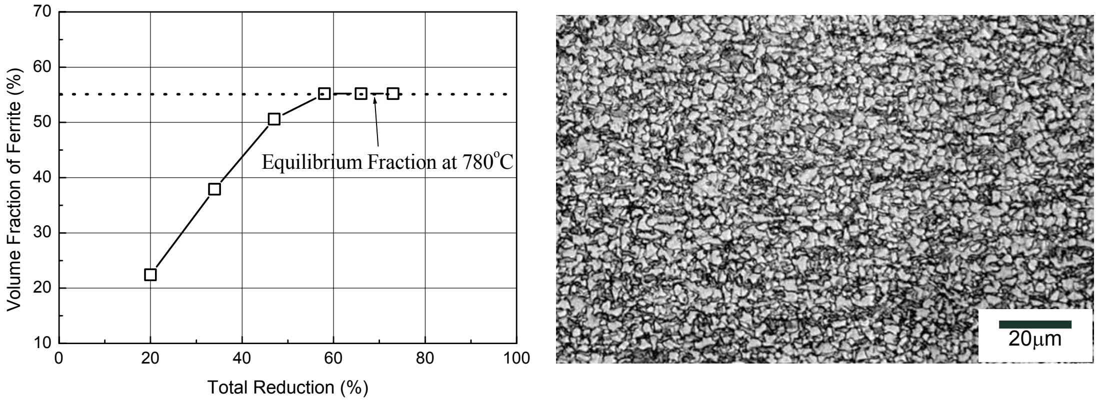
microstructure can be combined with conventional steels to exhibit synergistic performance for variety of applications.



(a) (b)

Fig. 3. (a) Evolution of ferrite volume fraction during multi-pass light deformation with 20% reduction per pass and 10sec interpass time at 780°C and (b) quenched microstructure after 4-pass deformation in 0.1C-0.25Si-1.5Mn-0.01Ti-0.04Nb-0.05V steel.

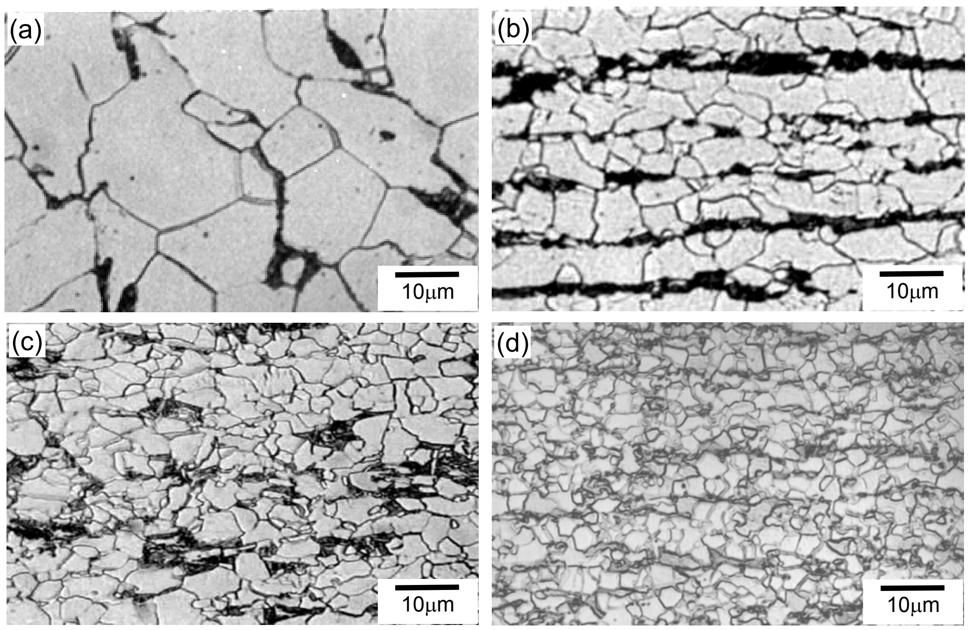


Fig. 4. Comparison of ferrite microstructures obtained by (a) conventional plate rolling, (b) TMCP plate rolling, (c) SIDT plate rolling, and (d) SIDT hot strip rolling of 0.1C-0.25Si-1.5Mn-0.01Ti-0.04Nb-0.05V steel utilizing existing rolling facilities for commercial mass production.

THERMALLY STABILIZED TiN AND IMPROVEMENT OF HAZ TOGHNESS

Usually, in order to increase strength level of plates, alloy system has been designed with high carbon equivalent which was especially crucial for thicker products. High-alloyed plates, however, show deteriorated HAZ performance. This problem becomes more serious when the heat-input is increased over 50kJ/mm during welding for the sake of cost-efficient ship building. This is caused by coarse ferrite side plates and/or upper bainite in HAZ where austenite grains are abnormally coarsened during the welding thermal cycle.

Conventional Ti addition technique for improving HAZ toughness cannot applicable to this high heat-input regime. In the coarse grain HAZ adjacent to fusion line, most of the TiN particles in conventional Ti bearing steels are dissolved and austenite grain growth is easily occurred during welding thermal cycle. Toughness of coarse grain HAZ can be improved by suppressing the growth of austenite grain which is a possible cause of coarse ferrite and/or upper bainite microstructure. Experience, however, has shown that it is the most difficult to control austenite grain size in coarse grain HAZ especially in high heat-input welding due to the very high peak temperature, e.g., over 1400℃ and slow cooling rate.

The austenite grain growth in coarse grain HAZ can be suppressed by increasing the thermal stability of TiN particles at high temperature[2)]. The growth of TiN particles will be minimized with a lower level of the metal solute in the matrix in equilibrium with the pinning particles. Increase of nitrogen content to make a hypo-stoichiometric Ti/N ratio in TiN steel is beneficial for decreasing the dissolved amount of Ti in austenite. Fig. 5 shows how moving towards hypo-stoichiometric state by increasing nitrogen content decreases the solubility of TiN precipitates in the austenite matrix, which in turn the TiN particles can effectively prevent abnormal grain growth of austenite in coarse grain HAZ.

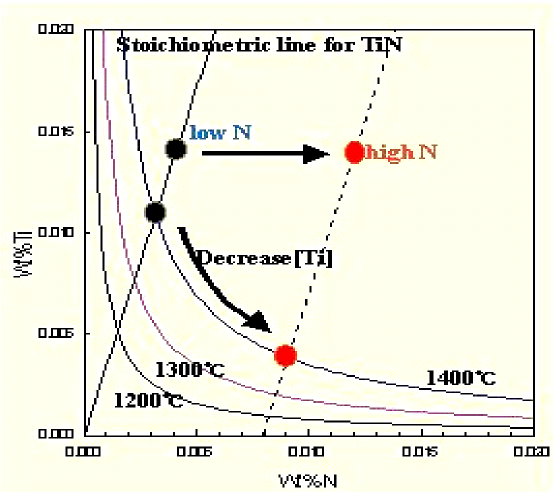


Fig. 5. Improved thermal stability of TiN particles by changing Ti/N ratio.

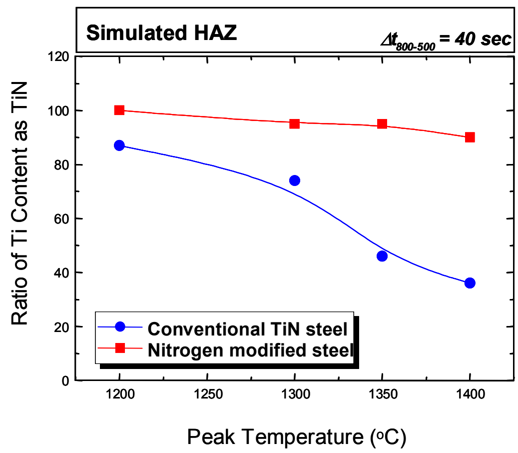


Fig. 6. Variation of ratio of Ti content as TiN particles in HAZ to that in base metal.

Conventional TiN steel and nitrogen-modified TiN steel were investigated to understand the effects of thermal stability of TiN particles in HAZ on the microstructure and impact toughness. The chemical compositions of materials used are shown in Table 3. Simulated HAZs were produced by induction heating in a computer controlled weld thermal cycle simulator. Prior austenite grain size of simulated HAZ by changing peak temperature was measured and TEM studies for precipitates were carried out on each steel. In order to compare the microstructures of coarse grain HAZ, microstructures of coarse grain HAZ in high heat-input SA(Submerged Arc) welded joint(50kJ/mm heat-input) were observed. Cold cracking susceptibility and HAZ toughness of high nitrogen steel were also evaluated.

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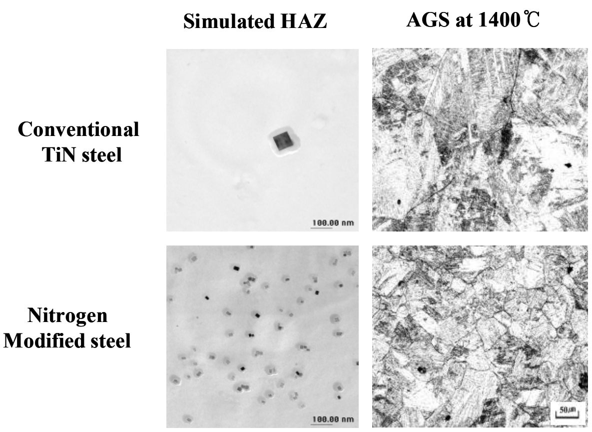
Table 3. Chemical compositions of steels used(wt. %).

	C	Si	Mn	Ti	N (ppm)	B (ppm)	Ti/N Ratio
Conventional TiN Steel	0.13	0.43	1.10	0.012	40	-	3.0
Nitrogen-Modified Steel	0.09	0.12	1.43	0.019	120	10	1.6

Fig. 6 shows the variation of ratio of Ti content as TiN precipitates in simulated HAZ to that in base metal as a function of the peak temperature ranging from 1200°C to 1400°C through the analysis of extracted residue. In conventional steel, Ti content in the precipitates rapidly decreases with increasing peak temperature and only about 40% of TiN precipitates of base metal remained under the condition of the peak temperature of 1400°C. In nitrogen-modified steel, however, Ti content as the precipitates shows almost unchanged with the change of peak temperature and about 90% of TiN precipitates of base metal survives at the peak temperature of 1400°C.

This fact supports the concept of Fig. 5 that TiN particles in conventional steel are easily dissolved at high temperature but those in high nitrogen steel are relatively stable at high temperature up to 1400°C. Fig. 7 shows TEM micrographs of extraction replica of TiN particles of two steels in simulated HAZ under the condition of peak temperature of 1400□ and $\Delta t_{800\text{-}500}$ of 40sec. In conventional TiN steel, very few TiN particles existed in simulated HAZ, whereas high nitrogen TiN steel had a large number of fine TiN particles with diameters of 10~20nm in simulated HAZ. The change of austenite grain size with peak temperature in simulated HAZ is shown in Fig. 8. The austenite grain size of simulated HAZ in high nitrogen steel was much smaller than that of conventional steel. It can be known that the austenite grains are kept fine in high nitrogen steel at high peak temperature up to 1400°C. From these observations it can be said that the TiN particles of high nitrogen steel become so stable at high temperature up to 1400°C as to effectively pin the austenite grains and suppresses grain growth in HAZ.



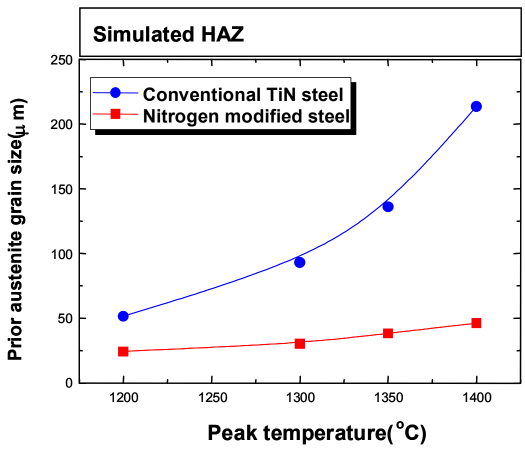


Fig. 7. TEM micrographs of extraction replica of TiN particles of conventional TiN steel and nitrogen-modified steel.

Fig. 8. Change of austenite grain size with peak temperature in simulated HAZ.

Fig. 9 represents the microstructures of weld metal/HAZ junction in high heat-input (50kJ/mm) SA weld joint. In high nitrogen TiN steel, very limited grain coarsening is observed near the weld fusion boundary whereas significant austenite grain growth takes place in relatively wide range of

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HAZ region of conventional TiN steel. The microstructure of coarse grain HAZ in high nitrogen steel consists mostly of fine ferrite and pearlite, while that in conventional steel consists of upper bainite and coarse grain boundary ferrite.

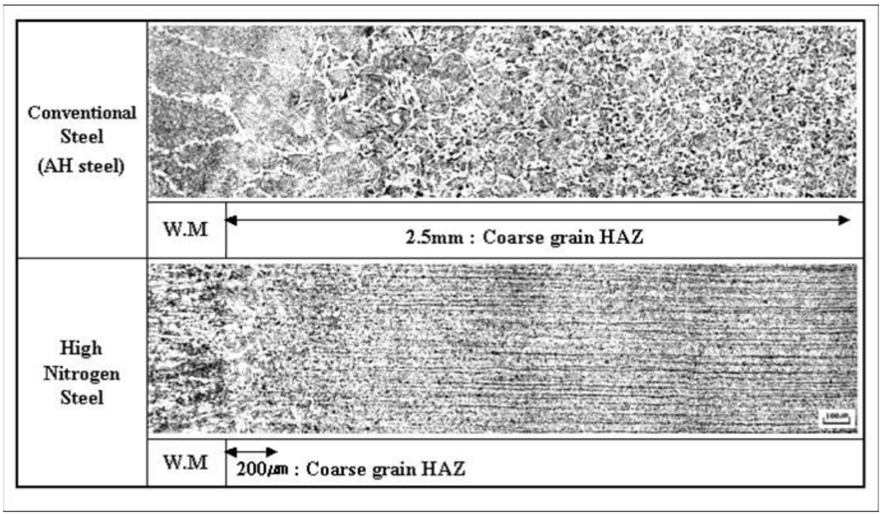

Fig. 9. Microstructures of weld joints of conventional TiN steel and nitrogen-modified steel welded by high heat-input submerged arc welding.

This technology was successfully applied to thick gauge shipbuilding plate with yield strength over 355MPa used for very large container ships of capacities more than 8,000TEU. Required plate thickness and heat-input rate are over 80mm and over 50kJ/mm, respectively. Alloying elements were so designed for the mechanical properties of plate to satisfy the required levels of ship classification and nitrogen content was optimized to ensure thermal stability of TiN particles in HAZ. Other minor elements were adjusted to minimize the free nitrogen level after welding which can be detrimental to HAZ toughness.

WEATHERING STEEL FOR SEASIDE ENVIRONMENT

Weathering steel gradually forms a dense protective rust layer on the surface through a long time exposure in an atmosphere and corrosion rate is reduced to an extremely low level. A protective rust layer is known to form on the surface of steel by addition of small amounts of chromium and copper. This Cu-Cr-P steel is called conventional weathering steel and can be used as structural materials without coating. Weathering steel applications have an advantage in reduction of initial and long-term maintenance cost. However, in coastal environment where airborne salt content is high, protective rust layers to increase corrosion resistance are hardly formed on conventional weathering steels because of Cl^- ions. Consequently, the alloy design for advanced weathering steel are mainly focused on the formation of a dense and stable rust layer even in high Cl^- environments.
The effects of various alloying elements such as Si, Ni, Mo, and W, etc., on the seaside corrosion resistance have been investigated. Especially, a focus was put on the effect of Ca addition on the corrosion behaviour. The investigated steels were exposed to seaside area and also tested in cyclic corrosion experiments. In the present section, some experimental results of the effects of alloying elements are briefly introduced. Table 4 shows the chemical compositions of alloys to investigate the effect of Ca content on the change in pH value of thin water film.

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Table 4. Chemical compositions of tested specimens(wt%).

No.	C	Si	Mn	Cu	Al	Ni	Ca
Ca1	0.097	-	1.01	0.396	0.035	0.98	0.0003
Ca2	0.100	-	1.20	0.300	0.042	1.00	0.0015
Ca3	0.052	-	1.43	0.296	0.014	1.00	0.0053
Ca4	0.094	-	0.98	0.386	0.029	0.97	0.0070

Fig. 10 shows the change in pH values of thin water films of distilled water and 0.1M NaCl solution covering the specimen[3)]. The general effects of Ca content on pH value of water film containing 0.1M NaCl are different from those observed in distilled water. Although the pH values for all specimens decreases, Ca3 specimen shows the highest pH values while Ca1 shows the lowest. These results indicate that the beneficial effect of Ca-modification is observed although it decreases with the increase in Cl^- ion content.

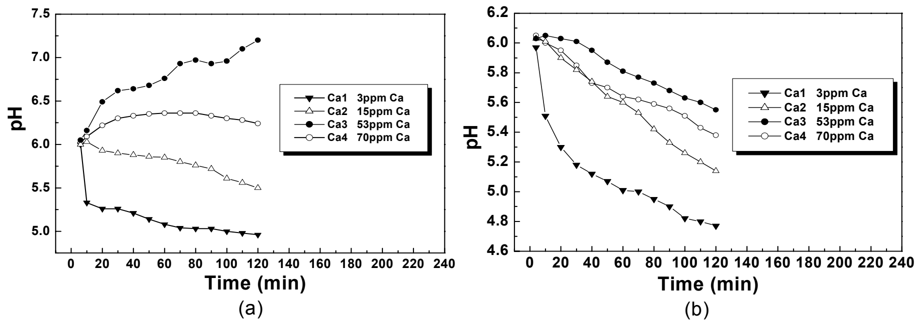

Fig. 10. Change in pH value of thin water film measured at room temperature using a micro-pH electrode (a) in distilled water, and (b) in 0.1M NaCl.

In order to observe the existence of CaO and CaS, inclusions formed in the Ca-modified steel was analyzed using the EPMA. As can be seen in Fig. 11, most inclusions are (Al, Si, Ca)O type complex oxides and some parts of inclusions are covered with CaS. The (Al, Si, Ca)O type complex oxides do

not contribute to the increase in pH value of the water film because they are insoluble in the water. Only a small portion of Ca is attributed to increase pH value of the water film by formation of CaS in the Ca-modified steel. Therefore, the important factor for increasing pH value of the water film is not the total Ca content in the steel but the fraction of CaS in the inclusions.

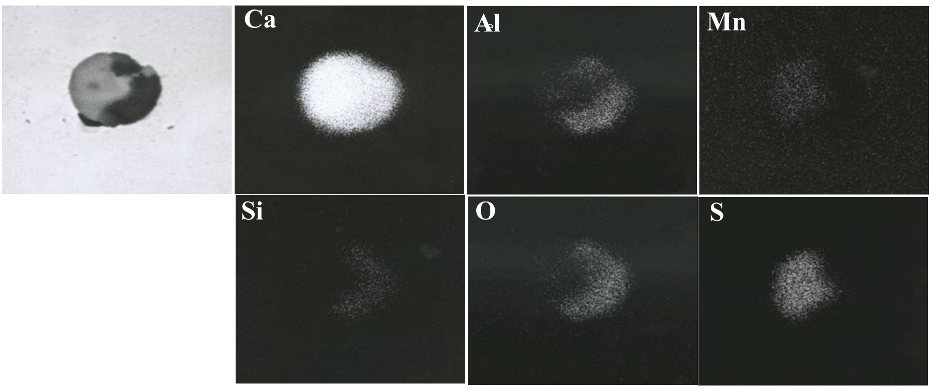

Fig. 11. EPMA analysis of inclusion formed in the Ca-containing steel

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Corrosion resistance of the weathering steel for seaside environment depends upon the Cl^- ion permeability through the rust layer. The Cl^- ion permeability can be evaluated by measuring the liquid-junction potential set up by the difference in the Cl^- ion concentration between the two different compartments separated by the rust layer which serves as a permeable membrane. Fig. 12 shows the liquid junction potential measured for the rust membranes prepared by cyclic corrosion test. The permeability of Cl^- ion through the rust membrane could be qualitatively interpreted and categorized by three groups; easily permeable group(N1), impermeable group(Mo2 and W2), and intermediate group(others).

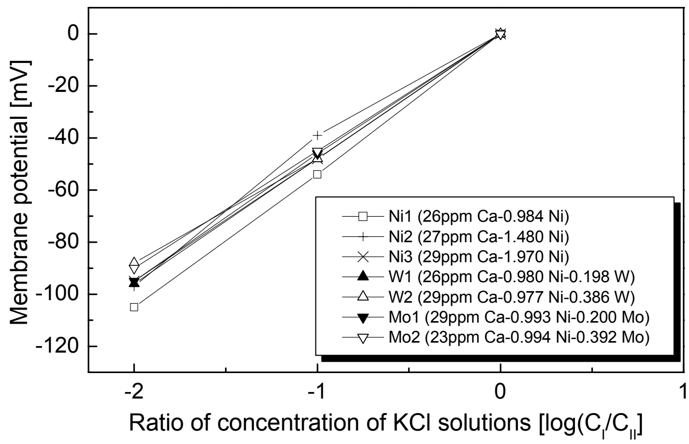

Fig. 12. Liquid-junction potentials measured for various rust membranes formed by cyclic corrosion test.

Fig. 13 shows chloride element distributions in the rust layers formed on each specimen. From this result, it is clear that addition of Ni does not effectively inhibit the permeation of Cl^- through the rust layer. On the other hand, the effects of W and Mo on the Cl^- permeation through the rust layer are obvious. In Ca-modified Mo and W containing steel, chloride element is concentrated near the outer layer of rust. Therefore, it can be said that a small amount of Mo and W addition can significantly improve the corrosion resistance in coastal environment.

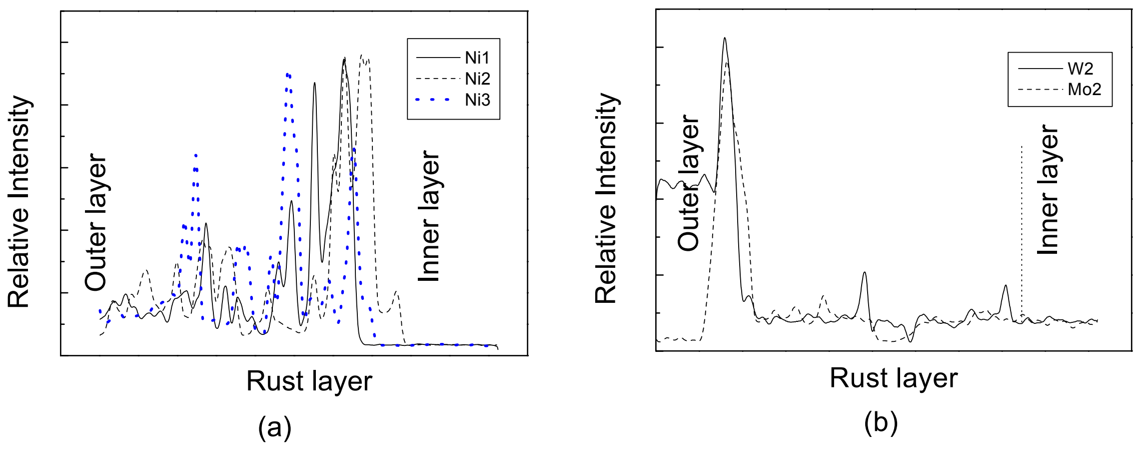

Fig. 13. Chloride element distributions in the rust layers formed (a) on the Ca-modified steels with different Ni contents and (b) on the Ca-modified steels with Mo and W.

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NEW MICROSTRUCTURES RESISTANT TO DELAYED FRACTURE

Two types of microstructure were developed for high strength bolt steels with good resistance to hydrogen delayed cracking. One is mixed microstructure of ferrite and tempered martensite. In order to retard the intergranular crack propagation due to hydrogen embrittlement, soft ferrite phase was located along the prior austenite grain boundary. The other is mixed microstructure of austenite and bainite. In this microstructure, crack propagation is retarded by austenite which has better resistance to delayed fracture than martensitic phase. Constant load tests have been performed under severe corrosive atmosphere(5%NaCl + CH_3COOH solution, pH 2.0) to evaluate delayed fracture resistance of new multi-phase microstructures and the superior resistance to hydrogen delayed cracking was confirmed.

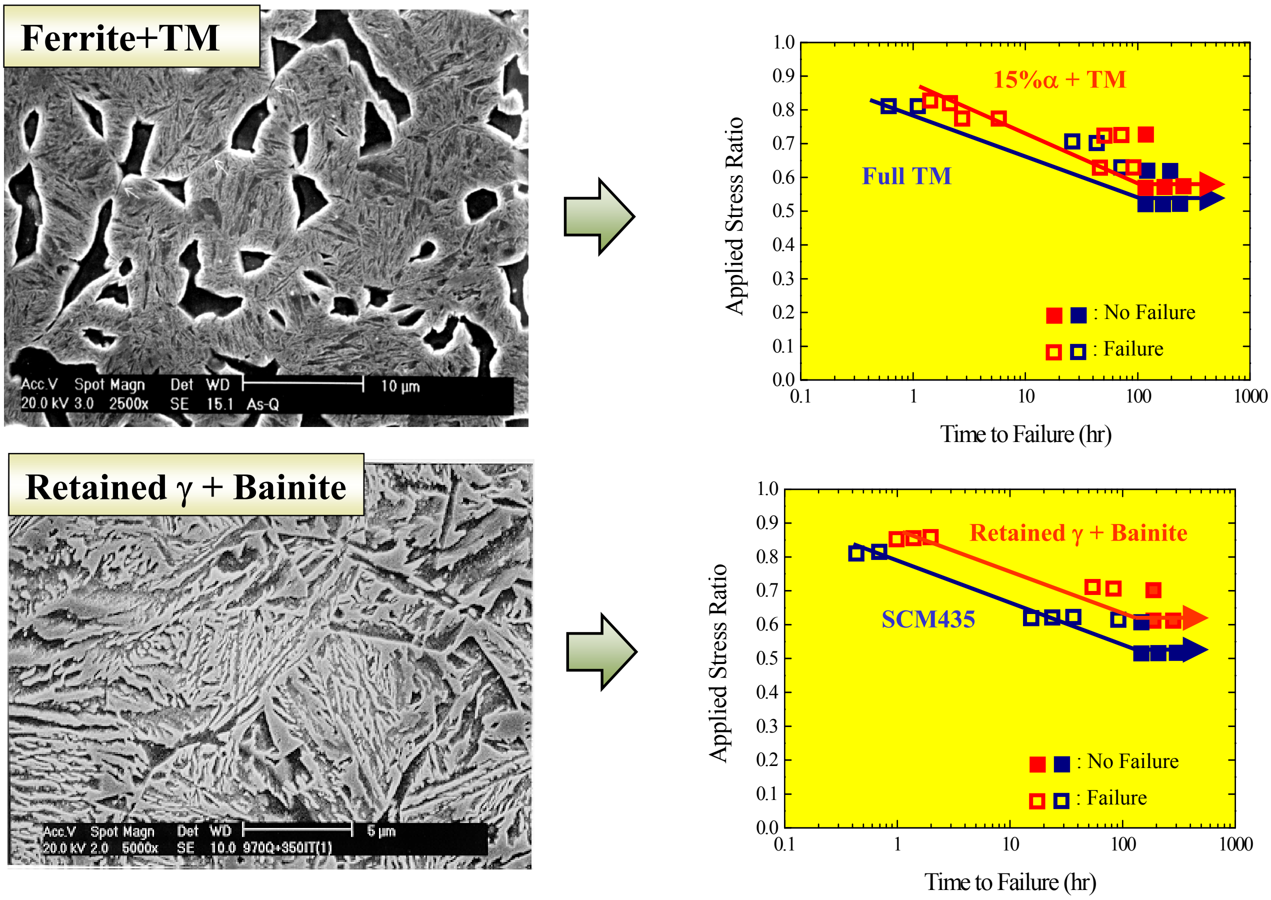

Fig. 14. Two types of microstructure which are resistant to hydrogen delayed cracking as compared to conventional tempered martensite microstructure.

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