Technical Review

Manufacturing Technology of Titanium and Titanium Alloys

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Abstract

Nippon Steel Corporation efficiently manufactures titanium products based on the advanced manufacturing technology developed in steel and provides high quality and a wide product range of sizes that surpass competitors in the field of commercially pure titanium for general industry. Especially in the field of aircraft where higher quality is required, Nippon Steel have developed manufacturing technology for airframes and premium engine quality. Furthermore, Nippon Steel is one of the world's leading titanium manufacturers with almost all titanium products such as sheets, plates, welded pipes, wire rods, billets, bars, and extrusion and with an integrated manufacturing process such as melting, forging, hot rolling, and cold rolling.

1. Introduction

The following three organizations are responsible for the manufacture and shipment of titanium products of Nippon Steel Corporation: Naoetsu Area (Niigata Prefecture) of East Nippon Works; Osaka Area of Kansai Works; and Yawata Area including Hikari (Fukuoka and Yamaguchi Prefectures) of Kyushu Works. The R&D laboratories that technically support these manufacturing centers are the Research & Engineering Center in Futtsu (Chiba Prefecture) and Amagasaki Research & Development Center (Hyogo Prefecture). This paper presents the system and technology of the titanium manufacturing of Nippon Steel.

2. History and Characteristics of Nippon Steel's Titanium Business

In 1952, six years after W.J. Kroll succeeded in producing titanium on an industrial scale by the Mg reduction method, Osaka Titanium Co., Ltd. started trial production of titanium sponge for the first time in Japan, and began its commercial production in 1954. After that, Nippon Steel started to manufacture titanium thin sheets in the Naoetsu Area in 1968, then, thin sheets, welded pipes, and wire rods at Hikari Titanium Production Div. of the Yawata Area (hereinafter referred to simply as Hikari, separately from the rest of the Yawata Area) in 1984, and heavy plates in the Yawata Area in the same year.

Naoetsu manufactures mainly thin sheets of pure titanium, and the plant has acquired the accreditation of Airbus SE for the supply of pure titanium thin sheets for aircraft use, for which high quality and a system for strict quality control are required.

On the other hand, most of the titanium thin sheets, welded pipes, wire rods, and heavy plates produced at Hikari and Yawata are made of commercially pure titanium (CP titanium) for industrial use.

Production facilities for titanium alloys were newly built in the Osaka Area of Kansai Works in 1984 (hereinafter Osaka means the Osaka Area, not the city), the plant obtained accreditations from aircraft-related heavy industry companies of Japan in 1985, and is manufacturing and shipping high-quality titanium alloys for the fan blades of aircraft engines.

3. Titanium Demand and Future Prospects

Figure 1 shows the historical change in the shipment tonnage of wrought (rolled, forged, or extruded) titanium products from Japanese producers to domestic users. Although there were temporary decreases owing to economic downturn due to the Great East Japan Earthquake, the Euro crisis, and most recently, the pandemic of the new type of corona virus, COVID-19, the overall trend is increasing, and in the last few years, the total shipment is approaching 20 000 t/y (all the units herein are metric). **Figure 2** shows the shipment ratios of Japan's titanium products by demand sector in 2019.

In appreciation of its excellent resistance to corrosion especially by seawater, titanium is widely used for plate heat exchangers (PHEs) and the condensers for thermal power plants that exchange heat with seawater.

Pure titanium accounts for most of the domestic demand, and the demand for aircraft use is roughly 13% of the total. On the other hand, in the global titanium market, the demand for aircraft use ac-

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counts for about one half, and most of it is for titanium alloys. Although the demand from the aircraft industry is currently sluggish owing to the COVID-19 pandemic, it is expected to recover within a few years.

China has been demonstrating a remarkable rise in the world market over the last few years. The annual shipment of wrought titanium products of China is increasing recently; it increased by 19% to 75 000 t/y from 2018 to 2019, roughly five times the growth of Japan in the same period.[1] It is desirable for the Japanese titanium industry to aim at expanding the sales of high value-added products such as those for aircraft and automobiles, for which high quality is required in particular.

As for the future of titanium products, new demands are expected to arise in the market sectors related to environment conservation such as fuel cells, hydrogen facilities, and flying automobiles.

Although titanium is excellent in terms of lifecycle cost owing to its corrosion resistance and consequent long service life, in consideration of carbon neutrality in relation to the recent environmental problems, further improvement is required for the production process of titanium sponge.

In the Kroll process, in particular, to produce titanium sponge, which is the raw material of wrought titanium products (see **Fig. 3**[2]), major problems are direct emission of carbon dioxide during the formation of $TiCl_4$ in the ore chloridizing process and its indirect emission (the electric power required especially for the electrolysis of $MgCl_2$ to regenerate Mg and Cl_2). According to a survey conducted by the National Institute for Materials Science of Japan, 6.9 t of CO_2 is emitted for producing 1 t of titanium sponge, of which roughly 60% is for the power required for the electrolysis of $MgCl_2$.[3] Technical innovations such as process improvement of the reduction of titanium ore (TiO_2) to obtain metallic titanium and that of refining of metallic titanium are urgently awaited. In addition to the above, while the manufacturing efficiency has been improved in the processes after the refining down to the manufacture of wrought titanium products by applying the technology accumulated through steel production, further improvement is required.

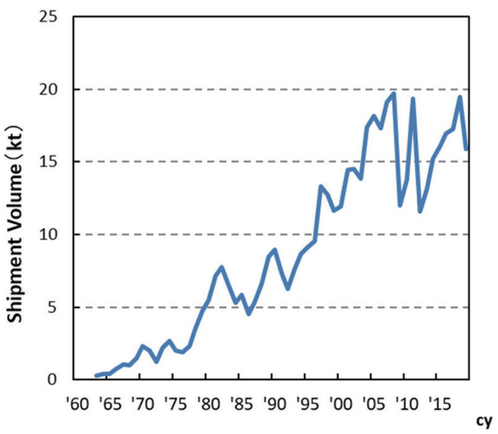

Fig. 1 Historical change in domestic shipment of titanium products

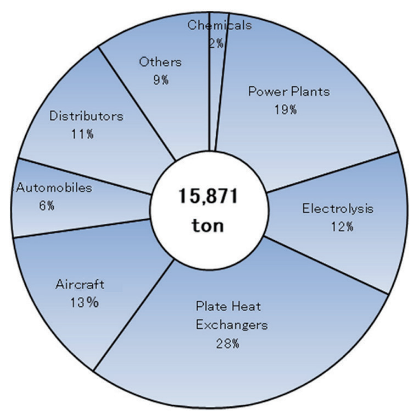

Fig. 2 Domestic shipment by demand sector in 2019

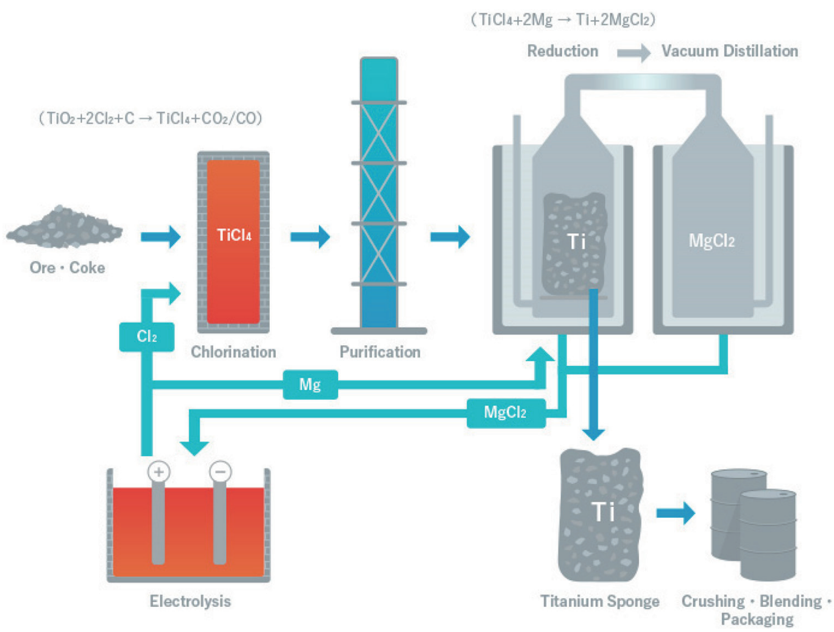

Fig. 3 Manufacturing processes of titanium[2]

4. Manufacturing Technology

4.1 Manufacturing centers

Figure 4 shows the shipment tonnage of titanium products from Japanese producers in 2019 by product shape. Flat products (thin sheets and heavy plates) account for roughly 70%, followed by welded tubes, bars, and wire rods. Nippon Steel manufactures and ships virtually all types of titanium products.

Steel manufacturing facilities are also used for titanium production, and to cover a wide variety of product types including sheets, plates, pipes, bars, wire rods, etc. Besides the three organizations mentioned in Section 1 (Naoetsu, Osaka, and Yawata including Hikari), three more, namely, the Kimitsu Area and Kashima Area of East Nippon Works and Hirohata Area of Setouchi Works (Setouchi meaning the Inland Sea), are involved in the production and shipment of titanium products, making six organizations in total.

As a world leading integrated titanium producer, Nippon Steel operates production facilities such as melting furnaces, breakdown rolling lines, forging presses, hot rolling mill lines for sheets, those for heavy plates, cold rolling mills for thin sheets, pipe welding lines, and rolling lines for bars and wire rods, and manufactures virtually all types of titanium products from ingots.

4.2 Raw materials and melting process

Titanium sponge, the raw material for the melting process, is porous metallic titanium obtained by reducing titanium ore. In Japan, Toho Titanium Co., Ltd. and Osaka Titanium Technologies Co., Ltd. produce titanium sponge, and titanium ingots are manufactured by melting it in vacuum arc remelting furnaces (hereinafter referred to as VARs) of the consumable electrode type or electron beam refining furnaces (hereinafter referred to as EBRs or EBMCHRs) and casting the molten metal. The quality of the titanium sponge and ingots of these companies is among the best in the world, and Nippon Steel purchases them mainly from these two.

Schematic illustrations of a VAR and an EBR are given in **Fig. 5**. A VAR is a melting furnace in which a consumable electrode made of pressed titanium sponge is melted by an electric arc in a vacuum, and the molten metal is solidified in a water-cooled mold of copper into ingots. On the other hand, EBR is another type of melting furnace, whereby raw materials such as titanium sponge and scrap are melted by electron beam in a vacuum, impurities in the molten metal are removed in a water-cooled copper hearth, and then the molten metal is continuously cast into a mold and solidified into ingots. Structurally, EBRs have the advantage of being able to use more titanium scrap as a raw material than VARs, while VARs have the advantage of being superior in terms of the mixing of component elements owing to the deep molten pool. It is possible to use either VARs or EBRs in consideration of the requirements of users.

Nippon Steel manufactures titanium ingots at Naoetsu using a VAR and an EBR. The new type EBR of Naoetsu is more flexible regarding the size and shape of titanium scrap used as a raw material, and the mixing ratio of titanium scrap has been increased from that with the old EBR. The technologies and experiences of metal melting, refining, and solidifying accumulated over many years of steel production, especially the technology of thermo-fluid analysis based on numerical simulation, have been instrumental in the improvement of titanium manufacturing processes.

Reducing carbon dioxide emissions during the refining of titanium sponge and cutting manufacturing costs by increasing the mixing ratio of titanium scrap and lowering the ratio of titanium sponge are the objectives.

Some manufacturers melt titanium using plasma arc remelting furnaces (hereinafter referred to as PARs or PAMCHRs). Whereas, in an EBR, an electron beam is irradiated in a vacuum, in a PAR, a plasma arc is irradiated in an Ar atmosphere at normal pressure, and for this reason, the loss of raw materials due to evaporation during melting can be lowered with the latter. On the other hand, gas remaining in titanium sponge cannot be degassed with a PAR because of the normal atmospheric pressure, and degassing in a VAR is required as post-treatment. **Table 1** compares the characteristics of these three types of titanium melting furnaces.

4.3 Thin sheets

Figure 6 shows the process flow of thin sheet production. Ingots are forged into slabs at Naoetsu using a press machine, then the slabs are hot-rolled into coils at Hirohata or Yawata, and the hot-rolled coils are pickled, cold rolled, annealed, and finished at Naoetsu or Hikari.

The yield of slab production by forging at Naoetsu is high thanks to forging pass schedules based on extensive experience and process simulation.

In cooperation with Toho Titanium, Nippon Steel has developed a process to melt ingots and cast them directly into slabs (DC Slabs™[*1]) by using EBRs as the first case in the world, and succeeded in commercially manufacturing cold-rolled sheets from the DC Slabs™ through the processes of hot rolling, cold rolling, and annealing.

The hot rolling of titanium slabs is conducted mainly at Hirohata. Although the hot rolling mill line of Hirohata is a compact one, it has a vertical rolling mill (VRM) to apply reduction in the width direction with vertical rolls, and its finishing mill train consists of

[*1] DC Slab is Toho Titanium's registered trademark.

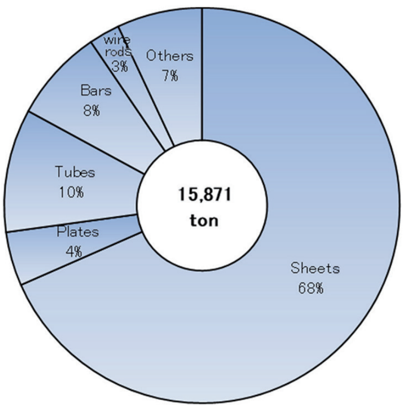

Fig. 4 Domestic shipment by product type in 2019

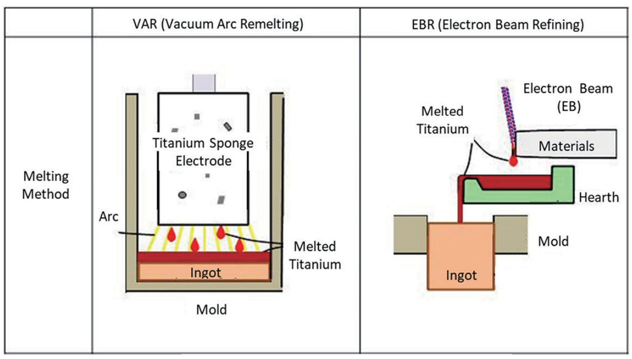

Fig. 5 Titanium melting furnace: VAR and EBR

Table 1 Characteristics and evaluations of titanium melting furnaces

Type of furnace	Vacuum arc remelting (VAR)	Electron beam melting cold hearth refining (EBR or EBMCHR)	Plasma arc melting cold hearth refining (PAR or PAMCHR)
Melting process	Melting consumable electrode by electric arc	Melting raw materials by electron beam	Melting raw materials by plasma arc
Raw material requirements	Poor • Preparation of electrodes: necessary • Scrap shape: blocks not acceptable • Scrap ratio: limited to low	Excellent • Pretreatment of raw materials not necessary • Scrap shape: blocks acceptable • Scrap ratio: high mixing ratio possible	Excellent • Pretreatment of raw materials not necessary • Scrap shape: blocks acceptable • Scrap ratio: high mixing ratio possible
Number of times of melting	Poor • Normally twice, sometimes three times, for degassing of titanium sponge (consumable electrodes) and improving ingot surface quality	Excellent • Normally once • Post-treatment by VAR, when necessary	Poor • VAR required after PAR for degassing of titanium sponge
Degree of vacuum (Pa)	10^{3}–10^{-1}	10^{0}–10^{-4}	10^{5}–10^{3}
Degassing efficiency	Good • Insufficient by one melting	Excellent • Sufficient because of melting under high vacuum	Poor • Insufficient because of melting in normal atmosphere
Melting cost	Poor • Two or more meltings necessary • Low scrap ratio only	Excellent • Normally one melting • High scrap ratio possible	Good • Two or more meltings necessary • High scrap ratio possible
Solidifying segregation	Good • Deep molten metal pool and long solidification time	Excellent • Shorter solidification time • Temperature control of molten metal pool possible	Excellent • Shorter solidification time • Temperature control of molten metal pool possible
Compositional homogeneity	Excellent • High homogeneity owing to good mixing in deep molten metal pool	Good • Low homogeneity owing to shallow pool • Homogeneous raw materials required	Good • Low homogeneity owing to shallow pool • Homogeneous raw materials required
Inclusion removability	Good • Dissolution in mold	Excellent • Dissolution or separation in cold hearth	Excellent • Dissolution or separation in cold hearth

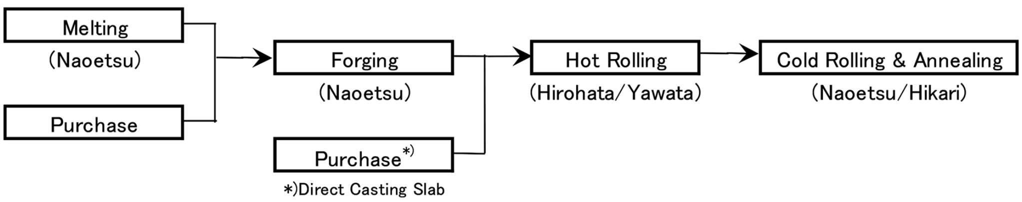

Fig. 6 Manufacturing processes of sheet products

pair-cross mill stands, which are capable of controlling the sheet thickness deviation in the width direction (sheet crown). The VRM and the pair-cross mills greatly contribute to accuracy improvement of the width and sheet thickness of hot-rolled and cold-rolled sheets. From the viewpoint of the business continuity plan, hot rolling is also conducted at Yawata, albeit in a smaller amount.

Hot-rolled coils are transported to Naoetsu and Hikari, undergo processes of pickling (or descaling), cold rolling, annealing, and finishing, and are then shipped as final products.

Pure titanium is used for heat exchangers and the like because of its excellent corrosion resistance, and thinner and wider cold-rolled sheets are required for the application. **Figure 7** shows the relationship between the thickness and width of Nippon Steel's titanium sheets. When the material is Class 1 or 2 commercially pure titanium under JIS (Gr. 1 or 2 under ASTM, respectively), cold-rolled coils 0.3 mm in thickness can be supplied up to a width of 1219 mm, and when the thickness is 0.6 mm, up to a width of 1524 mm; this size range is one of the best in the world.

Titanium foils thinner than thin sheets are also available: the minimum thickness of the material equivalent to JIS Class 1 is 20 μm, and when the thickness is 100 μm, the maximum width is 600 mm (up to 630 mm subject to consultation) (see **Fig. 8**).

The Naoetsu Area has obtained the accreditation for JIS Q 9100 "Aerospace Quality Management System," and also that under the National Aerospace Defense Contractors Accreditation Program (Nadcap), an international process certification program for the aerospace industry. In appreciation of its excellent product quality and quality control system, Naoetsu has obtained Airbus's certification, and is supplying cold-rolled coils of pure titanium to the company in large quantities.

To reduce the manufacturing costs of thin sheets, some processes have been omitted, and aiming at decreasing the surface defects of cold-rolled sheets, technical development has focused especially on measures to minimize the defects during hot rolling. Specifically, the mechanism by which hot-rolling defects arise has been examined from a metallurgical perspective, and the effects of the standards for ingot surface conditioning, slab grinding, etc., and those of the conditions of hot rolling on the occurrence of the surface defects of cold-rolled sheets have been clarified.

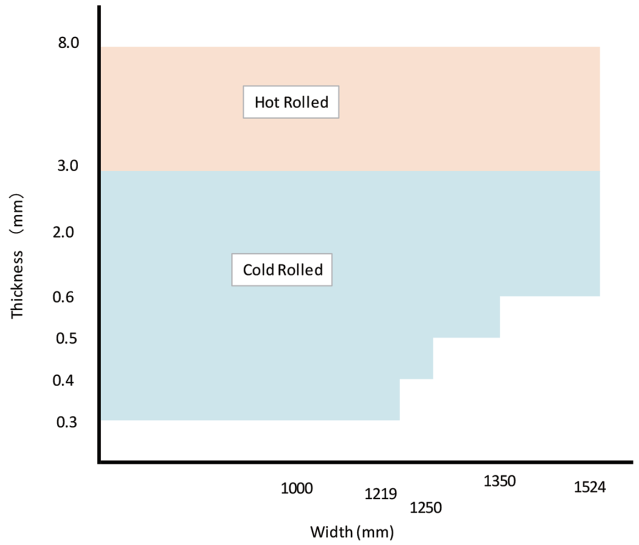

Fig. 7 Size range of hot- and cold-rolled sheets (JIS Classes 1 and 2 CP titanium)

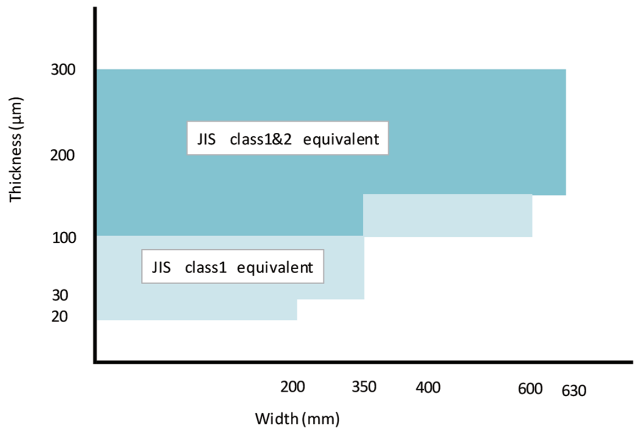

Fig. 8 Size range of foils (JIS Classes 1 and 2 CP titanium)

For PHEs, which are the largest use application of pure titanium thin sheets, press formability is important. Owing to adequate composition design and quality control in the processes of cold rolling and annealing, the product for the application has strength and ductility to customers' satisfaction and homogeneous material quality.

For titanium thin sheets for building applications such as roofs and other exterior finishing, the field of which Nippon Steel has cultivated over many years, the appearance design of the surface is important, and a wide variety of surface finishes have been developed to meet the tastes of designers. Typical surface finishes include dull finish, which is produced by making the surface of work rolls of the skin pass mill uneven by shot blasting and printing the unevenness on the sheet surfaces, alumina blasting, and coloring by anodizing. As a result, Nippon Steel's titanium thin sheets for building use hold a high share in the field. Recent supply references include the exterior finishing of the National Grand Theater in Jiangsu Province, China, which is one of the largest projects of Nippon Steel's supply of titanium building materials, covering a total area of 73 000 m^2, and the roof of the Katase Enoshima Station Building of Odakyu Electric Railway in Kanagawa, Japan, for which green-blue sheets and ion-plated sheets based on Nippon Steel's titanium coloring technology were used.

Titanium is used also for the exhaust system parts for motorcycles and four-wheel vehicles from the viewpoints of improving fuel efficiency by weight reduction and good appearance. To meet the needs for high strength at high temperature, Nippon Steel has developed unique copper-added titanium alloys for thin sheets such as Super-TIX™10Cu (Ti-1Cu), Super-TIX™10CuNb (Ti-1Cu-0.5Nb), and Super-TIX™10CSSN (Ti-1Cu-1Sn-0.35Si-0.25Nb).

4.4 Heavy plates

Titanium slabs for heavy plates are produced at Naoetsu by forging ingots, like those for thin sheets; they are then rolled into heavy plates at Yawata (see **Fig. 9**). After the merger of former Nippon Steel Corporation and Sumitomo Metal Industries, Ltd. in 2012, the titanium plate production was concentrated at Yawata, the plate mill of Naoetsu was closed, and the plate manufacturing technology accumulated there was transferred to Yawata.

The plate mill of Yawata has a wide manufacturing range (see **Fig. 10**), and is among the best in the world in terms of product quality. As a plate mill exclusive for titanium, it was newly equipped with a vacuum creep flattener (VCF) capable of simultaneously an-

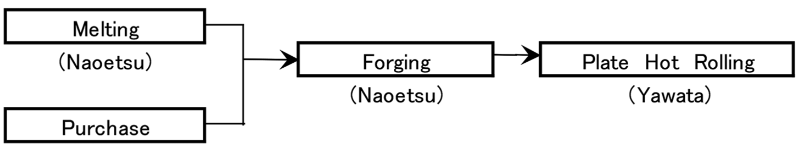

Fig. 9 Manufacturing processes of plate products

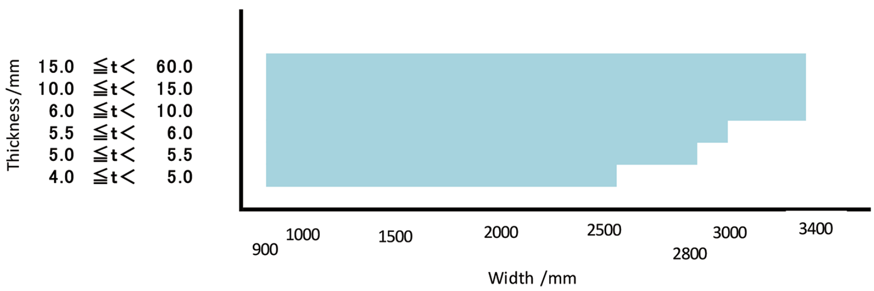

Fig. 10 Size range of heavy plates (JIS Classes 1 and 2 CP titanium)

nealing and hot-levelling to ensure good flatness. The high shape correction ability of the VCF has earned the high evaluation of customers.

Pure titanium plates are used for the drums for the manufacture of electrolytic copper foils for the printed-circuit boards of electronic devices; Nippon Steel's titanium plates for the application are highly evaluated in the market. The copper foils are manufactured by electrolyzing an aqueous solution of copper sulfate using a titanium drum as a cathode to have metallic copper deposited on the drum surface, and continuously winding it; high quality is required for the titanium drums. To satisfy the required product characteristics, the equipment and operating conditions of ingot casting, slab forging, and down-stream processes were precisely designed, and on that basis, technology to manufacture titanium plates that meet the required performance has been established. Further sales expansion is expected in the future in view of growing demands for electric vehicles and downsizing of home appliances.

4.5 Wire rods

Ingots are forged into blooms at Osaka, the blooms are rolled into billets at the section mill line of Kimitsu, and the billets are rolled into wire rods through the high-speed rolling mill line of Hikari (see **Fig. 11**). As with thin sheets, the manufacturing processes of wire rods are optimally controlled in a vertically integrated manner.

The size range is from 6 to 15.5 mm in diameter, and various surface finishes are available to meet different customer needs; such include Super Finish (SF) by special peeling and pickling finish.

The main application of titanium wire rods is for the frames of eyeglasses; in addition to pure titanium, titanium alloys such as Ti-3Al-2.5V and high-strength Ti-15V-3Cr-3Sn-3Al for forming into small diameters are used for spectacle rims.

4.6 Billets and bars

To manufacture products of pure titanium and titanium alloys, Osaka Area has a 3 000-t press, a high-speed forging machine, and a caliber rolling mill line (see **Fig. 12**). Osaka mainly manufactures titanium alloy products for aircraft use. It has established manufacturing technology and a quality assurance system for billets of Premium Grade Ti-6Al-4V for the rotating parts of aircraft engines for which extremely high quality is required, and obtained accreditations from aircraft builders.

4.7 Hot-extruded products

Nippon Steel has newly established a manufacturing process for hot-extruded products of titanium alloys (see **Fig. 13**). Applying the technology for hot-extruded products of stainless steel of Hikari, the material and shape of the dies were redesigned, heating temperature and lubricants were reviewed in consideration of the characteristics of titanium alloys, and on that basis, titanium alloy billets are extruded into products of different sectional shapes.

After hot extrusion and pickling, the bending and twisting of interim products are straightened in heat at Naoetsu. Besides shape correction, relieving of residual stress is important in this process.

To stably obtain products of high quality, the operation conditions for hot extrusion and straightening are determined based on FEM analysis of products of various sectional shapes.

Application procedures are under way to obtain accreditations of aircraft builders for the use of hot-extruded products of titanium alloys for the rails of aircraft seats. Since the products are made to near net shape, they serve to reduce the processing costs of aircraft companies.

5. Conclusion

Nippon Steel's titanium production processes range from melting to finishing of final products, which include thin sheets, heavy plates, welded pipes, wire rods, billets, round bars, and hot extruded sections. These products are used for general industrial applications, and also in the growing fields of aircraft, automobiles, building materials, and medical care. High quality is particularly required, in fields such as fuel cells, hydrogen-related facilities, and flying automobiles. As a world top runner, Nippon Steel will continue to aim at high quality and low costs of titanium products for such applications to meet the expectations of consumers, exercising its technical expertise.

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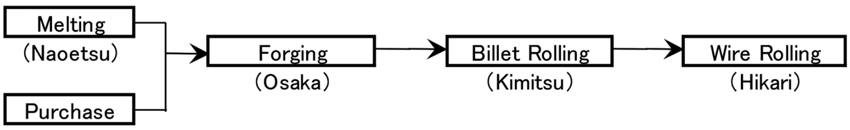

Fig. 11 Manufacturing processes of titanium wire rods

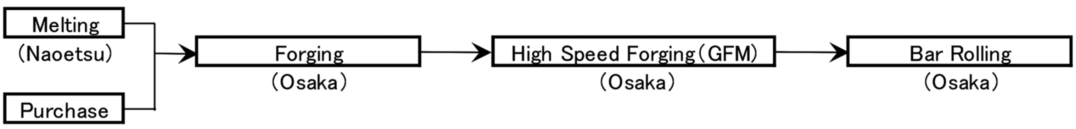

Fig. 12 Manufacturing processes of titanium billets and bars

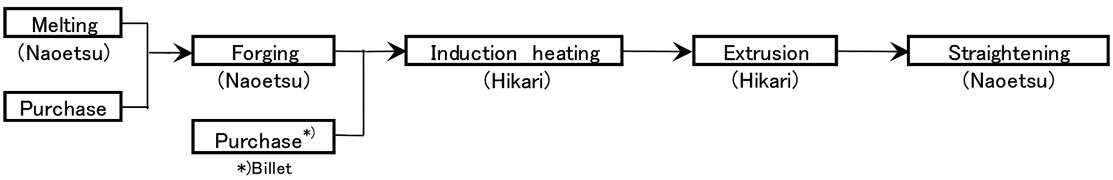

Fig. 13 Manufacturing processes of extruded titanium

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