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Development of Manufacturing Technology and Its Application in Titanium




Kinichi KIMURA*1 Motomi MASAKI*1 Masatoshi MURAYAMA*2 Yukihiro KAKO*1

Abstract

Approximately fifty years have passed since the industrial production of titanium started in Japan. One third of this period also has elapsed since Nippon Steel's entry into the titanium business in 1984 for the purpose of cultivating new demand through new product development and application processes. The company has succeeded in lowering the cost of titanium use, starting with raw titanium cost reduction and developing various application technologies. It also expended efforts in opening up new demands for titanium in building materials, automobiles and ships. As a result, titanium has become a metal familiar in daily life. This paper describes the present state of new applications for titanium as flat rolled, tubulars and wires.

1. Introduction

Titanium is the fourth most abundant metal on earth. With its effective reserve estimated at about 300 million tons, its resources may be said to be practically inexhaustible. Of the titanium ore used in Japan, about 70% is used as titanium oxide for pigment and other applications, and about 10 to 15% is used as titanium sponge for titanium metal.

W. Gregor of the United Kingdom discovered the element titanium in 1791, and M.H. Klaproth of Germany named the metal titanium after the Greek gods Titans in 1795. Titanium is so strongly combined with oxygen that it is difficult to separate. In 1910, M.A. Hunter of the United States successfully separated titanium by a sodium reduction process. In 1946, W. J. Kroll of Luxemburg succeeded in the commercial production of titanium by a magnesium reduction process. This is now the principal process of separating titanium from its natural state.

Japan started the commercial production of titanium in 1952 or six years after the successful commercialization of the magnesium reduction process by W. J. Kroll. In 1984, Nippon Steel Corporation entered into the titanium business as part of its multiple-business management. Titanium has an industrial production history of only about 50 years, and Nippon Steel has been engaged in titanium production for the last one third of that period. In recent years, titanium has come to be used in golf clubs and other sporting goods, eyeglasses, and even in camping equipment and frying pans. It is now being accepted as a familiar metal. In line with these trends, the demand for wrought titanium has been markedly growing, with its shipment reaching 13,000 tons in 1997. This growth is expected to continue, and the Japan Titanium Society announced its medium- and long-term titanium visions that estimate a doubling of titanium shipment to 30,000 tons in 2009.

Titanium demand prospects by sector are shown in **Table 1**[1]. Of the titanium consuming sectors, growth is remarkable in the existing

*1 Titanium Division

*2 Nittai Co.,

Table 1 Medium- and long-term visions of Japan Titanium Society

Existing sectors (ton/year)

	Aircraft	PHE	Electricity and water	Chemical	Architectural	Sales	Consumer goods	Others	Total
1998	567	2,252	2,742	3,180	176	901	852	1,798	12,468
2009	800	5,000	4,900	4,300	2,700	3,600	2,200	1,500	25,000

New sectors

	Automotive	Ships and offshore	Environment	Medical	Others	Total
1998	133	114	-	25	-	272
2009	700	1,700	800	1,000	800	5,000

sectors like chemical plants and plate-type heat exchangers, and the rate of growth is outstanding in the new sectors like automobiles and ships. Of these new sectors, environmental and other applications are still low in demand, but are expected to represent increasing titanium demand in the future. Among the environmental items are flue gas desulfurization equipment, water and sewage treatment plants, and spring water facilities. Titanium demand is also expected to increase in nuclear fuel and food processing plants[1].

Titanium is an excellent metal with very high corrosion resistance and very light weight. **Fig. 1** shows the relative property evaluation of titanium, chiefly as compared with iron or the most frequently used metallic material. The specific gravity, Young's modulus, and thermal conductivity of titanium are about 60%, 50%, and 30% of those of iron, respectively. Titanium is practically as strong as iron, and its r value, a deep drawability evaluation index, is higher than that of iron and its n value, another deep drawability evaluation index, is lower than that of iron. Generally, metals are evaluated as to working by reference to iron. From these relative evaluation results, it can be qualitatively understood that titanium undergoes greater springback than iron after working, has higher deep drawability, but is more difficult to stretch than iron is.

The demand for titanium is growing in Japan, but this demand is not as high as that for stainless steel and aluminum. One large factor responsible for this situation is its high price. Lowering the manufacturing cost and price of titanium is considered to contribute to the expansion of the titanium market.

Fig. 2 shows main manufacturing processes for Nippon Steel's main titanium products, or plate, sheet, welded tube, and rod. Ingots as raw material are purchased from another company. The ingot is

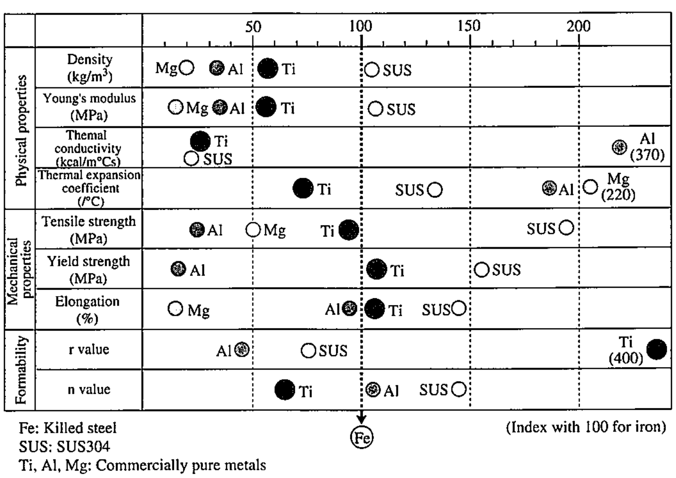

Fig. 1 Relative property evaluation of representative metals

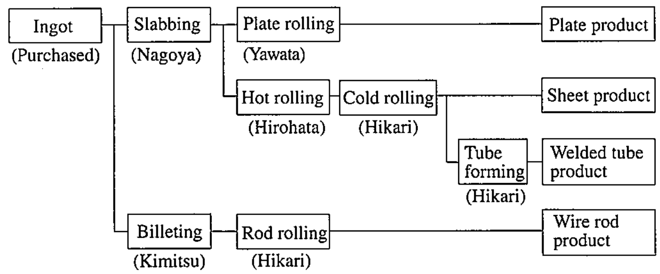

Fig. 2 Main manufacturing processes

processed to plate after slabbing and hot rolling, and to cold-rolled sheet after cold rolling and annealing. The cold-rolled sheet is formed and welded to tube. The ingot is also rolled to billets and then to rods.

When entering into the titanium business, Nippon Steel made it its policy to develop new demand for titanium through new product development and through utilization and fabrication technology development. It is still expanding its titanium business according to that policy.

This report describes the main steps recently taken by Nippon Steel to reduce the manufacturing cost of commercially pure titanium products and gives an overview of Nippon Steel's product development and manufacturing technology development.

2. Raw Materials

Nippon Steel has no titanium melting equipment and thus purchases most of its raw materials as melted ingots or slabs from Toho Titanium Co., Ltd. The material cost accounts for a large percentage of Nippon Steel's cost of manufacturing cold-rolled sheet and other products of commercially pure titanium. A sizable cost savings can be achieved by reducing the material cost. There are only two manufactures capable of supplying titanium raw materials in Japan. Under these circumstances, Nippon Steel started to import raw materials from abroad. We are accumulating results with foreign-sourced titanium raw materials and expanding their application range while confirming their properties. Acquisition of purchase sources, including foreign manufactures, has enabled the Nippon Steel to achieve a composition of low-cost titanium raw materials.

3. Initiatives with Respective Types of Products

3.1 Cold-rolled sheets

A purchased ingot is hot rolled to a slab at the Nagoya Works, hot rolled to a band at the Hirohata Works, and cold rolled and finished to product sheet at the Hikari Works. Electron beam (EB) remelted slabs are also purchased. These slabs are first hot rolled to bands at the Hirohata Works.

The manufacturing cost was been reduced by eliminating some of the process steps and by developing and applying technology for reducing surface defects in the cold-rolled product. More specifically, the effects of ingot surface conditioning, rolled slab grinding criteria, and hot rolling conditions, among other factors, on the occurrence of surface defects were clarified. Especially, hot-rolled band defects were reduced, and the efficiency of defect removal at the Hikari Works was improved. The Hikari Works initially used a grinder to remove hot-rolled band defects, but then developed technology for reducing the occurrence of defects in the hot rolling process and for efficiently removing defects in the acid pickling process. As a result of these efforts, the coil grinding process, a large cost factor, was practically eliminated.

While implementing these cost-saving measures, Nippon Steel also developed new products. A large demand sector for cold-rolled sheet is press-forming material. The effects of chemical composition and manufacturing conditions on press formability were quantitatively tested and investigated. Press-formable titanium differs in quality build-in technology between parts like those of plate-type heat exchangers that are mainly formed by stretching and parts like mugs that are mainly formed by deep drawing. More recently, titanium has come to be used in personal computers and other information technology (IE) equipment. Unlike plate-type heat exchangers and other applications that prioritize the functionality or corrosion resistance of titanium, these IT equipment applications impose severe surface appearance requirements. There are exacting surface quality requirements as to absence of even small surface defects and surface roughening during press forming and as to good grindability, among other items.

To meet these requirements, a new titanium composition system with excellent stretch formability was developed for plate-type heat exchangers, and the manufacturing conditions and especially annealing conditions were optimized. For deep-drawn parts like mugs, a new cold-rolled sheet product was developed that is dull finished and skin pass rolled to lessen anisotropy and to ensure uniform deformation and good formability during press forming. This new sheet product is shipped in large amounts, especially to Tsubame, Niigata Prefecture, where are located many special sheet metal fabricators. Hot rolling and subsequent manufacturing conditions of cold-rolled sheet for personal computers and other IT equipment were optimized to meet stringent surface quality requirements.

Nippon Steel has put force into cold-rolled sheet products for building materials in addition to press forming materials. Titanium was adopted as building material for the first time about 25 years ago. Titanium was initially used for corrosion resistance. In recent years, titanium has been adopted for surface appearance in many cases. Nippon Steel has developed a menu of surface finishes to suit the preferences of designers. Representative manufacturing processes are illustrated in **Fig. 3**. Among the typical surface finishes are dull finish produced with shot-blasted rolls during skin pass rolling, aluminum blast finish, and colored finish. One recently highlighted problem with architectural titanium is color change from silver to brown in a few years after construction.

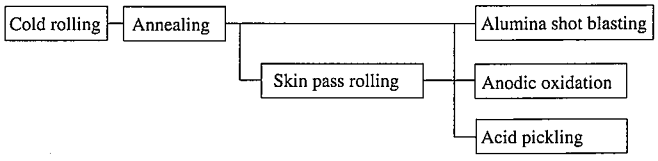

Fig. 3 Menu of surface finishes

Nippon Steel analyzed chemical composition and mechanical properties in detail, and established a method for quantitative evaluation of the degree of this discoloration. These efforts made it possible to complete the discoloration evaluation in a few weeks instead of a few years of exposure test, to quantitatively evaluate the relationship of the discoloration phenomenon with the manufacturing conditions, and to clarify the effects of environmental factors on the discoloration of titanium. According to the results, Nippon Steel developed a new grade of titanium with far higher discoloration resistance than that of conventional grades. The discoloration-resistant titanium was used in the roof of a main stadium built in a sports park in Oita Prefecture in the southern part of Japan.

Buildings materials have importance attached to the uniformity of architectural appearance. If the wall and other exterior panels of a building differ in color even partially, the entire appearance of the building suffers. Nippon Steel performs thoroughgoing lot control during manufacture and informs fabricators of the surface color of each lot (coil) during installation. The uniform surface appearance of architectural titanium is assured in this way.

3.2 Plate products

A purchased ingot is hot rolled to a band at the Nagoya Works, and the hot-rolled band is rolled, annealed and leveled to a plate at the Yawata Works. Some plates are produced directly from purchased as-rolled slabs.

To ensure high product flatness, a vacuum creep flattener (VCF) capable of simultaneously annealing and hot flattening plates was introduced 10 years ago. Because of its flattening capability being highly rated by customers, the VCF is now being put to full use.

In terms of product development, a titanium plate for electro-deposited copper foil manufacturing drums can be cited as one example. Electro-deposited copper foil is used in printed circuit boards for IT equipment and is sharply growing in demand. To meet the demand, copper foil plants are newly constructed or expanded in various parts of the world. Electro-deposited copper foil is made by conducting electrolysis in an aqueous solution of copper sulfate with a titanium drum as cathode, depositing copper metal on the drum, and continuously winding the resultant electro-deposited copper foil. The surface smoothness of the titanium drum is emphasized accordingly. If the drum has a surface pattern, it may be transferred to the copper foil surface to detract from the thickness uniformity of the copper foil and to adversely affect the quality of the copper foil for printed circuit boards. The titanium plate used as the cathode drum must be thus required to be free from any micro-structural patterns.

To meet these property requirements, Nippon Steel reviewed the manufacturing steps after ingot slabbing, added special steps, and succeeded in building the technology of manufacturing titanium plates with more uniform microstructure than obtainable in the past. The titanium plate products made by the newly developed technology have already come out on the market and are highly favored by customers. Nippon Steel further advanced the technology and established the technology of manufacturing titanium plates for sputtering targets used in the production of semiconductors and liquid crystal displays. Another new product, or corrosion-resistant titanium alloy TICOREX series, was added to the menu of titanium plate products. For the detailed description of TICOREX, refer to the article "Characteristics of High-Corrosion Resistant Titanium Alloy TICOREX and Its Applications" in this special issue.

3.3 Welded tube products

Welded titanium tubes are the product type whose market Nippon Steel has been trying to expand since its entry in the titanium business. The company installed two new TIG welded tube manufacturing lines for titanium at the Hikari Works. The welded titanium tubes produced at the new lines are shipped for chemical plant heat exchangers and adopted for nuclear power plant condenser tubes in Japan and abroad.

Welded titanium tubes for nuclear power plant applications must also be reduced in cost while maintaining high quality. Productivity, or more specifically, tube forming speed has been increased. Welded titanium tubes for utility power plants have especially stringent roundness control requirements to meet. To meet the requirements, the residual stresses in the respective portions of welded titanium tubes were determined, and techniques were developed for reducing these residual stresses. Tube forming rolls of soft copper alloy are used so as not to scratch welded titanium tubes. With usage, the rolls are worn locally to a slight degree. Since the deteriorating wear adversely affects the roundness and other geometrical properties of tubes, the relationship between the amount of roll wear and the geometry of tubes is quantitatively determined and used for constant roll wear control.

Any deposition of dust and contaminants at the skelp edges is likely to cause blowholes and other weld defects. To prevent such weld defects, the skelp is cleaned, and the skelp edges are deburred. Implementation of these measures and improvement of operating technology enable Nippon Steel to supply high-quality welded titanium tubes. Today's tube forming speed is considered to be close to its limit in view of low Young's modulus and other mechanical properties of titanium and the principle of TIG welding. It will be necessary to drastically review the titanium tube mills and to improve the production efficiency of the titanium tube mills by shortening the roll change time as required for each tube size change and aiming at size-free production.

As a new application, welded titanium tubes for the exhaust mufflers of motorcycles and automobiles are rapidly increasing in usage from the standpoints of weight reduction and aesthetic appearance. The heat of the exhaust muffler gives titanium a characteristic color. This color may delicately vary with the surface quality of titanium. For this reason, the effects of cold-rolled sheet manufacturing conditions on the color of titanium are clarified, and welded titanium tubes are shipped to suit the needs of customers. Muffler tubes are larger in outside diameter than heat exchanger tubes mainly with an outside diameter of 25.4 mm. Some sizes are too large to be produced at the titanium tube forming lines at the Hikari Works. These tubes are made by another manufacturer under the quality control of Nippon Steel and supplied to customers under the tradename of Nippon Steel.

A principal environmental control measure in recent years has been energy conservation for reduction in carbon dioxide emissions. Flexible titanium tubes were used in the highly efficient gas-fired household hot water supply and heating heat source machines "X PRIORL eco" of Osaka Gas and "ECOTECH Q" of Takagi Sangyo that were awarded the Fiscal 2000 Minister of Economy, Trade and Industry Energy Conservation Prizes sponsored by the Energy Conservation Center. The flexible titanium tubes are made of welded titanium that is produced by Nippon Steel and formed flexible by TIG Co. Ltd. They are used in heat exchangers in heat source machines. Nippon Steel developed thin-walled flexile titanium tubes with a wall thickness of 0.3 mm jointly with TIG Co. Ltd. Conventional titanium tubes for heat exchangers range from 0.5 to 0.7 mm in wall thickness, though there are a few comprising a wall thickness of 0.3 mm. When conventional titanium tubes for heat exchangers are made uneven in the surface and formed flexible for better heat transfer, their welds often crack.

In cooperation with TIG Co. Ltd, Nippon Steel designed a special chemical composition, and optimized rolling and annealing conditions so that the titanium strip skelp as tube stock could be made softer and more workable. Given the high probability of weld cracking during flexible forming, the weld shape was made smooth enough to ensure uniform deformation during flexible forming. Stabilization of smooth bead shape was accomplished by controlling the pressure of argon gas as the welding atmosphere and by applying tension during flexible forming. In addition to this manufacturing technology development, Nippon Steel performs the verification of weld integrity in the gas appliance environment and the verification of gas piping strength as well. The demand for titanium in this corrosive environment of heat recovery is expected to expand further in the future.

3.4 Bar and rod products

Bar and rod products are manufactured by rolling ingots to billets on a primary mill at the Kimitsu Works and rolling the billets to bars and rods on a high-speed mill at the Hikari Works. Initially, the rolled tonnage and coil weight were both small. As the usage of titanium wire for eyeglasses has increased in recent years, the rolled tonnage has increased concomitantly. The rolled tonnage by size has increased with increasing manufacturing volume, making it possible to roll different sizes together, and lowering the manufacturing cost together with improvement in rolling technology.

Bar and rod products are mainly used for eyeglasses. In addition to commercially pure titanium, the Ti-3Al-2.5V alloy is used in this application. Recently, the Ti-15V-3Cr-3Sn-3Al alloy that is high in strength and capable of being reduced in diameter has come to be used for rims of frameless eyeglasses by emphasizing fashionability.

Nippon Steel succeeded in the application development of the βc (Ti-3Al-8V-6Cr-4Mo-4Zr) alloy wire rod to the survey probe cables of deep-sea submersibles. The cables are mounted on the oceanographic research ship of the University of Tokyo, for example. The application of titanium to the automobile sector plays an important role in environmental load reduction. For instance, the use of titanium in the reciprocating parts of automotive engines reduces the engine weight and size and increases engine output, which in turn reduces the energy consumption and carbon dioxide emissions of the engine during travel. The quietness of the engine is said also to improve. Nippon Steel has built the system of domestically manufacturing titanium alloy wire rods for the intake and exhaust valves of automobile engines (e.g., Ti-6Al-4V and TIMETAL® 1100 (Ti-6Al-2.7Sn-4Zr-0.4Mo-0.45Si)) to meet the requirements of customers.

3.5 Development of other new products

Nippon Steel is endeavoring to develop titanium foil and develop titanium demand, not only limited to commercially pure titanium in the existing applications. The company also developed Ti-Nb-Cu plate-like multiple-layer composites for superconducting magnetic shields for the first time in the world. The composite is deep drawn into a joint-less multiple-layer cylindrical shield. These shields are used in medical MRI equipment and linear motor car experimental vehicles, among other applications, and are expected to have an expanding market in the future.

Nippon Steel started the application of titanium to ships as another application development and developed all-titanium ships jointly with ship builders. Since an all-titanium yacht was built in 1985, there were no titanium ship orders for some time. In 1998, an all-titanium fishing ship was built to the attention of those concerned.

A titanium ship working group was formed in the Japan Titanium Society. Thus the use of titanium in the shipbuilding industry is expanding.

Nippon Steel has been conducting research and development on the most popular Ti-6Al-4V alloy, the Ti-3Al-2.5V and Ti-15V-3Cr-3Sn-3Al alloys for eyeglasses and more recently on the high-strength beta alloy βc (Ti-3Al-8V-6Cr-4Mo-4Zr), the TIMETAL® 1100 (Ti-6Al-2.7Sn-4Zr-0.4Mo-0.45Si) with excellent heat resistance, and the low-cost beta alloy LCB (Ti-1.5Al-4.5Fe-6.8Mo). The technology of applying titanium to eyeglasses, golf clubs, and automobiles is under development in this way.

4. Conclusions

Titanium is used in power plant condensers and other heat exchangers, and chemical plants thanks to its excellent corrosion resistance. Titanium alloys with a high specific strength are used in large amounts in the aircraft industry. The usage of titanium and titanium alloys is rapidly growing, and their shipment is predicted to more than double or reach about 30,000 tons in 2009.

As discussed above, Nippon Steel has developed manufacturing technology and improved mill operation, centering on commercially pure titanium sheets, tubes, and wire rods. The company also has made efforts to develop new applications for titanium and has played a role in expanding the demand for titanium. We intend to contribute to the growth of Japan's titanium industry through development of various technologies.

Reference

1) Japan Titanium Society: Medium- and Long-Term Visions of Titanium Metal. May 1995