Niobium Bearing Structural Steels
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NIOBIUM IN STRUCTURAL STEELS

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Abstract

Since the widespread application of niobium (Nb) to linepipe steels started with the Trans Alaska Pipeline System (TAPS) project in the 1970's, the Nb-bearing technology has rippled across all the Thermo-Mechanical Control Processed (TMCP) steels due to its best-suited austenite conditioning effect. However, recent applications for steels have required not only ferrite-pearlite type microstructures but also bainite or martensite type high strength structural steels.

The Nb-added 950MPa tensile strength TMCP steel was supplied, for the first time, for the construction of the Kannagawa hydraulic power plant in 2002. Here the Nb was the key to increase strength without deteriorating the toughness of the martensitic structure. On the other hand, some ferrite (and bainite) based steel, such as offshore structure steels and LPG carrier hull steels, have contained Nb in order to increase low temperature toughness with decreased carbon content. The diverse applications of Nb-metallurgy for structural steels are presented in this paper from both mother plate and weldment points of view with actual project examples.

Introduction

In Japan, the wide spread application of the Thermo-Mechanical Control Process (TMCP) started with the production of API grade X65 steel pipes for the Trans Alaska Pipeline System (TAPS) project in the 1970's. TMCP enabled improvements in the toughness properties for low carbon steel pipes, as per the requirements for the TAPS project. At that time, the metallurgical value of microalloying had been found, and consequently, both TMCP and microalloying technologies have concurrently matured to the present key technology of steel plate manufacturing. Among the microalloying elements, the most popular and beneficial for TMCP has been that of niobium (Nb). It is well known that Nb has the strongest austenite conditioning effect over a large portion of the typical hot rolling temperature range [1]. Today, Nb is beyond any doubt the indispensable element for TMCP, not only for line pipe steels but also for structural steels.

For line pipes, a fair amount of Nb can be applied, for example, a 0.10%Nb containing steel plate was evaluated in full-scale test for application in a sour environment [2]. However, for the application to welded structural steels, care has been taken in selecting the appropriate microalloying content in steel because excess additions has some potential to deteriorate toughness in the weld metal and the heat affected zone (HAZ), especially after the PWHT. Therefore, Nb-bearing TMCP-type structural steels have generally been designed with judicious

Nb additions in the range that can satisfactorily bring about the required TMCP effect for the base metal.

The purpose of this paper is to provide a view into the modern steel design basis of Nb in TMCP structural steels. The fundamental metallurgy is reviewed and discussed from this point of view followed by examples of some actual applications of Nb to structural steels.

Niobium in Steel

Indispensable Element in TMCP

Today, there are a plethora of papers available within the literature that discusses the metallurgical role of Nb as a microalloying element. For example, see [1], [3]-[8], but from the steel maker's point of view there are three effects of Nb in the TMCP practice that need to be emphasized:

- Retardation of recrystallization;
- Retardation of γ-α transformation;
- Complete solid solubility with other microalloying elements*.

(* Remark: in this paper, the microalloying elements are defined as columns 4A and 5A in the periodic table.)

The retardation of recrystallization by Nb is the key to carry out controlled rolling effectively. The behavior exhibited in Figure 1 [9] represents this retardation effect for some elements, where it is quite obvious that Nb has the most significant effect. As can be seen from the figure, the recrystallization-stop temperature can be considerably increased with just a small addition of Nb. This has crucial practical value because it expands the temperature range during the practice of controlled rolling.

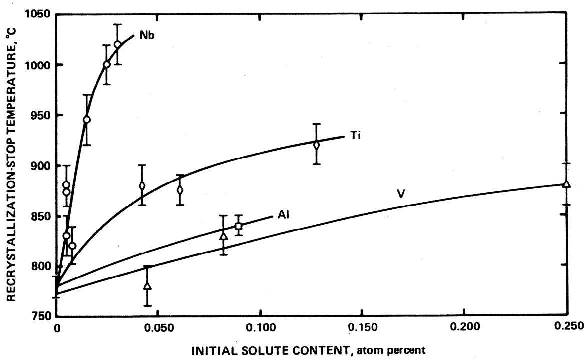
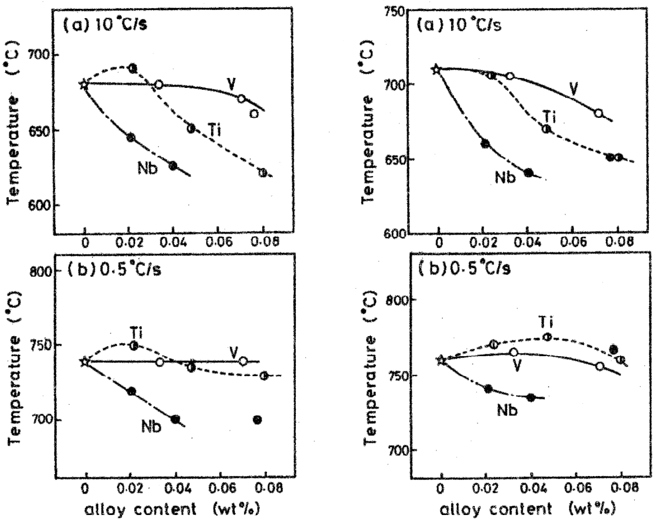


Figure 1. The increase in recrystallization temperature with increase in the level of microalloy solutes in a 0.07C, 1.40Mn, 0.25Si steel [9].



(1) Un-deformed (2) 50% deformed at 900°C

Figure 2. Corrected Ar_3 temperatures of microalloyed steels with standard austenite grain size of 100μm [10].

The retardation of γ-α (austenite-ferrite) transformation by Nb, on the other hand, is quite essential to the practice of accelerated cooling. Figure 2 shows the measured γ-α transformation temperatures for some microalloyed steels with 0.10%C-0.25%Si-1.5%Mn base chemistry. In every condition of deformation and cooling rate, the addition of Nb can noticeably decrease the γ-α transformation temperature. This effect of Nb can bring about remarkable strengths in steels with the accompanying practice of accelerated cooling.

The above-mentioned two metallurgical effects somehow relate to the solute drag effect by Nb atoms or the precipitation of Nb(C, N). It is the mobility of the boundaries (grain boundaries or interphase boundaries) that is interfered with by these solute atoms and precipitates. The above figures indicate that the maximum effects can be gained if Nb is selected among the microalloying element. However, as discussed later, the correct addition of Nb is required in relation to the chemistry to ensure good weldability. In some applications, V (vanadium) is also used in conjunction with Nb for optimum strengthening, and HAZ (Heat Affected Zone) toughness properties. Or, as often the case, Ti (titanium) is added with Nb, where Ti is usually applied as an austenite grain refiner or for the prevention of surface cracking on the continuous cast slabs. In these cases, Nb works very well with these other microalloys.

As a distinct definition of "microalloy" could not be found in the historical literatures, steelmakers usually call columns 4A and 5A elements of the periodic table as microalloys. These elements have some common characteristics, in that they have a strong affinity with carbon and nitrogen; the combined carbides or nitrides have a NaCl-type crystal structure (see Figures 3 and 4); these carbides or nitrides show complete solid solubility. Namely, in Ti-Nb-bearing steels, the observed precipitates are not simple TiN, TiC, NbN, or NbC but (Ti, Nb)(C, N) complex compounds.

Nb is considered to have medium affinity for carbon or nitrogen among the popular microalloying elements (Ti, Nb and V) as shown in Figure 5. Therefore, Nb additions with other microalloying elements in general go very well and it can change the various aspects of microalloying metallurgy. For example, since the equilibrium chemical composition of the formed carbonitride changes with temperature, as shown in Figure 6 for a (Ti, Nb)(C, N) system [12], the characteristics of the precipitates can be controlled by the pre-processing [22]. The size distribution of the precipitates can also be controlled to some degree by this multi-microalloy processing [13].

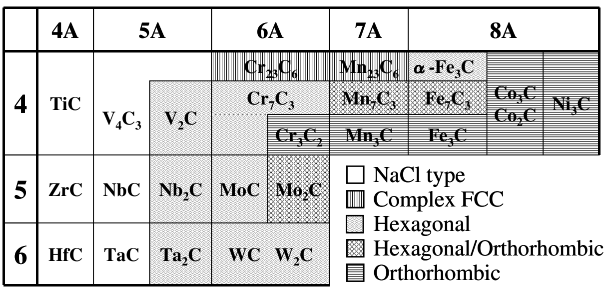


Figure 3. Crystal structures of carbides for some elements in the periodic table [11].

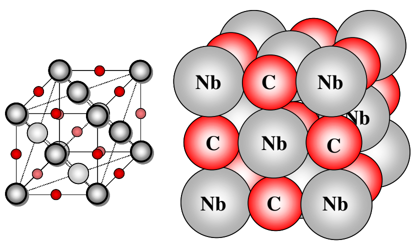


Figure 4. NaCl-type crystal structure of NbC.

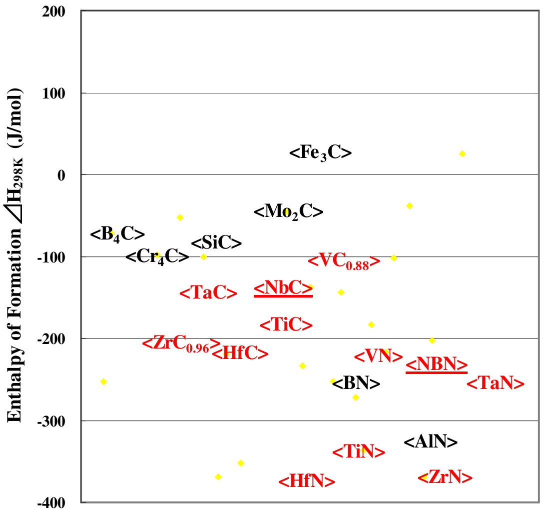


Figure 5. Enthalpies of formation for carbides and nitrides.

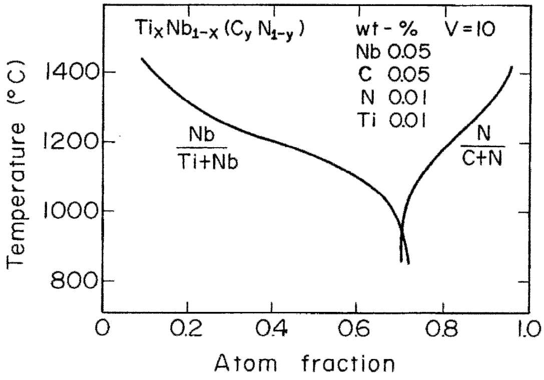
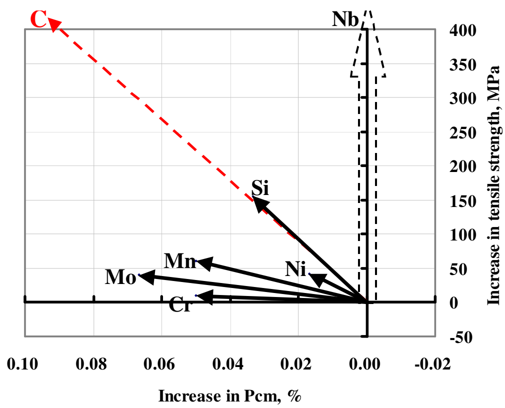


Figure 6. Atomic fractions of elements in the complex compound $Ti_xNb_{(1-x)}(C_yN_{(1-y)})$ precipitating from austenite over the temperature range 1400ºC-900ºC [12].

The three metallurgical roles of Nb in the practice of TMCP have been described above. However, from the practical point of view, the most prominent impact of Nb with TMCP is its significant strengthening effect without sacrificing weldability as the result of the above-mentioned metallurgical effects. When 12mm thick plate was controlled rolled in the γ-α two-phase region, just 0.03%Nb addition increased the tensile strength by more than 100MPa for a 500MPa tensile strength class carbon steels [14]. When a 100mm thick plate was accelerated cooled, 0.03%Nb was found to increase the tensile strength by about 50MPa for a 500MPa tensile strength carbon steel [15]. In spite of this significant strengthening of steel, Nb has no noticeable effects on general aspects of weldability such as HAZ hydrogen cracking, liquation cracking or weld metal solidification cracking [16]. Namely, Nb can increase strength distinctively without deteriorating the weldability. That means that Nb can permit a reduction in the carbon or carbon equivalent content to a great extent of many structural steels. Although some detrimental effects of Nb in the weldment can be anticipated, the carbon-reduction effect by Nb usually overcomes such effects. Essentially, this is the very reason why Nb-bearing TMCP became the mainstream production method for steel plates throughout the world.



Element	C	Si	Mn	Mo	Ni	Cr	Reference
Δσ (MPa/%)	4500	155	60	40	42	10	[17]
ΔPcm (%/%)	1	1/30	1/20	1/15	1/60	1/20	[18]

Figure 7. Comparison of strengthening vs. weldability vectors for some solute elements in steel.

Figure 7 compares the vectors of the strengthening effect vs. weldability deteriorating effect per one mass percent addition of element to steel. Here, only the solute strengthening effect was counted except for Nb, and the weldability was represented by the Pcm formula. The strengthening effects by carbon and Nb are extreme and they scaled over the range of Figure 7. It can be seen from this figure that each substitutional element can increase tensile strength of steel at some expense of weldability. Carbon has the same trend as that of Si but the effect per unit addition is extreme, but the most remarkable one is that Nb has a significant strengthening effect with no loss of weldability. This is the very reason why Nb is such an indispensable element in TMCP.

Welding of Niobium-Bearing Steels

Although Nb is indispensable to improve the properties of base metal in TMCP, Nb itself is sometimes detrimental at welding, especially for structural steels if added in the wrong amount for the intended application. The influence of Nb on the toughness of the weld metal and HAZ was well reported by Kirkwood [16]. He summarized that the detrimental effect by Nb could be anticipated for moderately high heat input conditions in high carbon steels, and also after PWHT (Post Weld Heat Treatment). Nevertheless, he also indicated that the beneficial effect of Nb could be derived in some circumstances such as low carbon and low heat input as welded conditions. He also mentioned that the complex role of Nb should be understood by checking what the microstructure was in the absence of Nb.

Unlike line pipe steels, structural steels tend to be fabricated with higher heat inputs during welding as well as low heat input, and sometimes PWHT is applied to reduce the residual stress along the welding lines. Therefore, structural steels suffer more severe conditions at welding in terms of Nb-microalloying additions. As a result, the maximum amount of Nb in steel has been often limited for these applications. Table 1 compared some representative Nb specifications for steel plates, in which it can be seen that the building and line pipe steels have the most lenient specifications on Nb, but the tank and offshore structure steels, in contrast, have the most restricted ones.

Table 1. Typical Nb Specifications for Steel Plates of 500MPa Tensile Strength Level

Structures	Codes	Specification for Nb
Ship	LR and other Ship Register, DH36-EH40	0.05 % max. (when used in combination with Al)
Building	JIS SM490, SN490	No restriction
Bridge	ASTM A709 Grade 50 Class 1& 3	0.005-0.05 %
Tank	ASTM A841 Grades A & B, Class 1 & 2	0.03 % max.
Offshore Structure	API Specification 2W Grade 50 & 60	0.03 % max.
Line Pipe	API Specification 5L X56, X60, X65	0.15 % max. (sum of Nb, V, and Ti)

The pessimistic side of Nb at welding lies in the intrinsic nature of Nb itself: part of which was already described above. The most influential one is the retardation effect of γ-α transformation by Nb. For a 500MPa tensile strength class steels, Nb in solution has a trend to enhance the upper bainite transformation in the HAZ during its cooling. The process of transforming upper bainite will also create the Martensite-Austenite constituent (M-A). Namely where carbon-rich austenite, that was left behind the ferrite side plates, forms M-A. This M-A is frequently the major cause of the HAZ deterioration when welding at a fairly wide heat input range.

Tsukamoto et al. showed, as in Figure 8, that the amount of the formed M-A has a strong correlation with the amount of solute Nb [15]. This is one of the strong evidence that Nb plays an important role to increase the hardenability of steel HAZ in some circumstances. Once M-A is formed, the succeeding thermal cycles often deteriorate the HAZ furthermore because the plate-like M-A is divided into small M-A lathes, which make micro-cracks initiate easier [19]. However, the reduction of Si content also promotes the decomposition of M-A constituent in the lower peak temperature of subsequent thermal cycle. A similar effect is also observed in the reduction of phosphorus content.

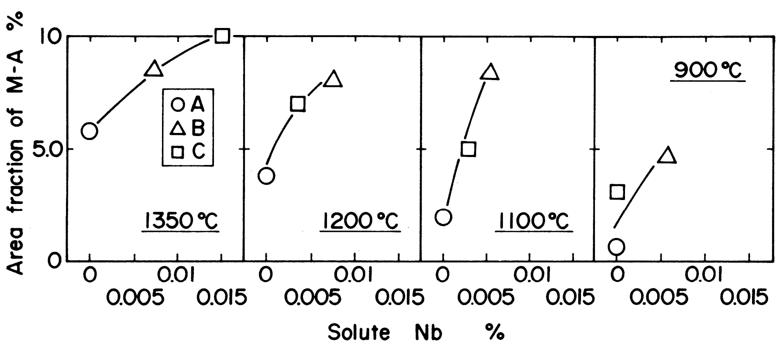
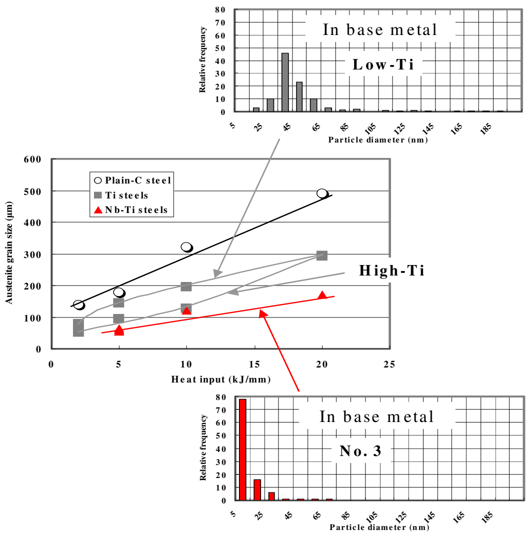


Figure 8. Effect of solute Nb content on the M-A constituent in simulated HAZ [15] (simulation of 100kJ/cm).

At these higher heat input welding rates, this adverse affect of Nb can be mitigated if a countermeasure action is adequately taken action against the formation of the M-A. Decreasing carbon or other M-A-friendly elements such as silicon is one of the most successful and widely applied measures, as described above. As a result the retained austenite at the upper bainite transformation will easily decompose into cementite and ferrite if the carbon content itself is low. When the higher Nb (0.10%) steel had been examined for line pipe application, the lower carbon content was essential in the success of that steel design [2]. For such structural steels, the simplest countermeasure is to limit the amount of Nb in solid solution and in fact it has been found that the toughness of the steel becomes superior with small additions of Nb and Ti than that with a single addition of Nb. The reason of this improvement in toughness by multi additions of microalloys comes from the formation of smaller nitrogen-rich precipitates. The application of Nb and Ti to steel with proper processing can decrease the size of carbonitrides considerably as illustrated in Figure 9 [13]. In the Nb-Ti-bearing steels, the precipitates are nitrogen-rich and these precipitates are more stable in the HAZ thermal history than those in the single Nb-bearing steels. These smaller stable particles in the matrix are effective not only in suppressing the grain growth but also in minimizing the amount of dissolved solute microalloys that contribute to M-A formation during the HAZ thermal cycles.

If the toughness of these steels is represented by the cleavage facet size [20], the characteristic of Nb and Ti multi-additions is well expressed by Figure 10 [21]. Here, the data for the same steels in Figure 9 are depicted. This figure says that the HAZ's of the Ti-bearing steels deteriorate in toughness depending on the austenite grain growth as the same tendency as those of the plain-C steel. When the heat input is small, Ti does not dissolve much in matrix due to the stability of TiN-rich particles; on the other hand, when the heat input is large, although some Ti is expected in solid solution, the solute Ti does not affect much on the transformation microstructure because the cooling rate is slow, as estimated by the slight influence of Ti on the γ-α transformation temperature at the slower cooling rate in Figure 2. In contrast to Ti-bearing steels, the Nb-Ti-bearing steels deteriorate more steeply with increasing austenite grain size than the Ti-bearing steels, stemming from the solute Nb. However, when the heat input is small, the austenite grain sizes are smaller in the Nb-Ti-bearing steels than in the Ti-bearing steels as shown in Figure 9, so the toughness of the Nb-Ti-bearing steels would be superior.



Steel		Chemical compositions (mass %)							
		C	Si	Mn	Ni	Ti	Nb	SolAl	N
Plain carbon		0.13	0.21	1.00	---	---	---	0.044	0.0020
Ti	Low	0.13	0.20	0.98	---	0.017	---	0.045	0.0035
	High	0.09	0.42	1.58	---	0.057	---	0.016	0.0030
Ti-Nb	No.3	0.12	0.31	1.47	---	0.015	0.016	0.024	0.0047
	No.4	0.05	0.21	1.29	0.25	0.019	0.013	0.061	0.0061
	No.5	0.08	0.19	1.28	0.24	0.018	0.016	0.027	0.0048

Figure 9. Austenite grain growth in the HAZ for various microalloyed steels.

The effect of Nb on the weld metal is similar to that effect on the HAZ, and is well reviewed by Kirkwood [16]. From the point of view of the steel design, as shown in Figure 11, the Nb content in base metal gives a significant effect on the weld metal tensile strength at large heat input SAW. Nb addition to steel, as with in common to Mn, Ni and Mo, is a good method to increase the tensile strength of the weld metal, but the amount of it should be judiciously applied when the involved risk is anticipated.

The other toughness deteriorating mechanism at welding is the precipitation of (C,N) microalloys in the ferrite phase. This is also of a great concern especially when the welded joint is thermally stress-relieved. It is reported that the toughness drops after PWHT with increasing Nb content [16]. This topic is also discussed in detail by Kirkwood [16].

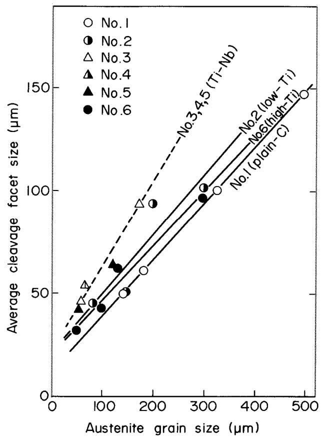


Figure 10. Relationship between average cleavage facet size and prior austenite grain size in the HAZ [21].

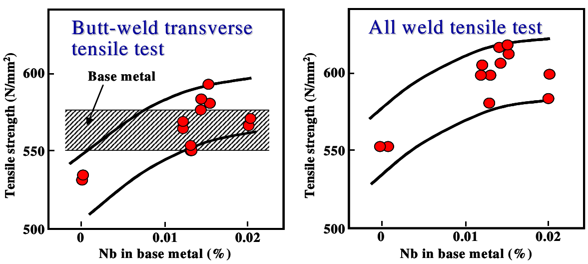
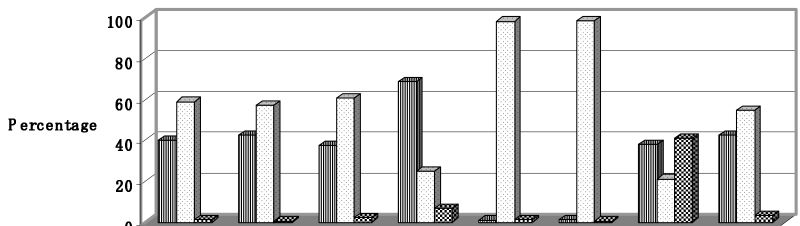


Figure 11. The influence of Nb content in base metal on tensile strengths of butt-weld joints and all-weld metals (Base metal: 0.11%C-0.3%Si-1.4%Mn, Welding method: SAW) [23].

Niobium-Bearing TMCP Steels

It is well established that Nb with the TMCP has improved the toughness of steel plates significantly by considerably decreasing the Ceq or Pcm value of the steel. The Ceq values of most structural steels must have decreased by more than 0.05% by the TMCP of Nb-bearing steels, compared to those of conventional steels. Today, users can fully enjoy the benefits of TMCP steels, assisted by Nb as an alloying element.

Figure 12 summarizes the percentage of as-rolled/TMCP/Heat-Treatment application in its plate manufacturing process for various industrial sectors in Japan in 2007. Although the TMCP was the minor manufacturing process of the steel plate in the field of construction and tanks, it was the major application for offshore structures and line pipes. Today, almost all of the steel plates for offshore structures and line pipes manufactured in Japan are TMCP steels. The total average TMCP application percentage was 54% in 2007. All of these TMCP steels are considered to contain some amount of Nb as an alloying element. This means that about half of modern steel plates need Nb for their good performance during application.



	Ship	Buld.	Bridge	Const.	Offshore	LP	Tank	Ave.
As-Roll	40	43	37	69	1	1	38	42
TMCP	59	57	61	25	98	98	21	54
H.T.	1	0	2	7	1	1	41	3

Figure 12. Application percentage of plate manufacturing processes in various industrial sectors. Data from Japanese steel plate mills in April-June 2007.

It is important to clarify that TMCP consists of some processing types: Thermo-Mechanical Rolling (TMR), Accelerated Cooling (and Tempering) (AC (+T)), and Direct Quenched and Tempered (DQT). By separating these types into the TMR and the other accelerated cooling processes, Figure 13 is obtained for some industrial sectors. This shows that the accelerated cooling types are the major methods to produce TMCP steel plates in the fields of shipbuilding, offshore structures and line pipes, but the ratios are opposite in the fields of building and bridges. In these latter fields, the applications of the steel requirements that need accelerated cooling, such as extra heavy high strength, large heat input welding, etc., are still rare. However, regardless of the TMCP types, Nb is of course the indispensable alloying element.

At present, the application of TMCP is still increasing due to its excellent cost effectiveness and its potential high-performance characteristics, and so is the application of Nb-microalloying.

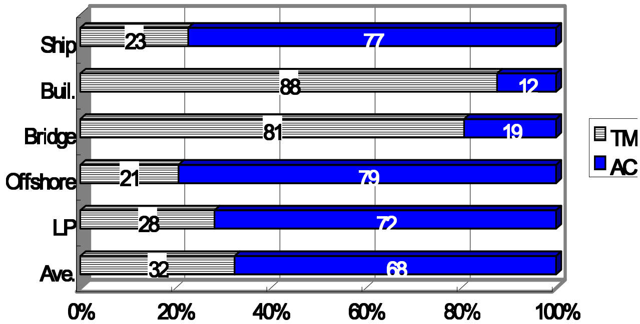


Figure 13. Rates of processing types in the TMCP practice in various industrial sectors.

Application of Niobium for Structural Steels

Toward Higher Strength -*Ausformed Steels (For Bridges and Penstocks)*

The austenite conditioning by TMCP has traditionally been used for the purpose of refining the transformed ferrite. However lately, it has been extensively applied to the refining of the transformed bainite or martensite structures. Here, Nb plays an important role by expanding the austenite un-recrystallized region as well in the practice of the TMCP.

During controlled rolling, lots of lattice defects are introduced in the austenite grains [24], and those defects, together with the increased grain boundary area of the flattened austenite grains, can multiply the ferrite nucleation sites [8]. This same mechanism also works for the bainite or martensite high tensile strength steels. For bainitic steels, the role of austenite conditioning on the bainite structure was examined by a thermal simulator [25]. Specimens were austenitized at 1100ºC in a vacuum chamber, deformed 0 to 50% at 900ºC, quenched by helium gas to 575ºC, kept isothermally, and then water quenched to room temperature. Figure 14 shows the SEM observation result of the thermally transformed bainite structures. They are on the primary stage of transformation, where the partially-decomposed bainitic ferrite laths and the transformed martensite from the austenite can be observed. Figure 14 (a) shows the typical BI type upper bainite. In contrast, the morphology of bainite structure changes significantly with deformation in the un-recrystallized austenite into refined ones in Figure 14 (b) and (c).

It was confirmed that this refinement of the bainite lath length by austenite deformation was not so effective at deformations less than 30%, but was significant with more than 50% deformation. This nonlinear dependence of the bainite lath size on the deformation in austenite is quite different from the linear dependence for the ferrite structure (Figure 15) [26]. This remarkable refinement of bainitic ferrite lath in the case of heavier deformation was considered to closely relate to the formation of dislocation cell structures within the deformed austenite grains.

Chemical compositions of steel (mass %)

C	Si	Mn	P	S	Ni	Nb	Ti	B	Sol.Al	N
0.18	0.20	1.37	0.007	0.001	0.62	0.014	0.012	0.0008	0.026	0.0021

(a) 0% deformed. Transformed at 575ºC for 25 sec.

(b) 30% deformed. Transformed at 575ºC for 20 sec.

(c) 50 % deformed. Transformed at 575ºC for 15 sec.

Figure 14. Effect of reduction ratio at 900ºC on bainite morphology transformed at 575ºC [25].

The deformation in the austenite un-recrystallized region is also effective for the refinement of martensite structure, but different from bainite, martensite lath morphology does not change dramatically by the austenite conditioning. However, the flattened austenite grain makes the same effect of the refined grain [27]. Many martensite packets with different direction are initiated in the flattened austenite grain and produce a noticeable effect of improving toughness.

Figure 16 shows the SEM observation result of TMCP HT950 (950MPa in minimum tensile strength) steel [28].

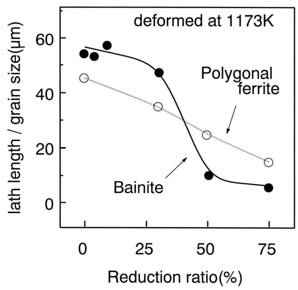


Figure 15. Effect of reduction ratio at 900 ºC on ferrite grain size and bainitic ferrite length [26].

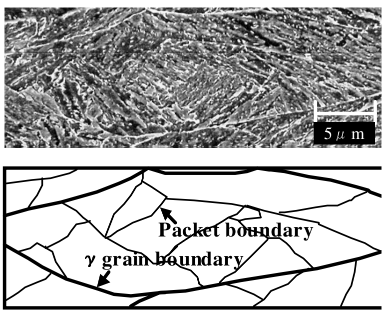


Figure 16. SEM observation showing martensite packet refinement of TMCP HT950 steel [28].

By utilizing the austenite conditioning effects on bainite or martensite, so called Ausformed Steels were developed [28]. The purpose of this processing was to improve the mechanical properties with an economical zero-nickel containing chemistry, which was only achievable with a Nb based chemical design. Increasing the austenite deformation in the un-recrystallized region can increase both strength and toughness of the ausformed steels. As a result these ausformed steels have been applied to bridges and penstocks.

As for penstocks in Japan, hydraulic plants started operation using HT570 in 1960, HT780 in 1975, and HT950 in 2005 [29]. This HT950 high strength steel was utilized in Kannagawa Power Plant (Tokyo Electric Power Co., Inc.) for the first time in Japan. The maximum plate thickness was 94mm, and about 2,330 tons of HT950 was used for the first term construction [29]. Following the Kannagawa Power Plant, Omarugawa Power Plant (Kyushu Electric Power Co., Inc.) utilized 1,600tons of HT950 in its first term construction. Since a high brittle crack arrestability is required for steel plates for penstocks in Japan [30], the developed ausformed martensite steels were applied for these big projects. The austenite conditioned Nb steel brought about a splendid improvement in the arrestability of steel against brittle crack propagation. This was the first time in the world that 950MPa tensile strength class steel plates were manufactured by TMCP of Nb-bearing steel and supplied for the actual projects. Interestingly, the same type TMCP martensite steels were supplied as a trial for X100-120 line pipes.

Kannagawa and Omarugawa Power Plants are now the only plants in the world, using HT950 in penstocks. Figure 17 and 18 outlined these penstocks. The steel materials used for these penstocks are shown in Figure 19, in which the ausformed bainite steels were also utilized as structural members of SM570.

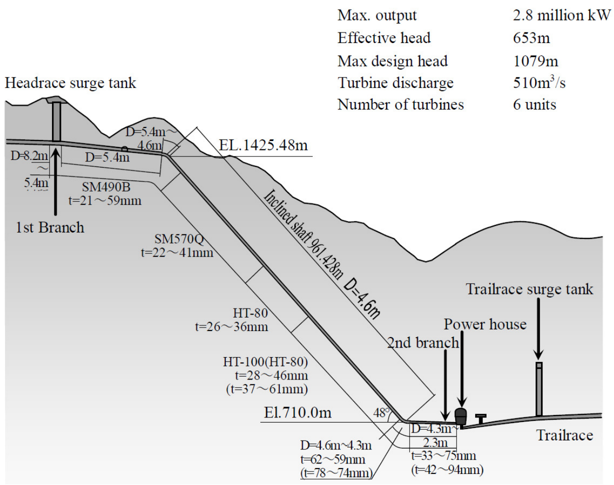


Figure 17. Overview of Kannagawa Power Plant penstock (Tokyo Electric Power Co.) [29].

The metallurgical effect of Nb on the ausformed martensite steels are illustrated in Figure 20. Nb addition to the steel expands the austenite un-recrystallized region, allows for the flattening the austenite grains, and thereby induces lattice defects inside the austenite grains. This austenite conditioning brings about the refined packet sizes in the transformed martensite during the accelerated cooling practice. The weldability of the TMCP HT950 steel was examined by the y-groove restraint-cracking test. The preheating temperature required to prevent cold cracking was 100ºC for SMAW and 75ºC for GMAW respectively. It should be noted that the HAZ toughness was good enough at –10ºC. Nb enhances the hardenability of steel in the HAZ but it goes along in the right direction for HT950 steels, assisting the martensite transformation. In addition, large heat input welding is not applied to HT950, so the HAZ toughness deterioration story by Nb does not hold for the HT950.

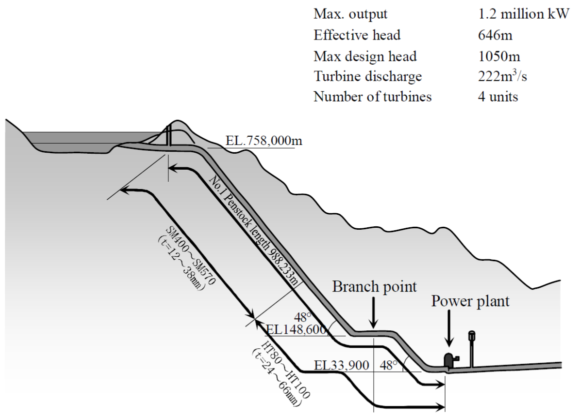


Figure 18. Overview of Omarugawa Power Plant penstock (Kyushu Electric Power Co.) [29].

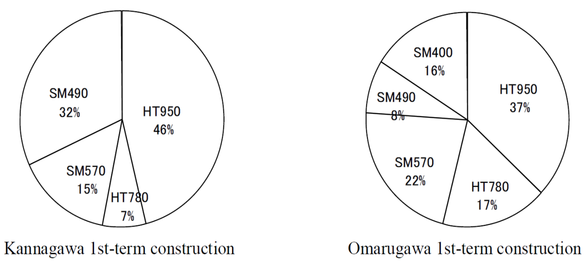


Figure 19. Configuration of materials utilized [29].

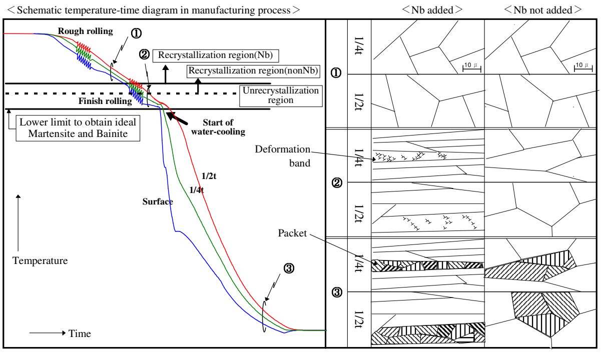


Figure 20 Enhancement of toughness by ausforming in austenite un-recrystallized region [28]

Towards Higher Safety - *Brittle Crack Arrestability (For Ships)*

In the ship building industries, the concept of arresting brittle cracks in steels has rightly received more emphasis than in the other steel structure's sectors. This originated from the famous Liberty ship accident during World War II [31]. Liberty ships were cargo ships built in the United States, constructed with welded steel sections. They were cheap and quick to build, necessary for the war effort, but early Liberty ships suffered hull and deck cracks. There were nearly 1,500 instances of significant brittle fractures. It is reported that twelve ships broke in half without warning but with a loud noise of explosion [31]. After World War II, the Charpy test requirement for ship steels was standardized based on the data analyzed for the fractured steel structures of the Liberty ships. At the same time, this accident stirred people to undertake research work in the area of brittle fracture. One outcome of this research was Figure 21, obtained by Machida, Aoki, et al. [32-33].

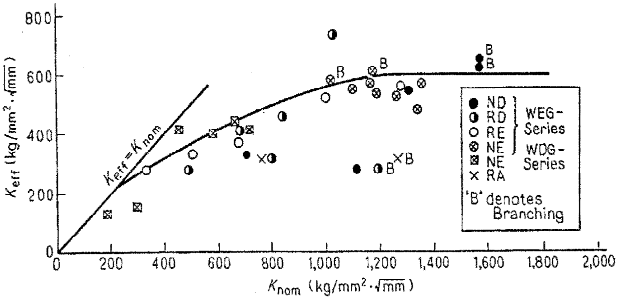


Figure 21. Relation between nominal K and K_{eff} [33].

Figure 21 demonstrates that if a steel plate had the K_{ca} value (stress intensity factor to arrest brittle crack propagation, obtained by ESSO test) of more than 6,000N/mm$^{3/2}$ (nearly equal to 600kg/mm$^2\sqrt{}$mm), any long propagating brittle crack can be arrested in the real steel structure. Since the publication of this research, the 6,000N/mm$^{3/2}$ in K_{ca} value had been the guideline for the crack arrester plate for the hull and deck. However, the recent growing constructions of larger container ships have caused a stir in the reasoning of Figure 21. This is because the experiments in Figure 21 had been done with steel plates of less than 30mm thickness, but the plate thickness of the recent large container ships easily reaches 80mm at the hatch and coaming portion. For the safety of the modern large container ships, the investigations on the brittle crack propagation behavior of heavy thick shipbuilding steel plates have started again in Japan lately. One of the objectives of these new investigations was to develop heavy steel plates that achieve one-step higher K_{ca} values.

It is well known that the K_{ca} property of steel plate is strongly dependent on the crystalline texture developed by controlled rolling in the plate, in addition to its dependence on the ferrite grain refinement. Figure 22 shows Ishikawa's double-tension tensile test result for structural steel plates [34]. Here, the temperature at which the K_{ca} value equals to 4,000N/mm$^{3/2}$ ($TK_{ca=4000}$) decreased significantly in the longitudinal stressed test with the development of the plate texture. This indicates that the K_{ca} value at a temperature above $TK_{ca=4000}$ would increase with developing the texture, in general. It was observed in the textured specimens that the brittle cracks propagated in an undulating manner, and the tear ridge thickness rose sharply with the crack extension. This is the evidence that the crystalline anisotropy created by the developed texture interrupts the straight propagation of brittle cracks.

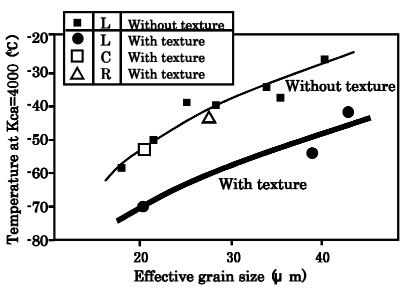


Figure 22. Relationship between effective grain size (cleavage facet size) vs. crack arrest toughness ($TK_{ca=4000}$) [34].

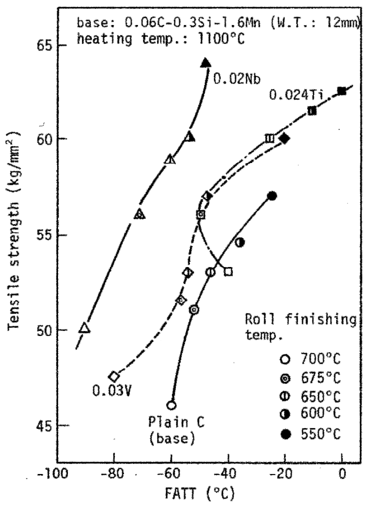


Figure 23. Comparison of effect of microalloying elements on strength and 2V Charpy FATT with hot rolling in (γ+α) region [14].

The texture that is effective to arrest brittle crack propagation develops predominantly with rolling the plate in the γ + α two-phase region. However, this rolling practice cannot be done effectively for plain carbon steels because the deformed austenite re-crystallizes easily; the deformed ferrite recovers quickly and sometimes re-crystallizes due to its high γ-α transformation temperature; consequently, the temporarily-developed texture recovers towards the random one before cooled down. On the other hand, Nb makes this controlled rolling in the γ + α region quite effective. The deformation slip bands in the austenite and ferrite grains are retained without recovery if the steel contains a small amount of Nb. Therefore, cumulative rolling strain retains the desired texture.

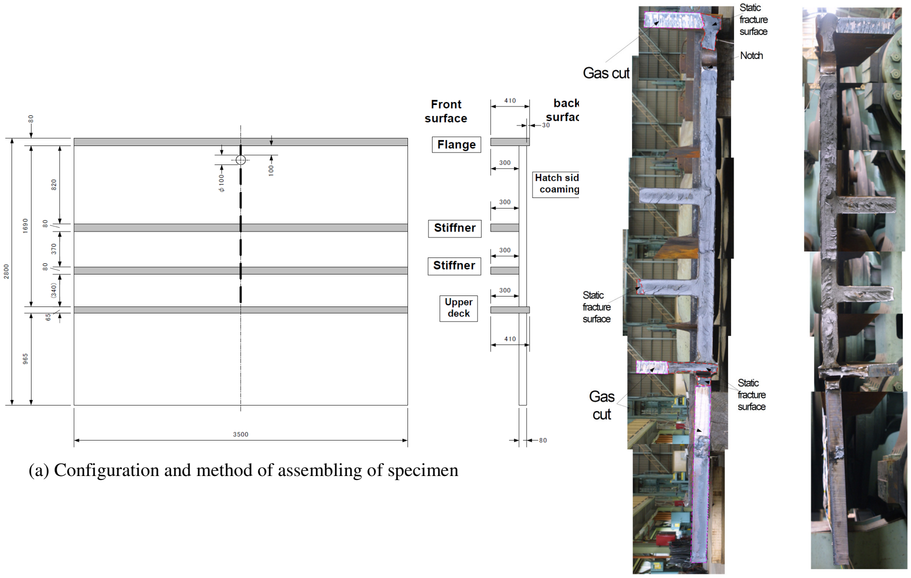
Figure 23 compares the effects of some microalloys on strength and Charpy transition temperature with rolling in the γ + α region [14]. The significant effect of Nb is again obvious in the rolling in the γ + α region, too. This shows that Nb can achieve both grain refinement and ferrite work hardening. The same mechanism by which Nb works in developing the texture.

The intentional texture control by the Nb-bearing TMCP has been applied to heavy thickness plates for the latest large container ships; here, the arrestability of brittle crack propagation has been examined for the developed 65mm thickness EH36 (355MPa in minimum yield strength with Charpy test requirement at –40ºC) steel plates [35]. This Nb-bearing steel was designed without nickel but it revealed that it had the K_{ca} value of more than 10,000N/mm$^{3/2}$ at –10ºC by the temperature-gradient type ESSO test. This K_{ca} value was much higher than the old guideline value of 6,000N/mm$^{3/2}$ for the thinner arrester plates in Figure 21. However, the brittle crack arrest had not been verified with this K_{ca} for 65mm thickness heavy plates yet; the required K_{eff}

value had been estimated to be around 7,000N/mm$^{3/2}$ for 65mm thickness, though [36]. So the mock-up type large brittle fracture test was carried out [37].

In this mock-up type fracture test, the worst case was assumed; namely, the long running crack initiated in the hatch side coaming was supposed to plunge into the upper deck plates. If this brittle crack propagated through the upper deck, then, that means, the container ship would break into half. In this experiment, the developed 65mm thick EH36 plate was put to the upper deck portion, and the conventional 80mm thick EH40 (390MPa in minimum yield strength) plate was used for the hatch side coaming and the other parts. Figure 24 shows the mock-up test specimen configuration and the fracture appearance after the test [37].

The fracture test was carried out under the applied stress of 257MPa and at –10ºC, using a 10,000tonf horizontal type tensile test machine. The uniformity of the applied stress was verified by the FEM analysis in advance (Figure 25). The specimen was kept for more than 1 hour at -10ºC except the top notch initiation part where the steel was rapidly cooled down to –140ºC locally for the brittle fracture initiation. Then the specimen was broken in a brittle manner. The measurement showed that the crack propagated at a speed between 500 and 1,500ms^{-1}. The running brittle crack was arrested in the upper deck just after plunging 5mm into the developed plate, as shown in the close-up photo of Figure 26.



(a) Configuration and method of assembling of specimen

(b) Appearance of fracture surface

Figure 24. Mock-up fracture test specimen and the result [37].

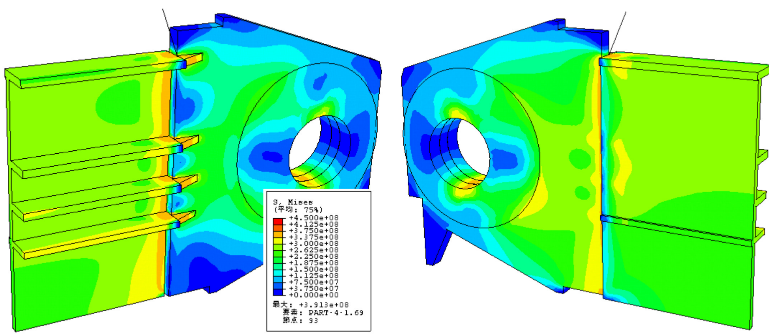


Figure 25. Final condition of joint of tab and specimen [37].

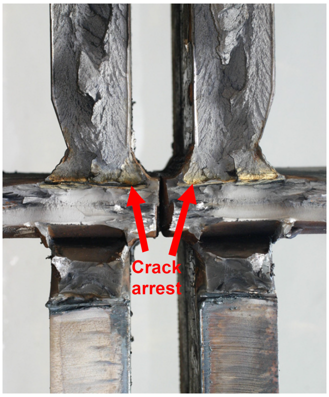


Figure 26. Close-up photo of fracture surface [37].

This mock-up fracture test demonstrated that the remarkable contribution of Nb to the construction of modern and safe container ships. However, it should be noted that the conventional steels used for the hatch side coaming portion in the test also contained Nb but the K_{ca} value of which was more or less 3,800N/mm$^{3/2}$ at –10ºC because the Nb in this steel was mainly used for increasing strength in its TMCP practice. So the important point in the application of Nb, like with all alloying elements, is that it exhibits the real practical value only when it is properly processed in the TMCP.

Toward Superior HAZ Toughness

Small Heat Input Welding (For Offshore Structures)

The most difficult design of Nb-bearing steels is for its application to the steel of low temperature service with superior HAZ toughness requirement. For these low temperature steels, the first priority is the superior low temperature toughness in the base metal with good weldability. So, the selection of Nb-bearing TMCP steel is the natural fit. However, if the requirement for the HAZ toughness is severe or large heat input welding is applied, then special care must be taken to mitigate any detrimental aspects of Nb at welding. The countermeasure to this varies with the applied heat input because the toughness controlling factors changes with weld heat input [13]. When the heat input is small, the formation of the M-A constituent is the main culprit of the toughness deterioration, but when the heat input becomes very large, the microstructure itself that is derived through the transformation from the large austenite grain is the main factor to be controlled. First of all, the case of low temperature steels fabricated with low heat input welding is considered.

Steel plates for offshore structures is a typical example, for which the superior HAZ CTOD toughness shall be verified by prequalification testing in accordance with API RP 2Z [38] or EN 10225 [39], as well as the high base metal toughness. This toughness requirement for the HAZ is the severest one among the current material standards for carbon steel plates. Generally, the required CTOD test temperature is 0ºC to –10ºC, but it goes down to –40ºC for the Sakhalin projects, and –60ºC for the latest arctic development projects. Needless to say, the Nb-bearing TMCP steel is the appropriate selection for these heavy plates, but an additional technology that can keep the high and stable HAZ toughness makes a difference.

In the qualification testing according to the API RP 2Z, the weld heat input shall encompass at least 0.8 to 4.5kJ/mm. This minimum heat input of being equal to or less than 0.8 kJ/mm is a very small one for heavy plates, where the local brittle zone caused by the formation of the M-A becomes the main issue to be overcome for the better HAZ toughness. As was discussed, under certain circumstances, Nb in solid solution enhances the formation of M-A. Therefore to mitigate any likely effects, some countermeasures have been developed so far; although the sheer essences of those technologies have not been fully disclosed. Nevertheless, the most conventional method is to suppress the austenite grain growth in the HAZ. This will decrease the hardenability of the steel and suppress the M-A formation through enhanced ferrite transformation. The technology of dispersing small TiN particles has also been applied in the plate production, but other countermeasures have also been devised such as the use of low-aluminum chemistry. The concept was based on experimental evidence that reducing the aluminum content in steel accelerates carbon diffusion in steel. If so, it would reduce the retained austenite and help the M-A decompose.

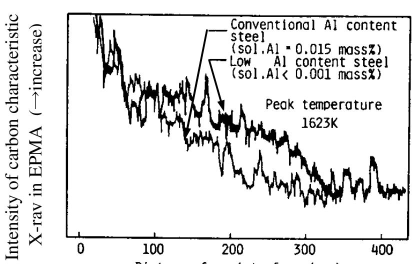


Figure 27. Carbon profiles adjacent to interface between carbon-powder and steel [40].

Fukada and Komizo [40] prepared small dilatometry specimens filled with graphite powder at the centre of the specimens, then rapidly heated to 1,350ºC in vacuum and cooled them down. They observed that carbon diffused farther inside from the surface for the low-aluminum steel than for the conventional-aluminum steel. Figure 27 is the observed carbon profiles of EPMA from the surface for these two steels. The result shows the difference in the rate of carbon diffusion between low-aluminum and conventional-aluminum.

The high quality heavy plates for offshore structures were developed based on this concept and were first applied to the SHELL MARS Tension Leg Platform (TLP) in 1994 [41]. The developed low-aluminum-Nb steels revealed very low Charpy transition temperatures for 4" thick 345MPa yield strength (YS) grade steel and 3" thick 414MPa YS grade steel. The production history for the MARS deck steel order showed that the shear area percentages in transverse mid-thickness Charpy impact test at –80ºC of all steel plates were more than 50% with their absorbed energy range of 130-460 Joule [41]. This level of low temperature toughness can only be achieved by the Nb-bearing TMCP technology for low carbon low alloy heavy plates.

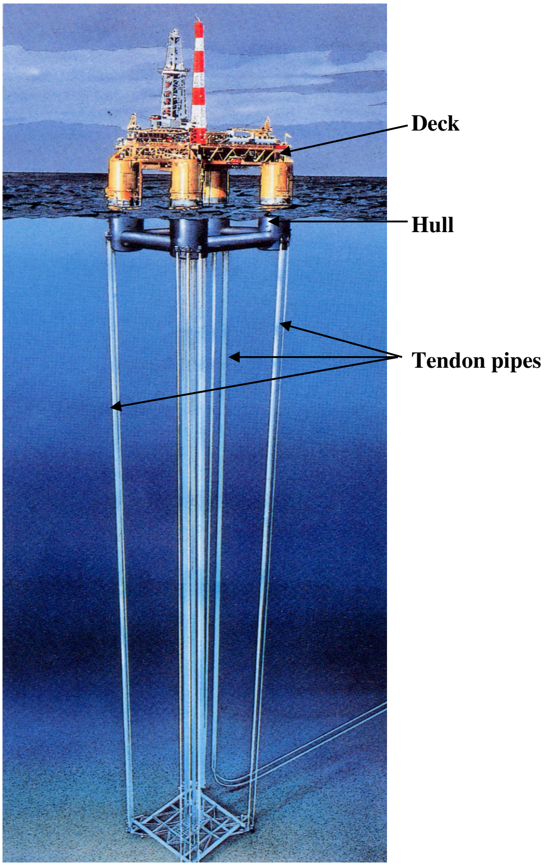


Figure 28. Structure of a Tendon Leg Platform (TLP).

Figure 29 shows the prequalification HAZ CTOD test result for 3" thick 414MPa YS plate. The high CTOD values at –10ºC were verified for the welded joint test of different heat inputs.

Since the MARS projects, the low aluminum-Nb TMCP steels have been applied for most of the modern TLP's. Figure 30 is the world TLP construction record as of March 2006. The nine numbered large TLP's adopted the developed steel plates for their deck and/or hull portion.

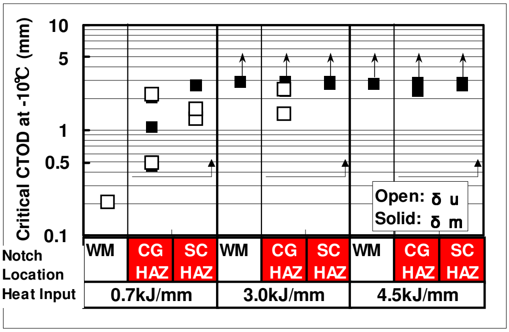


Figure 29. HAZ CTOD test result for 3" 414MPa YS steel plate in the MARS prequalification test.

As well as the deck and hull plates, the UOE formed pipes of the same chemical design basis were applied to the tendon portions (Figure 28.) First, those pipes were developed for CONOCO Julliet Tension Leg Well Platform (TLWP) in 1987 [42], followed by the SHELL Auger TLP in 1994 [43], and then applied, as the tendon pipes, to the same TLP's that were numbered in Figure 30.

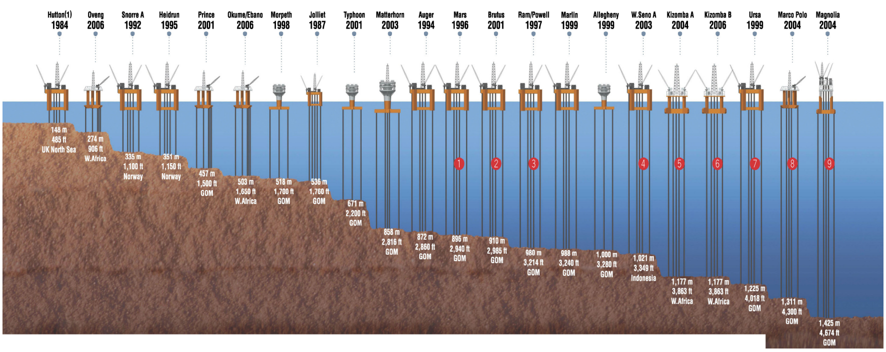
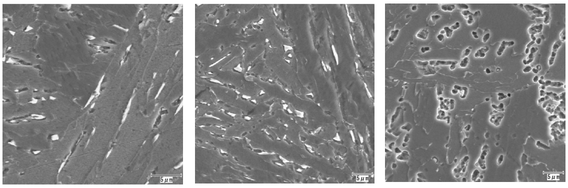


Figure 30. TLP- sanction, installed or operating in the world (As of March 2006)

Large Heat Input Welding (For Ships)

When welding heat input increases, the role of the M-A disappears because it is unlikely to form with such a slow cooling rate. Figure 31 shows the observational results of M-A after welding simulation tests of different heat inputs [13], where the M-A was revealed by the two-step electro-polishing technique [44]. From this observation, the M-A could not be distinguished for the 60kJ/mm high heat input welding. The influence of austenite grain growth on the HAZ toughness also diminished with increasing heat input [45]. When the heat input increases, the HAZ microstructure itself becomes the dominant factor to control the toughness.



C	Si	Mn	Cu	Ni	Nb	Ti	Ceq
0.07	**0.22**	**1.40**	**0.22**	**0.36**	**0.015**	**0.018**	**0.35**

Figure 31. Observation of M-A constituent for different heat input thermal cycles [45].

If the nucleation of intra-granular ferrite is enhanced, the toughness generally improves. The one way to increase intra-granular ferrite nucleation is to disperse small oxides in steel. The oxides are so stable that even in the severe welding thermal history they could be effective for ferrite nucleation, if they are present as small particles. In the past, REM oxides [46] and Ti-oxides [47] have been utilized for this purpose. However, if boron is utilized with the optimized microalloys, the intra-granular ferrite transformation can be also enhanced [48]. Boron diffuses very fast in steel like carbon and nitrogen, but the ability to form its carbide or nitride is not so strong. So the solute boron diffuses to the austenite grain boundaries and segregates there. This results in reduction of the interfacial energy of the austenite, and suppresses the ferrite nucleation from the austenite grain boundaries; and consequently, it would indirectly enhance the formation of the intra-granular ferrite. In the case of the microalloy-carbonitrides, they precipitate on the austenite grain boundaries but they easily grow at the very slow cooling rates of large heat input welding. So they do not contribute much to decrease the grain boundary energy.

Nb is vital in decreasing carbon/carbon equivalent for the low temperature steels, but the amount of it must be judiciously applied for large heat input welding applications. Table 2 shows the chemical composition of the boron-based steel for LPG carriers. This steel contains no alloys other than Nb, Ti, and boron, thanks to the thermomechanical effect by Nb it can achieve the superior toughness both in the base metal and in the HAZ at the LPG storage temperature.

Figure 32 is the HAZ Charpy absorbed energy at –51ºC of this steel for two kinds of single-pass welds. The Charpy absorbed energy values were high and stable in the HAZ. Many LPG carriers have been successfully constructed by the uses of such economical steel plates.

Table 2. Chemical composition of boron-Nb type steel for large heat input application.

C	Si	Mn	Nb	Ti	B	Ceq	Pcm
0.06	0.13	1.41	0.012	0.011	0.0010	0.30	0.14

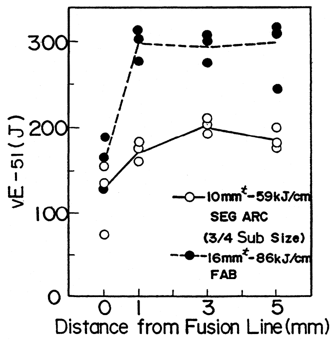


Figure 32. Charpy absorbed energy in the HAZ of high heat input single-pass welds of the boron-Nb type steel [48].

Summary and Conclusions

Today as nearly half of the steel plates produced in Japan utilize Nb as an alloying element, a review has been presented on the role and application of Nb for the production of steel plates. The superb advantage of Nb lies in its significant strengthening effect without sacrificing weldability.

In this paper, structural steels were focused on as its application fields. Different from line pipe steels, the structural steels take the toughness of the weldment into due consideration when designing Nb in the steels because they are fabricated with high heat input welding or with PWHT, where there is a greater risk to deteriorate toughness. The state-of-the-art technologies to overcome this disadvantage were introduced in addition to the excellent advantages of Nb to the base metal properties.

The austenite conditioning by Nb was lately expanded to bainite and martensite microstructures. The applications to these high strength microstructures have made it possible to construct enormous huge steel structures. On the other hand, the full utilization of Nb for the controlled rolling in the $\gamma + \alpha$ region has brought about the development of the safest steel plates for modern large containers. These brilliant evolutions of Nb-bearing steels owe the consecutive developments in the Nb metallurgy that has been undertaken by many researchers concerned with Nb and steel.

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