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Steels for Energy Production and Transport

Ryuji UEMORI*
Takuya HARA
Yasuhiro SHINOHARA
Hitoshi FURUYA
Yasushi HASEGAWA
Takehiro INOUE
Hiroshige INOUE

1. Introduction

This technical review describes the development of steels used in the energy industry. Since this particular field covers a wide area, we shall focus here the development of steels to exploit fossil energy and as applied to power generation. The recent trends in the development of steels for wind power generation—one of the new energies—are described briefly. At the end of the review, we offer our prediction for the future of steels for energy industries.

2. Activities to Develop Steel Materials Used in the Energy Industry

2.1 Steel trends for exploitation of energy

Oil, coal and natural gas, which are fossil fuels, account for the great majority of energy resources. Therefore, it is extremely important to produce and transport them at reasonable cost. In particular, high-performance steels are indispensable for the production and transportation of crude oil and natural gas.

Steel pipes for oil wells are used to extract crude oil and gas from underground oil-rich strata (both oil and gas wells are referred to as oil wells hereafter). Steel pipes for oil wells are used under severe conditions—in particularly deep oilfields, this can mean 10,000 meters underground, in oilfields exposed to high temperatures, high pressures and acidic gases (corrosive atmosphere), in offshore oilfields several thousand meters below the surface of the sea, or in horizontal wells contorted with many sharp bends. Therefore, various types of steel pipes for oil wells which afford superior strength, collapse resistance, sour resistance and corrosion resistance, have been developed and applied. In addition, to develop undersea oilfields, an offshore structure (e.g. platform) is constructed. Since offshore structures process flammable substances, they are required to have a high degree of safety. For those structures, steel plate with high heat-affected zone (HAZ) toughness is applied. In recent years, many oilfields are being developed nearer or in the Polar Regions and hence, the development of new steels for offshore structures with excellent low-temperature toughness has been actively pressing ahead.

Line pipe is used for pipelines to transport crude oil and gas extracted from the oilfields. The eventual user of these resources may be thousands of kilometers away from the production site. Furthermore, globally, ninety percent of natural gas is transported by pipelines. Therefore, it is important to ensure stable supply of line pipes which have the potential to reduce transportation costs. To that end, steels for line pipe which can be used under severe conditions—for high-pressure transportation, in deep seas, in a wet hydrogen sulfide atmosphere—have been developed and manufactured. In Japan, however, natural gas has so far been imported in the form of liquefied natural gas (LNG) because of the convenience of transportation by sea. The amount of natural gas transported in a liquefied state is increasing on a global basis. Special steels for LNG tanks are applied in this particular exploitation. Of these, 9%Ni steel, which has high toughness even at extremely low temperatures, is widely employed. Recently, activities to further enhance the performance of 9%Ni steel and reduce the addition of Ni, which is an expensive alloying element, have been pursued.

In industries such as thermal, nuclear and hydroelectric power generation, positive efforts have also been made to enhance the performance of steels. They include the development of new steels with superior high-temperature strength, new corrosion-resistant steels for boilers that use heavy oil or biomass as their fuel, and the study of thicker heavy-section steels with greater strength and toughness which allow for an increase in the hydroelectric power generating capacity of dams.

2.2 Development of products

2.2.1 High-performance steel pipe

(1) Oil country tubular goods (OCTG)

As OCTG, seamless steel pipe and electric resistance-welded (ERW) steel pipe 2-3/8 to 20 inches in diameter are used. Aiming for a high degree of safety under severe working conditions, new products with high strength and good corrosion resistance, including threaded joints, have been developed. As seamless steel pipes, Nippon Steel Corporation has developed a number of environment-friendly, high-performance products, including high-strength, sour-resistant steel pipe,[1] corrosion-resistant 13Cr OCTG,[2] high-torque, gastight threaded joints,[3] and dope-free threaded joints friendly to the environment.[4] As ERW steel pipes, the company has been pressing ahead with the development of collapse-resistant products taking advantage of its thermo-mechanical control process (TMCP) technology in hot-rolling and ERW process control technology. Since the company ended production of seamless steel pipes for export in 2001, it has been active in the development, production, and marketing of new ERW steel pipes on a priority basis. Concerning high-strength steel pipes, it has become possible to manufacture products up to C95 grade.

As an example of functional enhancement, steel pipe capable of

* General Manager, Dr.Eng., Plate, Pipe, Tube & Shape Research Lab., Steel Research Laboratories
20-1, Shintomi, Futtsu, Chiba 293-8511

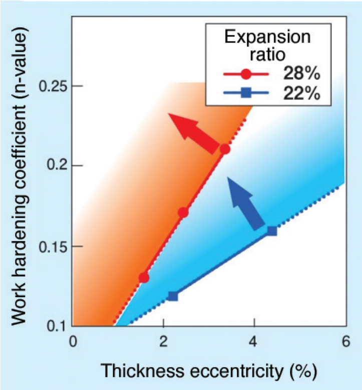


Fig. 1 Design diagram of the thickness eccentricity and work-hardening coefficient for expandable tubular (22% the current maximum expansion rate, 26% the maximum expansion rate in future)

Fig. 3 View of field construction of X120 line pipe

withstanding pipe-expanding work in the oil well (expandable tubular) can be cited. With excavation technology using this steel pipe, it is possible to cut excavation costs significantly and allow more freedom in oil-well design. Therefore, the scope of its application is expected to expand in the future. As shown in **Fig. 1**, the smaller the wall thickness eccentricity (the higher the wall thickness uniformity) and the larger the n-value (work-hardening coefficient) of the material, the higher the pipe expansion rate can be made.[5] Taking advantage of the small wall thickness eccentricity of ERW steel pipe, Nippon Steel has developed and manufactures expandable steel pipe for oil wells incorporating the company's advanced materials technology. In addition, the company has proposed a solution including a technique to predict the collapse characteristic of steel pipe after pipe expansion,[6] and is striving to promote the sales of its expandable steel pipe for oil wells.

(2) UOE line pipe

(i) Line pipe for high-pressure transportation

Since the volume of gas transported by a pipeline can be increased by raising the internal operating pressure of the pipeline, it is common practice to transport gas at high pressure. In order to implement high-pressure transportation, increasing the wall thickness and strength of the steel pipe used is effective. Ultra-high-strength line pipe, such as API (American Petroleum Institute) X120/X100, or ultra-heavy line pipe, such as API X80, meets such needs. **Fig. 2** shows how the properties required of line pipe have changed so far. In addition to high strength and ultra-low-temperature toughness, composite properties are required of line pipe. X120 is an ultrahigh-strength line pipe developed by Nippon Steel through joint research (1995-2005) with ExxonMobil, the world's largest oil company. In 2007, it was registered in the API Standard. In order to create the X120 equipped with both the required low-temperature toughness and good field weldability at reasonable cost without sacrificing the as-TMCP strength, the company adopted a low-carbon bainitic structure with boron added. The addition of boron significantly improves the hardenability of steel, making it possible to obtain high steel strength with a comparatively small amount of alloying element. On the other hand, manufacturing X120 by TMCP on a stable basis requires a high level of technology. In particular, the addition of boron to line pipe was limited by the above standard because it would impair the field weldability of the pipe. Thus, there was a major obstacle to practical application of the low-carbon bainitic structure with boron added.

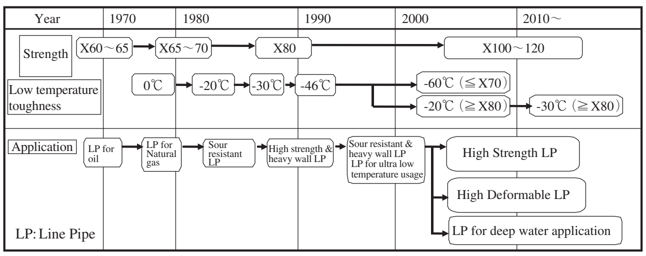


Fig. 2 Changes in line pipe property requirements

Accordingly, Nippon Steel established a technique to add boron on a stable basis by taking advantage of its analytical technology. Eventually, it was approved by ExxonMobil and the B-added steel was adopted.[7] The development of X120 was a major project that called for extensive R&D on UOE forming and seam welding, too.[8] Ultimately, following a small-volume commercial production test, ExxonMobil laid out an experimental X120 pipeline over a distance of 1.6 km in northern Canada during the severe winter of 2004 (**Fig. 3**). During that time, X120 proved to be comparable to conventional API grades in terms of efficiency of pipe laying and the quality of welds. That experimental X120 line pipe is still used as part of the pipeline. X100 was originally developed as a high-strength line pipe.[9, 10] Ultimately, it was completed as a high-deformability line pipe applicable to strain-designed pipelines.[11] Nippon Steel applied its high-precision cooling technology to the continuous on-line control process- μ (CLC- μ) to control the steel's structure, thereby achieving high strength and good deformability. X100 was adopted for part (5-km section) of a pipeline constructed in Canada in 2007.

X80, an ultra-heavy line pipe, hardly has the high-speed ductile fracture-arrest capability that is indispensable for line pipe. Nippon Steel developed an X80 line pipe 56 inches in diameter with 27.7-mm thick walls by optimizing the steel's chemical composition and TMCP conditions and utilizing high-precision cooling in CLC- μ.[12] In a full-scale burst test carried out in Russia, the X80 line pipe proved to be capable of arresting a high-speed ductile crack in a short distance (within 12 m).

(ii) Deep-water line pipe

For pipelines laid in the Gulf of Mexico, the Black Sea, and the Mediterranean, etc. at depths exceeding 2,000 m, collapse resistance is an important factor in its design. Large-diameter line pipes can hardly be subjected to collapse tests. Therefore, it was common practice to estimate the collapse resistance of such a line pipe from the results of a small-scale collapse test. However, the prediction accuracy using that method was insufficient. Accordingly, Nippon Steel established a technique to accurately estimate the collapse value from a small test using a large-scale collapse test and finite element analysis (FEA)[13]. For the development of new materials, the company offered a design technique that utilizes strain aging more positively with the addition of molybdenum and low stop-cooling temperature in the TMCP. Using that technique, the company developed a line pipe with good collapse strength, which was applied in the MEDGAZ Project (Algeria to Spain).

(iii) Sour-resistant line pipe

Hydrogen-induced cracking (HIC) can occur with pipelines used to transport fluids containing wet hydrogen sulfide (sour) gas. Sour-resistant line pipe which restrains the occurrence of HIC requires a steel plate which is made from high-quality, continuously cast slab, and whose structure is suitably controlled by TMCP. Nippon Steel has developed a technology to restrain the occurrence of elongated sulfides, which can initiate cracks for HIC, by controlling the sulfur concentration to within 10 ppm, and to control the forming of sulfides and reduce their precipitation by adding calcium.[14] Thus, the manufacturing of sour-resistant line pipe has advanced steelmaking technology markedly in terms of the control of nonmetallic inclusions and center segregations. Today it is possible to manufacture sour-resistant UOE line pipes of API grades up to X70. Concerning ERW steel pipe too, API grade X65 for sour-resistant undersea pipelines, which require exceptionally high quality, is manufactured.

(iv) Line pipe for strain-based design

In areas which contain discontinuous permafrost or which are susceptible to landslides and faults, etc., pipelines are subject to plastic deformation. Therefore, it is necessary that the pipeline should be designed so as to restrain any fracturing of circumferential welds and buckling of the pipe body. Design of such pipelines is called strain-based design (SBD), and this must ensure that neither fractures from the welds nor buckling of the pipe body occurs up to the required strain decided for each individual project. The important point in designing to prevent fractures from circumferential welds is overmatching the strength of the circumferential weld metal and the longitudinal strength of the steel pipe. Ordinarily, steel pipe is subjected to thermal coating for corrosion prevention. Therefore, it is necessary to restrain the increase in steel pipe strength due to strain aging. The low limit for steel pipe strength is the minimum strength of the required grade, and the high limit for steel pipe strength must be lower than the minimum strength of the weld metal used in the field. Therefore, a steel pipe manufacturing process that allows for a narrow range of strength must be worked out.

On the other hand, in order to enhance the buckling resistance of steel pipe under flexural deformation, it is indispensable to improve the uniformity of elongation and lower the yield to tensile ratio of steel pipe.[15] In order to secure high deformability of steel pipe, Nippon Steel applied a composite steel structure of ferrite (soft structure) with good work hardenability and bainite (hard structure).[16] In addition, with the aim of assuring low-temperature toughness at −40 ℃, the company developed a high-deformability steel pipe for ultralow temperature service ("Super Tough-Ace") with a fine composite structure having an average grain size of 5 μm or less (ASTM method) as its base, since high deformability of steel pipe is demanded most strongly in extremely cold regions.[17, 18] For the Super Tough-Ace steel pipes, manufacturing technology has been established for API grades X60 to X100. For example, the company has developed a steel pipe of X60 grade which has a yield to tensile ratio of 88% or less and a uniform elongation of 8% or more and which guarantees low-temperature toughness at −40℃. 17,000 tons of steel pipe of this grade were manufactured for Russia in 2009.[17] In addition, X100 high-deformability steel pipe for low-temperature service was laid over a distance of five km in Canada.[11]

There is no doubt that pipeline to transport natural gas will continue increasing in length. Accordingly, better composite properties, such as higher toughness and deformability, will be required of line pipes. Accordingly, it is considered that the Super Tough-Ace steel pipe will be demanded in large quantities in the future and that its application will contribute to stable supplies of natural gas.

(3) Pipe-forming and solution technology

With the increased strength and wall thickness of materials, there are cases in which conventional pipe-forming technology can hardly be applied in terms of forming capacity or product shape. As a result, it has become necessary to develop new pipe-forming technology and introduce new forming indexes. In addition, it is necessary to evaluate marginal service performance of steel pipe so as to supply reliable products.

Manufacturing a high-strength line pipe (e.g., X120) using the UOE process involves a number of problems, such as cracking during pipe expansion, a geometric imperfection caused by excessive spring-back, and insufficient bending at the plate edge (for pipes with thick walls). In order to resolve such problems, Nippon Steel optimized the pipe-forming conditions on the basis of the results of a numerical analysis for accurate spring-back predictions and an experimental simulation in the laboratory (**Fig. 4**)[19] and thereby, it has established a technology for the stable supply of high-strength line pipes.

As one solution technique, for deep-water line pipe, which is required to have high collapse resistance, the company derived an equation to evaluate the collapse strength taking into consideration the Bauschinger effect in cold forming. In addition, for line pipes for strain-based design which are laid in discontinuous permafrost and which require resistance to bend buckling, the company built a numerical analysis technique that takes the orthogonal anisotropy of the steel pipe into account. The technique has contributed to improved reliability of strain-based design.

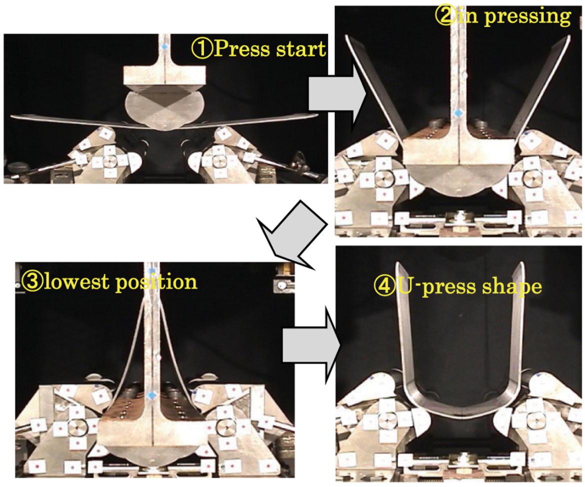


Fig. 4 Experimental simulation in U-press (X120)

2.2.2 High-performance steel plate

(1) High-strength, high-toughness steel for offshore structures

Offshore structures relating to oil/natural gas can be classified according to the purpose (excavation, production) and the water depth and other conditions of the marine area in which they are installed. Namely, they are divided into three types: stationary (e.g., jacket platforms (**Fig. 5**) and jack-up rigs) used in depths up to about 300 m; floating (e.g., semi-submersible platforms and tension leg platforms (TLP)) used in deep-sea areas exceeding 1,000 m in depth; and a flexible type that falls between the two aforementioned types. In almost all offshore structures, steel plate plays an important role. Characteristically, many steel plates for offshore structures are stronger and thicker than steel plates for shipbuilding.

In recent years, more and more offshore structures have been built in deeper seas and colder regions. Accordingly, higher quality and superior performance are required of steel plates for offshore structures ("offshore structural steel"). In particular, since the calamitous overturn of the Alexander Kielland in the North Sea in 1980, preventing fractures became a significant issue. Eventually, the crack tip opening displacement (CTOD) test—a fracture toughness evaluation technique based on fracture mechanics—was applied in earnest as an index to evaluate offshore structural steel. Conventional offshore structural steels manufactured by normalizing could hardly meet the CTOD criterion. Accordingly, attempts were made to apply the TMCP that had been actively developed by Japan's major steelmakers in those days. Nippon Steel studied not only how to optimize the TMCP, but also the entire plate manufacturing process from casting and reheating to rolling and water-cooling and then tempering under the concept of integrated process metallurgy. As a result, the company succeeded in developing a CTOD-guaranteed YP 350 steel applying TMCP for the first time in the world. The steel was used for the Oseberg-I offshore structure in 1984.

In addition, in response to the ever-growing demand for higher-strength steel plates with the expanded scale of offshore structures and increased drilling depths in the background, Nippon Steel supplied YP 420 Steel to the Draugen project in the North Sea in 1990,[20] YP 460 Steel to the Bayu Undan project in the Timor Sea in 2000, and YP 500 Steel to the Grane project in the North Sea in 2000,[21] all ahead of other steelmakers in the world. Furthermore, as a material for the rack applied to the legs—the most important member of a jack-up rig for oil drilling, the company successfully developed an ultra-heavy, high-strength 210-mm-thick steel plate, the world's thickest plate for racks, achieving the Charpy impact energy requirement of 800-N/mm^2 class at −60℃.[22]

Fig. 5 Stationary platform made of steel plates for offshore structures

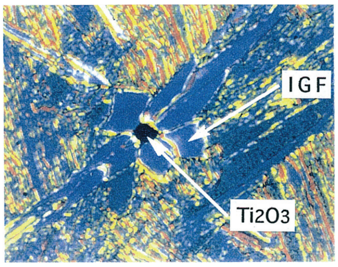


Fig. 6 Example of the intragranular ferrite formed from a titanium oxide

As mentioned above, more and more offshore structural steels of higher strength have been developed. On the other hand, the development of marine resources in icy seas around the Arctic Ocean, where some thirty percent of the world's undiscovered gas resources are thought to exist, has become active. As a result, it became necessary for Nippon Steel to develop new steels that display good properties even at extremely low temperatures. The temperature used for CTOD evaluation is generally −10℃. For steel materials to be used in the Polar Regions, however, the CTOD criterion is much more severe, that is, −40℃ to −60℃. Since the CTOD value is governed by locally embrittled regions, it is extremely important to prevent any deterioration in the toughness of the heat-affected zone (HAZ) by properly controlling the microstructure of steel. Throughout the development of new offshore structural steels, Nippon Steel conducted an important study on the improvement of low-temperature toughness of HAZ.

In the 1970s, Nippon Steel studied technology that utilized TiN in its offshore structural steels.[23] In the 1980s, the company put into practice a TiO steel for offshore structures.[24] In the TiO steel, the structure is refined as a large proportion of intragranular ferrite (IGF) is formed from a titanium oxide that is stable at high temperatures and which is present in γ grains (**Fig. 6**). As a result, good CTOD values were obtained on a stable basis. From the standpoint of improving the low-temperature toughness of steel, it is important to control the martensite-austenite constituent (M-A). In this respect, the mechanisms of M-A formation and the basic concept of the effect of alloying elements on HAZ toughness have been clarified.[25] In the 1990s, taking advantage of those HAZ toughness control techniques, Nippon Steel succeeded in developing YP 350 Steel and YP 420 Steel,[26,27] both CTOD-guaranteed at −50℃. Recently, an improved version of TiO steel with a reinforced HAZ structure was put to practical use. It was developed in 2004 as a −40℃ CTOD-guaranteed joint steel of YP 355-N/mm^2 class for a project in the northern Caspian Sea. It is expected that in the future the application of the steel will expand as a thick, high-strength offshore structural steel that is capable of ensuring good toughness even under extremely severe conditions, such as the demand for guaranteed CTOD in icy seas.

(2) Low-temperature steel for LNG tank

The steel material for the inner tank of an LNG (liquefied natural gas) tank is required to have fracture resistance at low temperatures down to −160℃. In the 1940s when the world's first LNG tanks were constructed and put into service, the technology for preventing brittle fractures based on fracture mechanics was not completely reliable. For example, for the world's first LNG tank that was constructed in Cleveland, U.S.A., 3.5%Ni steel was used. Eventually, the LNG tank fractured, leading to a massive fire.[28,29] After that disaster, in 1946, International Nickel Co. developed a 9%Ni steel.[30, 31] This steel rapidly became widespread once U.S. Steel, INCO and Chicago Bridge & Iron Co. proved through their extensive fracture tests (“operation cryogenics” in 1960)[32] that the steel did not require stress-relieving annealing.

In Japan, Nippon Steel began fundamental research into 9%Ni steel early on. As a result, in 1969, 9%Ni steel manufactured by the then Yawata Iron & Steel Co., Ltd. was used for the first time for an LNG tank at the Negishi plant of Tokyo Gas Co. In the 1970s, the safety of 9%Ni steel came to be suspected in the wake of a series of large-scale fractures of LPG tanks. In order to dispel that suspicion, various large-scale fracture tests were carried out. In the 1980s, it was proved that 9%Ni steel had sufficient brittle fracture resistance and crack propagation arrest performance as a steel material for LNG tanks.[33-35]

Since Japan’s first LNG tank (capacity: 45,000 kl) was constructed in 1969, tank capacity has continually expanded. Today, LNG tanks with capacities up to 180,000 kl are manufactured. Accordingly, the maximum thickness of steel plate used has changed from 20 mm for a 45,000-kl tank to 30 mm for an 80,000-kl tank, then to 40 mm for a 140,000-kl tank, and now to some 50 mm for a 180,000-kl tank. In order to respond to this steady increase in steel thickness, Nippon Steel developed a new 9%Ni steel,[36] applying the dual-phase heat treatment (L-treatment) [37, 38] described later. In addition, for thick, very tough steels, the company developed Super 9%Ni Steel (9%Ni steel containing less Si and with Mo added) with the L-treatment applied.[39]

The L-treatment is a dual-phase heat treatment performed between the conventional quenching and tempering processes as shown in **Fig. 7**.[36-38] This technology enables the steel’s toughness to be improved by refining the steel structure and forming stable austenite. With this technology, it is possible to reduce the consumption of nickel, which is an expensive alloying element. In the 1970s, Nippon Steel developed a 5.5%Ni steel (N-TUF CR196) using this technology.[40] N-TUF CR196 was a radical Ni steel in that it reduced the Ni content to 5.5% while offering good base metal/weld properties comparable to those of 9%Ni steel through the addition of appropriate amounts of chromium and molybdenum. Although N-TUF CR196 was used for ethylene tanks, etc., it was not employed for LNG tanks owing, at least in part, to the fact that the reliability of even 9%Ni steel was not completely verified in those days. Eventually, in 2008, the company resumed the development of low nickel steels. Recently, it has created a 6%Ni steel applicable even to large-scale LNG tanks by applying the TMCP and L-treatment.[41] The new 6%Ni steel is expected to be put to practical use in the near future.

2.2.3 Steel for power generation

(1) Steels for power plants (steel pipe and steel plate)

In the field of steels for power generation, there is brisk demand for heat-resistant steels with high-temperature creep strength which are mainly used for fossil fuel-fired power plants. Since 1990, in particular, there has been a growing need for steel piping and its members for use under “ultra-supercritical pressure” conditions—with the turbine inlet steam temperature at 600℃ to 610℃ and steam pressure of 250 N/mm^2 to 300 N/mm^2—so as to enhance the efficiency of power generation. The other properties required of heat-resistant steel include a low thermal expansion coefficient and resistance to steam oxidization. As a creep-resistant ferritic steel with all those composite properties, Oak Ridge National Laboratory developed around 1985 a new steel that contained 9% or more chromium and had good high-temperature durability achieved by controlled dispersion of a fine carbide or nitride which is stable at high temperatures. That was a 9Cr-1Mo-Nb-V-N steel (ASME Gr. 91, intended maximum service temperature: 593℃). Through study on the mechanisms to improve the high-temperature strength of that steel,[42] Nippon Steel clarified the alloy design concept of creep-resistant characteristics. On the basis of an extension of that design concept, the company and the University of Tokyo co-developed a new heat-resistant steel with tungsten and boron added, that is, 9Cr-1.8W-0.5Mo-Nb-V-N-B steel (Gr. 92, intended maximum service temperature: 610℃).

During the period 1995 to 2000, through a domestic project (Joint Research Phase II with Electric Power Development Co.) and international joint research with the Electric Power Research Institute (EPRI) of the United States, Nippon Steel pressed ahead with standardization of the above steel and testing of a boiler made from it (in Denmark). Eventually, the steel was applied to domestic plants (Tachibanawan Nos. 1 and 2 in Shikoku). As shown in **Fig. 8**, the creep rupture strength of the steel exceeds 100 N/mm^2 at 600℃ for 100,000 hours of service. As one of the heat-resistant ferritic steels for industrial use, the steel boasts the world’s highest creep rupture strength.[43] In addition, for superheaters that are exposed to higher temperatures, the company has developed heat-resistant austenitic steels, 22.5Cr-20Ni-1.5Mo-Nb-N (TP310MoCbN) and 18Cr-9Ni-2W-Nb-V-N (TP347W), which have been applied at home and abroad. In the future, Nippon Steel intends not only to expand the application

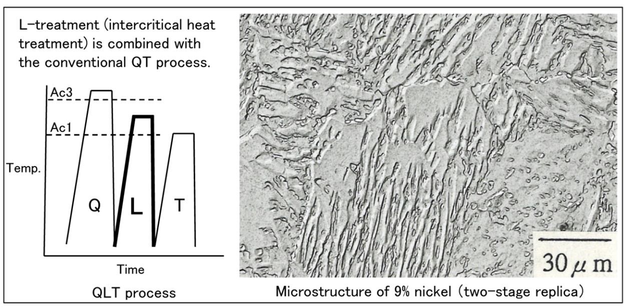


Fig. 7 Schematic illustration of QLT-process and microstructure of 9% nickel steel manufactured by QLT-process[36]

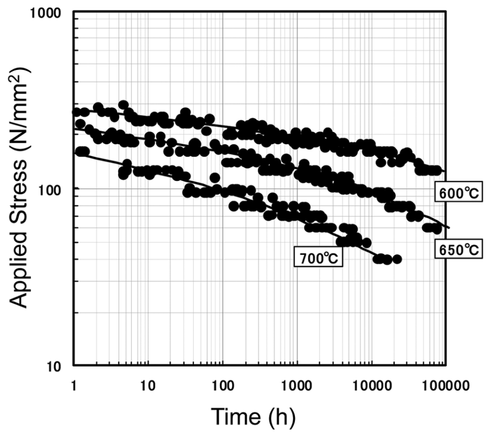


Fig. 8 Creep rupture curves of the ASME Gr.92 steel

scope of the above steel grades, but also to concentrate on the development of new steel materials with superior high-temperature creep strength that help to reduce CO_2 emissions from thermal power plants and enhance the efficiency of those plants.

(2) Steel for oil refineries

At petrochemical plants that refine and process crude oil into various types of petroleum products, the operating temperature of the desulfurization reactor, which becomes especially high, has become an environmental issue. Accordingly, more and more larger reactors with thicker walls have been constructed since the 1990s. Since there is a certain limit to the maximum thickness of steel that can be fabricated in a reactor, using a stronger steel plate was preferable to using a thicker steel plate. Although the working temperature of the reactor is lower than that of a power plant (450℃ to 500℃), it became necessary to increase the high-temperature strength of 2.25Cr-1Mo steel, which is a low-alloy steel with the highest resistance to hydrogen attack. Eventually, Nippon Steel established technology to manufacture a new steel plate with 0.25% V added for reactors.[44] At present, the company also conducts research to improve the high-temperature strength of steel required to meet the revised standards for reactors.

(3) Steel resistant to sulfuric acid/hydrochloric acid dew-point corrosion

In the smoke exhaust system of a boiler plant, depending on the temperature at the surface of the steel material making contact with the exhaust gas and the moisture contained therein, gaseous acidic substances (SO_x, HCl, etc.) which are contained in the hot exhaust gas condense, causing corrosion. This phenomenon is called acid dew-point corrosion. Equipment adversely affected by acid dew-point corrosion includes, for example, the smoke exhaust and heat-recovery systems of heavy oil-fired boilers and chemical plant reheating furnaces. Specifically, economizers, air pre-heaters, dust collectors (electric precipitators, bag filters), flues, chimney internal tubes, etc. are subject to acid dew-point corrosion.[45, 46] In recent years, as described later, acid dew-point corrosion by SO_x/HCl has also occurred with waste incineration plants, etc.[47]

The environments in which acid dew-point corrosion occurs can roughly be classified according to the type of substance burned. With heavy oil- and coal-fired boilers, sulfuric acid dew-point corrosion can occur. In the case of LNG-fired boilers, so-called water corrosion can occur since LNG contains very small amounts of sulfur and chlorine.[48] At waste incineration plants and resource recycling plants, sulfuric acid and hydrochloric acid dew-point corrosion occurs.[47]

In order to meet contemporary needs, Nippon Steel has actively developed and commercialized new corrosion-resistant steels for boiler plants using various types of fuels. During the period of rapid economic growth in the 1960s, individual steelmakers were pressing ahead with the development of sulfuric acid-resistant steels as measures to cope with sulfuric acid dew-point corrosion of heavy oil-fired boilers. Nippon Steel developed and commercialized "S-TEN1," a COR-TEN-based steel resistant to sulfuric acid dew-point corrosion.[48-50] In the 1990s, water corrosion at thermal power stations became a new problem in the wake of the change in fuel to LNG. As a solution to that problem, the company developed and commercialized a cold-rolled, corrosion-resistant steel for gas-fired air-heating element,[51] as well as a corrosion-resistant plate, WELACC5, for combined cycle generation.[52]

In recent years, from the standpoint of realizing a sustainable, recycling-based society, reducing the environmental burden and improving the productivity of resources have been strongly called for. As a result, the objects of reuse have rapidly become more diverse.

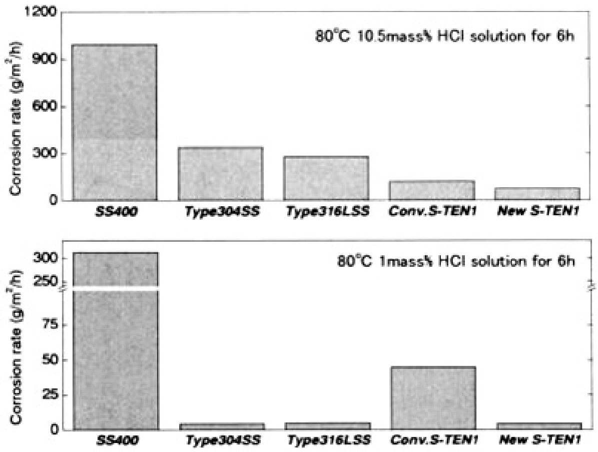


Fig. 9 Immersion test results under HCl solutions at 80℃

In many cases, the objects of reuse, such as incineration ash and waste tires, contain chloride ions. In addition, with the rapid progress of technology for environmental protection in recent years, at waste incineration plants and various resource reuse plants, instances of corrosion of smoke exhaust treatment equipment due to an acidic hydrochloric atmosphere are increasing.

In October 2002, Nippon Steel developed "New S-TEN1" as a measure to combat hydrochloric acid corrosion of smoke exhaust treatment equipment at waste incineration plants and various waste recycling/reuse plants. **Fig. 9** shows the results of an immersion test of various types of steel materials in 10.5% and 1% HCl solution at 80℃. It can be seen that New S-TEN1 has far superior hydrochloric acid resistance compared to conventional S-TEN1, especially in 1% HCl solution. A comparison between New S-TEN1 and SUS steels shows that New S-TEN 1 has superior corrosion resistance especially when the HCl concentration is high. Since New S-TEN1 is resilient against acids containing chloride ions, it has a wider scope of application than the conventional sulfuric acid-resistant steel (which only has good resistance to environments containing sulfuric acid). The new steel has increasingly been applied to smoke exhaust treatment equipment which are subject to acidic chloride ions and equipment for storing/transporting sulfuric or hydrochloric acid. In particular, smoke exhaust treatment equipment in the field of waste reuse/recycling is susceptible to corrosion by hydrochloric acid/chloride, and this new steel is being applied to plants in diverse fields.

At present, Nippon Steel is selling the newly developed steel (New S-TEN1) as S-TEN1. This steel is a unique corrosion-resistant, low-alloy steel that has excellent corrosion resistance to hydrochloric acid and affords comparable usability and availability to SS 400. Because of those advantageous characteristics, it is expected that uses for the steel will expand in the future.

(4) Steel for penstock for hydropower generation

The penstock for hydropower generation plays the role of leading water stored in the dam to the generator. With the increase in scale of dams, the conduit head for hydropower stations has increased, causing the internal pressure of penstocks to rise. Accordingly, the wall thickness and strength of penstocks have been increased. In addition, with the increase in demand for electricity in recent years, very strong steels for penstocks have been increasingly used in the construction of pumped-storage hydropower stations which are designed to store

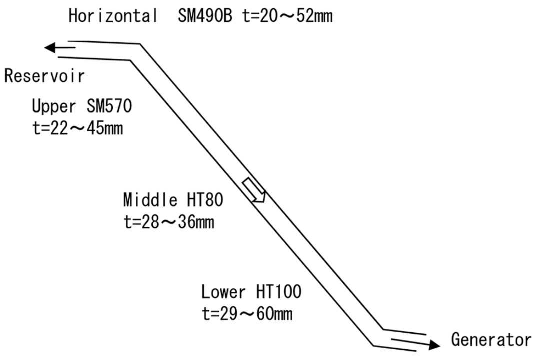


Fig. 10 Example of steel plates for penstocks [53]

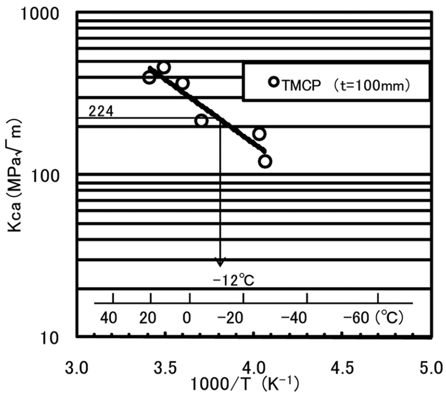


Fig. 11 Arrest toughness Kca of HT100 steel (t = 100mm) [54]

surplus electricity at night.

At the Ohira Pumped-Storage Hydropower Station built in 1975, a steel of 780-N/mm^2 class (HT80) was used for the penstock for the first time in Japan. In 2005, at Kannagawa Pumped-Storage Hydropower Station, a steel of 950-N/mm^2 class (HT100) was put to practical use for the first time in Japan. Penstocks represent one of the fields in which very tough and strong thick steel plates have been employed. A penstock is presented schematically in **Fig. 10** [53].

Looking at overseas hydropower plants, at the Bieudron Hydropower Station in Switzerland that came into operation in 1998, the Cleuson-Dixence penstock made from HT100 for the first time in the world ruptured in 2000. It is said that the accident was caused by delayed cracking of a weld. However, the unexpectedly serious damage caused by that accident is considered ascribable, at least in part, to the fact that the concept of arrestability—the ability to "arrest" a propagating brittle crack—is not applied to steels for penstock overseas.

In Japan, the "Technical Standards for Penstocks" specifies the properties that are required of steel grades up to HT80 for penstock. Those requirements are based on the concept of double integrity. In the first place, they need to prevent the occurrence of brittle cracks from the welds. Secondly, even if a brittle crack occurs in a weld, it should be arrested by the base metal. Specifically, the Technical Standards demand that: "The welds shall prevent initiation of brittle fractures at 0℃" and "The base metal shall arrest a propagating brittle crack at 0℃." The Japan Welding Engineering Society's Standard WES 3003 provides for Type G, that requires brittle fracture characteristics, and Type A, which requires arrest characteristics. Those requirements have been converted in terms of Charpy impact values by using the correlation between brittle fracture characteristics and Charpy impact values and the correlation between brittle crack arrestability (arrest characteristics) and Charpy impact values, respectively, and the required Charpy impact values are specified.

Concerning the arrest characteristics of steel plate, in particular, WES 3003 requires confirming not only the Charpy impact value but also an arrest characteristic equivalent to Type A by carrying out an ESSO test as required. With respect to HT100 as well, the "Technical Guidelines on Application of High-Tensile Steels of 950-N/mm^2 Class (HT100) to Penstock" (published by the Association of Penstocks) demand properties similar to those required of HT80.

Nippon Steel has developed and commercialized an ultra-heavy HT100 steel plate (maximum thickness: 100 mm) for penstock, whose base metal meets WES 3003 Type A criteria (**Fig. 11**) and whose welding meets WES 3003 Type G criteria.[54, 55] The HT100 steel plate was employed for the first time at the Kannagawa Hydropower Station of Tokyo Electric Power mentioned earlier. Later, it was adopted for the penstock, including the branch-stiffening girder (HT100Z) of Omarugawa Hydropower Station of Kyushu Electric Power.

(5) Steel for nuclear power generation

The steel materials used at nuclear power generators include steel plates for steam generators and reactor vessels, etc. which are directly exposed to radioactivity, and steel plate for the containment vessel that contains the pressure vessel. The steam temperature is about 250℃ to 350℃ lower than for thermal power generation, and carbon steel or low alloy steel is used for those parts which are not exposed to a corrosive atmosphere. Since the 1980s, Nippon Steel has developed super-tough carbon steels, such as SGV480 and SPV490, and has delivered them mainly for containment vessels and other parts used at temperatures not exceeding 300℃. In the 1990s, from the standpoint of enhancing the pressure resistance and safety allowance of vessels, the company developed and commercialized a high-strength steel of SQV grade containing 0.5% Mo,[56] an SQV2B steel of 620-N/mm^2 class affording tough electron beam-welded joints,[57] and an SGV480 steel for containment vessels which applies TMCP technology and permits omitting post-weld heat treatment. In the future, a higher degree of safety will be required of such nuclear pressure vessels. Therefore, the demand for steel materials with high-temperature strength and toughness will become more stringent than ever before. It is considered, therefore, that the expectation for heat-resistant, low-alloy steels with good weldability and corrosion resistance, as well as good high-temperature properties, will rise.

2.2.4 Welding solutions in the energy field

In order for the above steel materials to be used for structures and manifest a social value, it is indispensable that they should afford welded joints comparable in performance to their base metal. Given below are examples of welding solutions for the line pipes described in 2.2.1 (2), the high-strength, high-toughness steels for offshore structures described in 2.2.2 (1), and the steels resistant to sulfuric acid/hydrochloric acid dew-point corrosion described in 2.2.3 (3).

(1) Welding solution for UOE line pipe

As steel pipes for pipelines, there are UOE pipes and high frequency resistance-welded pipes. These pipes have their seams welded. Here, we describe the seam welding of high-strength UOE line pipes of API Grade X100 or higher that are required to be

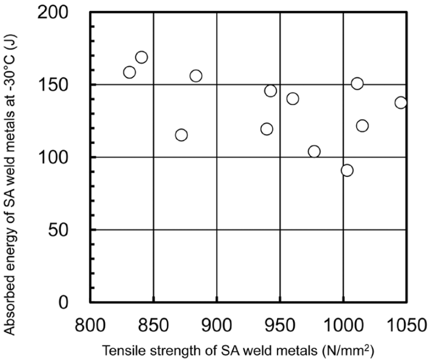


Fig. 12 Relationship between tensile strength of SA weld metals and absorbed energy of SA weld metals at −30℃

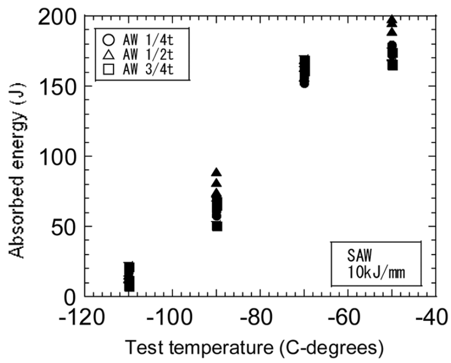


Fig. 13 Charpy impact test results of weld metal

especially strong.

In order to weld the seams of UOE line pipes, multi-electrode submerged arc welding (SAW) is generally used from the standpoint of welding quality and efficiency. The seam weld of a UOE line pipe consists of two welding layers, one on the outer side of the pipe and the other on the inner side, with the weld metals overlapping at the center.

For the seam weld metal of UOE line pipe, it is necessary to have higher tensile strength than that of the base metal and low-temperature toughness matching those of the base metal. In order to design a weld metal which meets the above requirements, we studied the relationship between weld metal strength and toughness. **Fig. 12** shows the relationships between tensile strength and absorbed energy at −30℃, obtained with SAW metals of varying chemical compositions.[58] As shown, the higher the tensile strength of the weld metal, the lower the absorbed energy. In particular, when the tensile strength exceeds about 1,050 N/mm^2, the microstructure of the weld metal changes from bainite to martensite, causing the steel toughness to decline. Thus, excessive strength of the weld metal makes it difficult to secure the required low-temperature toughness of the weld metal. Therefore, it is necessary to maintain the bainite structure of the weld metal by setting a high limit on the weld metal strength. Besides, with a high-strength weld metal having high oxygen content, the desired low-temperature toughness cannot be obtained. By keeping the weld metal oxygen content at around a level of 200 ppm and optimizing the oxide composition, we could obtain a fine bainite structure. As a result, it was found that even with a weld metal having a tensile strength of about 1,000 N/mm^2, it was possible to obtain a high toughness of about 150 J at −30℃ on average. In SAW, the dilution ratio of the base metal is relatively high and hence the chemical composition of the weld metal is more or less influenced by the composition of the base metal. Therefore, it is necessary to consider the base metal composition in designing the chemistry of the weld metal. Nippon Steel has developed new welding consumables for SAW with consideration given also to the base metal composition so that a weld metal chemical composition affording a fine bainite structure can be obtained.

The newly developed welding consumables for SAW made it possible to obtain seam welds of X100 and X120 UOE line pipes having high strength and good low-temperature toughness.[58]

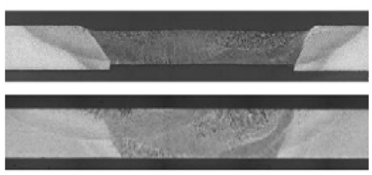
(2) Welding solution for high-strength, high-toughness steels for offshore structures

Concerning high-strength, high-toughness steel plates for offshore structures, high degrees of safety, such as a guarantee of toughness at extremely low temperatures, are required of welded joints. Besides, even thick steel plates need to be welded efficiently. For those reasons, welding with a large heat input is also being called for lately. Generally speaking, however, with the increase in heat input, coarse intergranular ferrite tends to form easily,[59] and acicular ferrite formed by intragranular transformation becomes coarse.[59] As a result, it becomes difficult to secure the desired toughness of the weld metal. In order to solve the above problem, we studied lowering the M-A volume fraction by reducing the carbon content, enhancing the toughness of weld metal by addition of nickel, and restraining the growth of intergranular ferrite by addition of boron.[59] As a result, as shown in **Fig. 13**, even in submerged arc welding with a large heat input of 10 kJ/mm, a high-toughness weld metal whose Charpy absorbed energy was higher than 100 J at −70℃ was obtained.[60] Weld metal containing an excessive amount of nickel is susceptible to hot cracking. In this respect, we performed calculations to predict hot cracking using a neural network and limited the nickel content of weld metal to about two percent. As a result, the occurrence of hot cracking with weld metal has been restrained.[60]

It has been reported that in one-pass submerged arc welding, the grain size of acicular ferrite varies according to the aluminum content of the weld metal.[61] The report suggests that in order to obtain a high-toughness weld metal with fine-grain acicular ferrite, it is desirable that a suitable amount of aluminum be contained in the weld metal.[61]

(3) Welding solution for new S-TEN1, which is resistant to sulfuric/hydrochloric acid dew-point corrosion

When welding the new S-TEN1 that is resistant to sulfuric/hydrochloric acid dew-point corrosion, Nippon Steel has developed welding materials in accordance with the guidelines on corrosion resistance similar to those applied to the base metal. As an example, **Fig. 14** shows the results of a test in which test pieces cut out from



Conv. S-TEN1+Conv. FCW

New S-TEN1+New FCW

Fig. 14 Cross-sectoin of welded joints after HCl immersion tests (10.5% 80C-degree HCl, 24 hour immersion)

welded joints were immersed in 10.5% hydrochloric acid at 80℃.[62] It can be seen that the welded joint obtained with a welding material developed exclusively for the new S-TEN1 steel was free from selective corrosion of the weld metal and was comparable to the base metal in corrosion resistance not only in a hydrochloric environment but also in a sulfuric acid environment.[62]

3. Steels for New Energies and Their Future Prospects

3.1 Steels for new energies (steel for wind turbines)

In view of the global movement to reduce CO_2 emissions and the mounting cry to abandon nuclear power generation in the wake of the disaster at Fukushima Daiichi Nuclear Power Plant, there is growing attention to new renewable energies, such as from wind, solar power, and biomass. So far, wind turbines have mainly been introduced on land. It is expected, however, that in the future more and more wind farms will be installed in marine areas out of consideration for the environment and local communities and the dwindling number of suitable installation sites. There are already plans for construction of large-scale wind farms mainly in the North Sea and the western part of the Baltic Sea.

Fig. 15 shows the steel materials used in a standard offshore wind turbine having a generating capacity of 3 MW.[63-65] A total of about 1,000 tons of steel, including steel plates, electrical steel sheets, bars and cast iron, is used per wind turbine. Since the scale of these wind turbines is continually being expanded, it is considered that the quantity of steel materials used per unit will increase accordingly. In the U.K.'s Round 3 Project that plans to start construction of an offshore wind farm in 2015, it is expected that more than one million tons of steel materials will be demanded annually.

The tower and foundation (mono-pile type) are made from very thick welded steel plates. They are fabricated by circumferentially connecting welded plate units of YP355-class steel. The steel materials for the foundation are required to have higher properties than those for the tower. The typical tower requires a steel plate having a thickness of 40 mm or less and a Charpy impact energy at 0℃ to about −20℃. On the other hand, the foundation requires a steel plate 50 to 120 mm in thickness. Besides, both the base metal and welds are required to have a Charpy impact energy at −40℃ almost comparable to that of a middle-grade steel plate for offshore structures or F-grade steel plate for shipbuilding. Nippon Steel has already

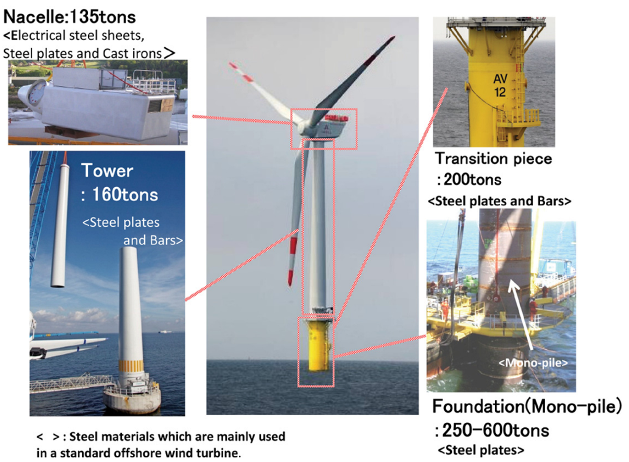


Fig. 15 Steel materials used in a standard offshore wind turbine[63-65]

started supplying steel plates for wind turbines.

3.2 Steels for large-capacity, high-efficiency power generation in the future

3.2.1 Prediction of future energy supply-demand environment

The energy to maintain and develop social infrastructure comes from resources that are mainly used for electricity generation and transportation. At present, we are largely dependent on fossil fuels for that energy. In Japan, annual electricity generation is about 100 million kWh, sixty percent of which comes from fossil fuel-fired power plants and about thirty percent from nuclear power plants. The conventional modes of power generation are now being critically reviewed. In the future, it is estimated that the proportion supplied by renewable energies, such as wind and sunlight, will expand and that dependence on thermal power generation will increase. In particular, as a comparatively clean and highly durable power plant combined with CO_2 separation and recovery technology, much is expected of high-efficiency thermal power plants fueled by coal, which remains abundant almost everywhere and which is relatively inexpensive.

3.2.2 Steel for large-capacity, high-efficiency, coal-fired thermal power generation

Since the oil crisis in the 1970s, efforts to improve the efficiency of coal-fired thermal power generators have been made, with the focus on developing technology that permits increasing the temperature and pressure of the steam used. However, with the increase in steam temperature, the creep strength of the applicable steel becomes an obstacle to improving the efficiency. At present, it is difficult to raise the steam temperature above 600℃.

Raising the steam temperature to implement high-efficiency operation of the plant is important since it helps reduce CO_2 emissions. Therefore, new materials that are capable of withstanding very high steam temperatures are highly sought after. Accordingly, R&D into optimizing the various elements contained in heat-resistant steels has made remarkable progress. For example, as the optimum concentration of chromium, about nine percent has been proposed recently. At present, in addition to the above proposal, introduction of such reinforcing elements as tungsten and boron, and controlling the initial structure of steel, etc. are being studied to come up with new heat-resistant ferritic steels capable of standing steam temperatures above 650℃. It is estimated that if the steam temperature can be raised to 650℃, the efficiency of energy conversion will improve by three percent. If the steam temperature can be raised to 700℃, the efficiency is estimated to improve another three percent. Then, the CO_2 emissions can be reduced accordingly.

On the other hand, temperatures around 650℃ are near the point of transformation for heat-resistant ferritic steels. Even when a factor which helps increase deformation resistance at high temperatures is introduced to the steel structure, it has only a limited effect. Thus, it is extremely difficult to increase the high-temperature strength of heat-resistant ferritic steels. Therefore, it is important to build a new structural control technology that permits not only existing standard steels, but also new steel grades, to retain their strength at higher temperatures or for a longer period. Basic studies in that direction have been conducted in projects under the Ministry of Economy, Trade and Industry, etc. Namely, in addition to the conventional concept of strengthening the initial dislocation structure and of intragranular precipitation strengthening, new steel materials based on new ideas, such as using the grain boundary to locally disperse precipitates densely, or using a structure that is subject to minimal time-serial change, are being sought.

In research on those heat-resistant steels, evaluating the creep characteristics is indispensable and many hours of testing are required for that purpose. In order to improve the accuracy of technology to predict the life of materials and shorten the time required to develop new materials, technology to predict the strength so as to permit determining long-term characteristics is also being developed. Through research on new materials that will maintain excellent creep characteristics for a very long period, Nippon Steel is investigating the supply of new steel materials to realize the concept of advanced ultra-supercritical steam condition (A-USC).

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Ryuji UEMORI
General Manager, Dr.Eng.
Plate, Pipe, Tube & Shape Research Lab.
Steel Research Laboratories
20-1, Shintomi, Futtsu, Chiba 293-8511


Yasushi HASEGAWA
Chief Researcher, Dr.Eng.
Plate, Pipe, Tube & Shape Research Lab.
Steel Research Laboratories


Takuya HARA
Chief Researcher, Dr.Eng.
Kimitsu R&D Lab.


Takehiro INOUE
Chief Researcher, Ph.D.
Plate, Pipe, Tube & Shape Research Lab.
Steel Research Laboratories


Yasuhiro SHINOHARA
Senior Researcher
Plate, Pipe, Tube & Shape Research Lab.
Steel Research Laboratories


Hiroshige INOUE
Chief Researcher, Dr.Eng.
Welding & Joining Research Center
Steel Research Laboratories


Hitoshi FURUYA
Senior Researcher
Nagoya R&D Lab.

Collaborator


Ryuichi HONMA
Senior Researcher
Plate, Pipe, Tube & Shape Research Lab.
Steel Research Laboratories


Eiji TSURU
Chief Researcher, Dr.Eng.
Plate, Pipe, Tube & Shape Research Lab.
Steel Research Laboratories


Michio KANEKO
Chief Researcher, Dr.Eng.
Plate, Pipe, Tube & Shape Research Lab.
Steel Research Laboratories

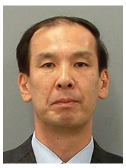

Tetsuro NOSE
General Manager, Dr.Eng.
Welding & Joining Research Center
Steel Research Laboratories


Hiroshi MORIMOTO
Chief Researcher, Dr.Eng.
Welding & Joining Research Center
Steel Research Laboratories


Kazuhiro KOJIMA
Senior Researcher
Welding & Joining Research Center
Steel Research Laboratories


Mitsuru SAWAMURA
Chief Researcher
Nagoya R&D Lab.


Naoki SAITOH
Senior General Researcher
Nagoya R&D Lab.


Hitoshi ASAHI
Manager, Dr.Eng.
Intellectual Property Div.