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Technical Review

Non-Ferrous Structural Materials (Titanium, Aluminum)

Hideki FUJII* Makoto SAGA

1. Introduction

Capitalizing on its technological assets in the field of iron and steel, Nippon Steel Corporation has also been contributing to progress in nonferrous structural materials technology. In this technical review, we discuss titanium and aluminum—two representative nonferrous structural materials.

2. History of Technological Development in the Fields of Titanium and Aluminum

In 1983, the Titanium Division of Nippon Steel started manufacturing titanium sheet, plate, wire rod and pipe by taking advantage of the powerful steelmaking facilities of the company. Since then, the division has continued to expand production and sales of titanium products that are characterized by excellent corrosion resistance, lightweight, and high strength, etc. Today the company is among the leading manufacturers of various titanium products, mainly pure titanium sheet for industrial use. Needless to say, the titanium refining and re-melting processes are markedly different from those for steel. Therefore, the company purchases ingots or slabs of titanium from outside and makes them into final titanium products mainly employing its steelmaking facilities, but partly using equipment exclusive to titanium production, in the hot rolling process and succeeding processes.

Incidentally, the material properties of the final titanium products are significantly influenced by the qualities of the titanium ingots, such as the added elements and impurities. In cooperation with Toho Titanium Co., Ltd.—the largest supplier of titanium ingots to Nippon Steel, the company has applied itself to the research and development of technology to manufacture sponge titanium, which is the principal raw material for metallic titanium, and titanium ingots (remelting process) and to research and development on ways to improve the material properties, including titanium alloys. By so doing, the company has delivered high-quality titanium products to its customers. In addition, armed with its high-quality titanium products and the results of the research and development it has conducted from a unique viewpoint, the company has come up with various original titanium products, including new titanium alloys, thereby further expanding existing markets—the chemical and electric power industries—and, at the same time, developing new markets in the field of so-called civil-life requirements—civil engineering, architecture, automobiles, home appliances. In that way, Nippon Steel has contributed to the development of the titanium industry and various other related industries.

On the other hand, the introduction to the aluminum business of Nippon Steel dates back to 1964, when SKY Aluminum Co., Ltd. was founded jointly by the then Yawata Iron & Steel Co., Ltd., Showa Denko K.K. and Kaiser Aluminum of the United States. In the early 1990s, in order to respond to a bill calling for stringent automotive fuel efficiency regulations that was being hotly debated in the United States, it became an important issue for Japanese automakers, too, to reduce the weight of their cars. Having foreseen that it would become indispensable not only to increase the strength of its steel products for automobiles but also to expand the use of aluminum alloys which are lightweight materials, Nippon Steel strengthened its ties with SKY Aluminum and started up an automotive aluminum joint venture. In 2003, SKY Aluminum and the light metals division of Furukawa Electric Co., Ltd. were merged into Furukawa-Sky Aluminum Corp.—Japan's largest aluminum rolling company. Today, Nippon Steel and Furukawa-Sky have established a cooperative business organization, the former being responsible for the marketing and R&D for the automotive aluminum joint venture and the latter for the manufacturing and R&D.

In the field of automobiles, the use of rolled or extruded aluminum materials for car bodies and undercarriages is especially noticeable. The application of aluminum in this particular field has been steadily increasing. The major drawback of aluminum as a material for automobiles is its "formability", which is inferior to that of steel. Nippon Steel and Furukawa-Sky have jointly developed the 5xxx series Al-Mg alloys for car bodies featuring high strength and good formability and the 6xxx series Al-Mg-Si alloy sheets offering both greater strength (bake hardenability) attained by the bake treatment during painting, and better formability.[1)] In addition, various types of extruded aluminum products, bumper reinforcement parts, and undercarriage components have been developed.

3. Development of Manufacturing Process for Commercially Pure Titanium Products and their New Markets

Commercially pure titanium is sufficiently ductile and relatively easy to work. Thus, it is a suitable material for manufacturing rolled products on a steel mill. On the other hand, it has quite a few properties which are inherently different from those of steel. Examples include: pure titanium is a very active metal which tends to adhere to the rolling rolls and surrounding equipment easily; the Young's modulus of the metal is small; the metal easily absorbs hydrogen and tends to be oxidized at high temperatures; the metal shows strong anisotropy in mechanical properties ascribable to its crystalline structure (close-packed hexagonal structure); and the metal is non-magnetic. Furthermore, as titanium is much more expensive than steel, improving the yield of titanium in the manufacturing process is vitally important in determining the success or failure of the titanium busi-

* Chief Researcher, Dr.Eng., Sheet Products Lab., Steel Research Laboratories
20-1, Shintomi, Futtsu, Chiba 293-8511

ness.

When it comes to manufacturing titanium on a steel mill, therefore, it is necessary to have a thorough understanding of those properties and issues of titanium listed above that are entirely different from steel. Nippon Steel's titanium manufacturing conditions might not be as good as those where titanium is produced using dedicated manufacturing equipment designed for titanium, but even so, the company has been producing high-quality rolled titanium products at its Nagoya Works (slabbing), Hirohata Works (hot rolling), Hikari Works (cold rolling, welded tube, wire rod) and Yawata Works (plate). At present, most of the processes at Hikari and all processes at Yawata belong to Nippon Steel & Sumikin Stainless Steel Corporation, which, as a member of the Nippon Steel Group, is striving for stable production of titanium products with a strong sense of solidarity.

As described in Chapter 2, by manufacturing pure titanium products using the above processes, Nippon Steel has supplied, on a stable basis, the ever-expanding titanium markets, including steam condensers of power stations, heat exchangers, and chemical plants. At the same time, the company has played an important role in exploiting new markets in the field of civilian requirements, including seawater desalination plants, civil engineering and architecture, spectacle frames and portable home appliances.

In the field of civil engineering, titanium is used in large quantities in bridges and offshore structures, since these are required to have exceptional corrosion resistance. For example, more than a decade ago, Nippon Steel's original titanium-clad steel plate using Cu as an insert was adopted to prevent corrosion of the bridge piers of the Trans-Tokyo Bay Highway ("Aqualine")[2] that are subject to rising and falling tides and exposed to seawater splashes (for the development of the titanium-clad steel, the company received the Ichimura Industrial Award in 1999). Recently, about 1,000 tons of titanium sheet were employed to prevent corrosion of the back and side faces of the pier of Haneda Airport D-Runway that came into operation in the autumn of 2010.

In the field of architecture, titanium materials with artistic surfaces including unique hues given by a special surface treatment or anodic oxidation are used for the roofs and walls of cultural structures and landmark buildings. For example, for the main building at Koetsuji Temple in Kyoto (see **Fig. 1**), a titanium roof with a comparable feeling to the traditional Japanese-tiled roof was created by special alumina blasting.[3] For the role the titanium roof plays in protecting the cultural asset against deterioration due to acid rain, etc. while securing the cultural value of the building, Nippon Steel received the 2003 Good Design Award (together with the late Koichi Kinoshita, master builder at Sukiya Kenkyusho Shindenan, and Tomoaki Yamashita, chief priest of Koetsuji Temple) and the 2004 Otani Art Museum Award.

Fig. 1 Main building with a titanium roof at Koetsuji temple

Many roofs on traditional buildings in Japan are made of copper sheets which are subject to verdigris. The unique hue of verdigris adds to the cultural value of those buildings. It has become possible to impart the color of verdigris to titanium roofs by means of alumina blasting coupled with anodic oxidation. The treatment was first applied to the roofs of the Homotsuden Treasury at the Kitano Tenmangu Shrine. Recently, examples of application of the treatment are increasing in number. Alumina-blasted titanium tiles have recently been used for the roofs of the Hozomon Gate at Sensoji Temple (**Fig. 2**) and the main building of the temple as well. Titanium is also employed for highly decorative ridge-end tiles called "onigawara" in Japanese (Fig. 2). Titanium tiles have a similar feeling to traditional Japanese tiles but are about one-fifth in weight. The use of titanium for roofing has helped improve the seismic resistance of the building. For the Hozomon, Nippon Steel received the 2006 Otani Art Museum Award, together with Shimizu Corporation, Caname Co., Roof System Co., and Hibiki Corporation. For the main building at Sensoji Temple, the company won the same award for 2010, together with Sensoji Temple and Shimizu Corporation.

The main drawback with titanium roofs was discoloration, that is, its gradual change in color as it aged. On the basis of its research, Nippon Steel clarified the mechanism causing the discoloration as follows: When TiC or F is deposited on the titanium surface, the oxide film formed on the surface grows when subjected to acid rain and eventually produces an undesirable color due to interference.[4, 5] Today, thanks to improvements in titanium manufacturing technology that ensures carbon is sufficiently removed from the surface layer, it has become possible to completely prevent such discoloration. **Fig.**

Fig. 2 Hozomon gate with titanium roofs at the Sensoji temple
Upper right: Close look at the corner of the roof, Lower right: Ridge-end tile "Onigawara" made of titanium

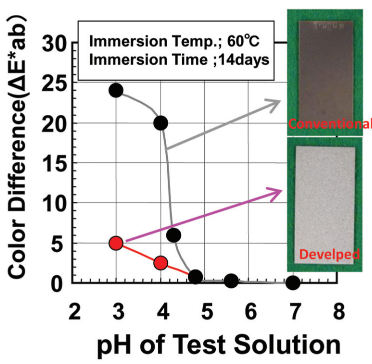

Fig. 3 Transition of color difference during exposure in acid circumstance for a developed colorfast titanium sheet and an ordinary one

3 shows the changes in color of a colorfast titanium sheet and an ordinary one when they were exposed to an acid environment. It can be seen that the colorfast titanium sheet has excellent resistance to discoloration. The above new technology won the 2004 Technology Award from the Japan Institute of Metals.[6)]

In the field of consumer electronics, as in the field of architecture, the beautiful surface of titanium sheet leads to its widespread use in the casings for various types of portable electrical products. Incidentally, in the press-forming process for titanium sheet, which has strong planar anisotropy, Nippon Steel's high-precision numerical simulation technology—which takes such anisotropy fully into account—is applied.[7)]

4. Development of High-Performance Titanium Alloys and Their Applications

The market for commercially pure titanium has been expanding remarkably thanks to its excellent corrosion resistance combined with aesthetic appeal and good formability. Concerning titanium alloys which are exceptionally light and strong, it could hardly be said that their application in the fields of general industries and civilian requirements had been brisk until the 1990s, although they were among the principal materials for the aerospace industry. The major reason for that was cost. Since the mid-1990s, Nippon Steel has been striving to expand the application of titanium alloys in non-aviation industries through comprehensive development of technology to reduce the cost of raw materials, technology to cut manufacturing costs, and technology to utilize the titanium alloys including the users' in-house processes.

One of the results of the company's R&D efforts is the Super-TIX® Series of original titanium alloys composed mainly of inexpensive, ubiquitous elements with no or only small amounts of expensive elements (V, Mo, etc.) which are used in considerable quantities in conventional titanium alloys.[8-10)] The alloying elements for most of those titanium alloys account for up to about 10% of the total cost of the raw materials. In addition, some improvements have been made in the manufacturing technology and several new functions have been added to those titanium alloys. Today, Nippon Steel's original titanium alloys have come to be widely used for various purposes, including automotive parts, shipping-related parts, high-speed rotary machine parts, sporting goods, and special outfits.

Fig. 4 shows the schematically represented relationship between strength and ductility, obtained with conventional titanium alloys and titanium alloys developed by NSC which replace all or some of the V/Mo with Fe—an inexpensive, widely used β-stabilizing element. In the figure, modified commercially pure titanium is, strictly speaking, a material which is considered to be classified as a kind of pure titanium. With a comparatively large proportion of Fe added to help to control the grain size, this material is used for motorcycle mufflers, etc. The Super-TIX® 800 is a Ti-1%Fe-0.35%O-based alloy with a tensile strength of about 800 MPa. Since this alloy does not contain Al which causes the hot formability of titanium alloy to deteriorate, it has good hot formability and is made into various products, including plate, hot- and cold-rolled sheet, and wire rod.

The Super-TIX® 51 AF is a Ti-5%Al-1%Fe-based alloy with O added for fine adjustment of strength. This alloy is comparable in strength to the most popular titanium alloy Ti-6%Al-4%V of extra low interstitial (ELI) grade to standard grade. It is lightweight and strong and is superior to Ti-6%Al-4%V in hot formability and Young's modulus. Round bars and hot-rolled strips of this alloy are mass-produced. An example of the application of this alloy is for golf clubs, as shown in **Fig. 5** (a). Concerning the Super-TIX® 523 AFM (Ti-5%Al-2%Fe-3%Mo), which is even stronger than the other developed titanium alloys, it was necessary to add 3% Mo—an expensive element—in order to avoid the influence of Fe solidification segregation that becomes a problem when manufacturing large ingots. However, the high strength and excellent fatigue life of this alloy more than offset the extra material cost. Wire rod made from this alloy is used for intake engine valves in motorcycles and four-wheeled vehicles, etc. (Fig. 5 (b)).

Super-TIX® 523 AFM can be further strengthened by a suitable heat treatment. In addition, it permits drastically reducing the 0.2% proof stress from about 950 MPa of ordinary annealed materials to about 420 MPa. (It is also possible to regain its original strength by working or heat treatment.) Furthermore, this alloy allows for some unique functions, such as facilitating cold working and reducing the normal Young's modulus of about 110 GPa to about 70 GPa which is comparable with that of β -type alloys.[10, 11)] At present, strenuous efforts are being made to develop new uses for the alloy, which has a number of advantageous characteristics as mentioned above. Incidentally, it has been clarified by a detailed structural analysis that the above unique phenomena occur as a result of the two-stage ($\beta \rightarrow \alpha'' \rightarrow \alpha'$) deformation-induced martensite transformation.[10, 11)]

In addition to the high-strength alloy series with Fe added, the Cu-added titanium alloys, Super-TIX® 10CU (Ti-1%Cu) and Super-TIX® 10CUNB (Ti-1%Cu-0.5%Nb), which offer comparable cold formability and heat resistance to pure titanium, have been developed.[12-14)] As shown in **Fig. 6**, cold-rolled sheets of those titanium

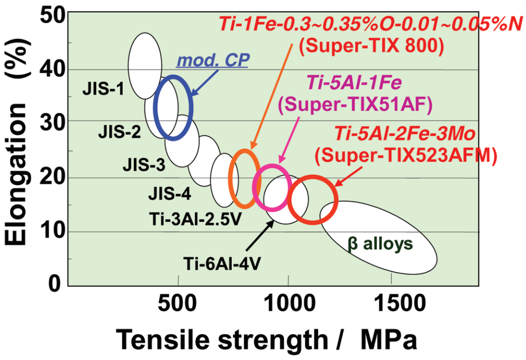

Fig. 4 Strength-ductility relationship of conventional titanium materials and some of the alloys developed by Nippon Steel containing Fe as an inexpensive and widely-used ubiquitous element (Schematic drawing)

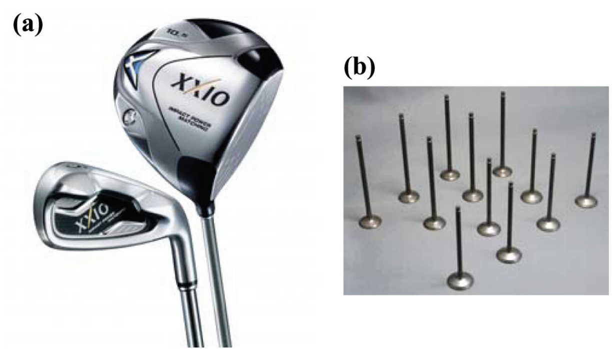

Fig. 5 (a) Golf club head made of Super-TIX®51AF (XXIO, SRI Sports Ltd.), (b) Intake engine valves made of Super-TIX523®AFM for motorcycles (Aisan Industry Co., Ltd.)

Fig. 6 Examples of mufflers made of Super-TIX®10CU (NB)

alloys are widely used for the mufflers and exhaust systems of automobiles. The excellent high-temperature strength of those titanium alloys is attributable to solid-solution strengthening by Cu, and their good formability at room temperature is based on the new knowledge that the addition of Cu does not affect the twin deformation that accounts for the superior formability of pure titanium. Namely, the above titanium alloys combine these convenient properties—low strength and good formability at room temperature and high strength at high temperatures. For the above new knowledge and the application thereof, the alloys won the 2010 Technology Award of the Japan Institute of Metals.[14)]

As has been described above, Nippon Steel has developed original titanium alloys utilizing inexpensive, widely used ubiquitous elements, rather than conventional titanium alloys for aircraft, and has expanded the scope of application of those original alloys. In particular, for its efforts to expand the use of its titanium alloys in the field of automotive parts, Nippon Steel won the first Titanium Application Development Award of the International Titanium Association (ITA) in 2007.

5. Developing New Aluminum Alloys for Automobiles

Aluminum alloys are inferior to steel in terms of press formability at room temperature. With the aim of compensating for that drawback, Nippon Steel, Furukawa-Sky and Honda Motor Co., Ltd. co-developed a high-speed, high-temperature blow forming technique that permits shortening the forming time by heating the material to a high temperature and thereby increasing its ductility (**Fig. 7**). Then, Nippon Steel developed the 5xxx series aluminum alloy sheets suitable for high-temperature blow forming. The ductility of the 5xxx series aluminum alloy is about 30% under ordinary tensile test conditions. Under high temperatures, however, it displays good formability thanks to the effects of grain boundary sliding and solute drag (i.e. dynamic drag of dislocation shift by solute Mg) (**Fig. 8**)[15)]. The 5xxx series alloy was developed based on Furukawa-Sky's technology incorporated in its "ALNOVI," a superplastic forming aluminum alloy for high-temperature blow forming, and by taking advantage of the above characteristic. Unlike ordinary superplastic aluminum alloys for high-temperature blow forming, the newly developed alloy does not require a special manufacturing process. Thus, it is an inexpensive material which can be manufactured with high productivity. In addition, the alloy composition is optimized to restrain grain coarsening during blow forming, since that weakens the alloy.[16)]

Formerly, the aluminum alloy sub-frame members of automobiles were, in many cases, fabricated by hydroforming the material tube at normal temperature. However, the formability was not sufficient. Therefore, Nippon Steel developed the "hot bulge forming process" which first heats the material to a high temperature to increase its ductility, and then forms it using compressed air. The process allowed for hot forming of aluminum alloy tube for the first time at a high temperature just below its melting point. We also developed the 5xxx series extruded aluminum material for hot bulge forming compatible with the above process. This material, too, maintains its high strength since the mixing ratio of added elements is optimized to restrain the coarsening of grains in the forming process .[16)]

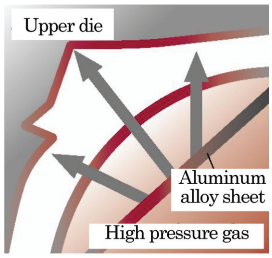

Fig. 7 Outline of high-temperature blow forming
The materials are formed at temperatures just below the melting point.

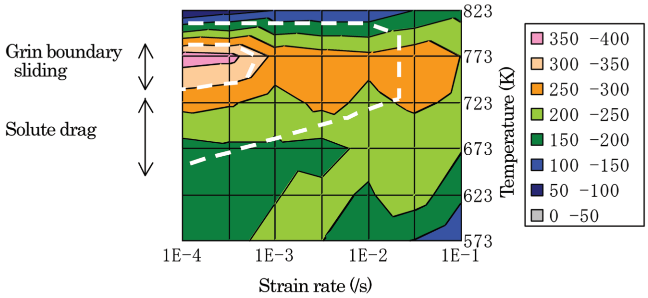

Fig. 8 Effects of temperature and strain rate on high temperature ductility on a 5xxx series aluminum alloy A5182

Thanks to the above R&D results, etc. which have dramatically lowered the hurdles in the way of forming aluminum alloys, it became possible to form even aluminum alloys into complicated shapes. In 2004, an aluminum alloy sheet was applied for the first time to Honda Motor's latest Legend model. As a result, the trunk lid frame was made 47% lighter than that made from steel sheet and the sub-frame member was made 38% lighter than that made from steel. In addition, it became possible to design and form aluminum alloy sheet into exquisitely curved shapes which would be impossible with steel sheet (**Fig. 9**)[17)].

For the remarkable R&D results mentioned above, Honda Motor Co., Ltd., Furukawa-Sky and Nippon Steel received the Nikkei Superiority Award for Excellent Products and Services in 2004 and the 2004 Technology Award from the Japan Aluminum Association.

The 6xxx series aluminum alloys, which allow for high strength due to its paint baking hardenability and lighter weight thanks to thickness reduction, has become a mainstream material for body panels. This series combines bake hardenability and various other properties required of materials for panels by virtue of the total control of the complicated phenomena of precipitation/cluster formation, the distribution of second phase in the crystal grains, and texture, etc.[18, 19)] For example, concerning bake hardenability, by appropriately controlling multiple clusters that are formed at around 70℃ and which significantly influence the precipitation of β" phase, which

Fig. 9 Trunk lid inner manufactured with high-temperature blow forming
A less expensive aluminum alloy developed by Nippon Steel and Furukawa-Sky is employed.

is the reinforcement phase during heat treatment, an aluminum alloy comparable in strength to soft steel is obtained as the result of work hardening during press forming and precipitation strengthening during paint bake treatment. For the engine hood and other parts for which 6xxx series aluminum alloys are abundantly used, bendability is required to make the outer and inner panels into a single unit by caulking. In this respect, the desired properties are imparted to the alloys by structural control while taking into consideration the influences of second-phase particles and textures, etc.[20, 21)]

When the 6xxx series of aluminum alloys is applied to automobile bodies, the quality of the body surface after press forming is one of the most important issues. If a large strain is applied to the material during press forming, parallel streaks known as ridging patterns can occur in the rolling direction, impairing the aesthetic appeal of the finished surface. This ridging pattern is considered to be a phenomenon whereby irregularities in the surface occur as grains of a specific orientation along the pattern show the same behavior of deformation.[18, 19)] In order to meet the strict quality requirements of users, by making the most effective use of the structure control technology accumulated in the development of aluminum alloys and

Table 1 Strain causing ridging pattern in the developed aluminum alloy and an ordinary one (○: hardly recognized, △: slightly recognized, ×: clearly observed)

	Strain (%)				
	4	8	12	16	20
Ordinary 6xxx series alloy	○	○	△	△	×
Developed 6xxx series alloy	○	○	○	○	△

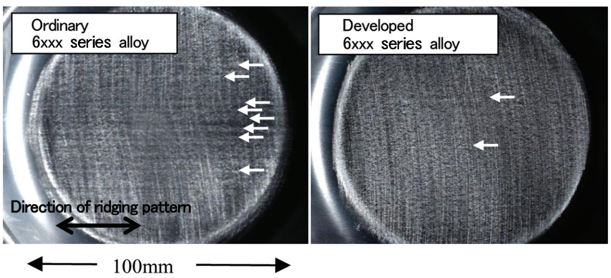

Fig.10 Ridging patterns after deformation at 16% of strain in the developed aluminum alloy and an ordinary one
Ridging patterns are emphasized by polishing the surfaces with emery paper after deformation.

steels, Nippon Steel and Furukawa-Sky have co-developed the 6xxx series aluminum alloys that hardly produces any ridging pattern even when subjected to strong forming (**Table 1**, **Fig. 10**). These 6xxx series alloys impart a good appearance even to those parts which require highly decorative work. It is considered a promising material which can further boost freedom of design.

Nippon Steel and Furukawa-Sky are also tackling the development of structures for automotive parts to which aluminum alloy material is applied. One of the most important performance issues regarding the engine hood, which represents the most advanced application of aluminum alloy to the car body, is the “pedestrian head-protection performance” by minimizing the impact to the head of a pedestrian in any accidental collision involving the engine hood, etc. of a car. By taking advantage of the knowledge obtained from the development of steel application technology, the two companies are also tackling development of hood inner structures which have the above performance and which retain the advantage of using an aluminum alloy, in other words, which benefit from being light in weight.

6. Conclusion

As has been described, titanium and aluminum have also experienced remarkable advances with the aid of the technology accumulated in the field of steel. In concluding this technical review, we discuss the future of those nonferrous materials.

Recent years have seen a marked increase in the demand for titanium alloys in the aircraft industry. In addition, there has been steady demand for pure titanium for seawater desalination plants and power station steam condensers, etc. There are even reports that demand for titanium will double in the next ten years. However, the outstanding properties of titanium have not yet been fully utilized. It is considered, therefore, that there is probably still more potential demand for titanium. In order for us to be able to fully benefit from the superb characteristics of titanium—exceptional corrosion resistance, small specific gravity, excellent strength—it is of the most important to cut the cost of this nonferrous material further. From the standpoint of assuring the progress of titanium in the future, it is indispensable not only to press ahead with reductions in the cost of the alloying elements added to titanium and the cost of manufacturing, but also to tackle the development of innovative new technologies for the upstream processes – from refining to re-melting.

Concerning aluminum alloys, it is expected that the application of aluminum alloys, as well as high-strength steel materials, will continue expanding in view of the automobile fuel efficiency regulations that are becoming increasingly stringent. In addition to the advantageous properties inherent to aluminum alloys—small specific gravity, excellent corrosion resistance, high thermal conductivity, the technologies that permit forming aluminum alloy into complicated shapes and maintaining a good surface quality even after forming—as described in the text, are expected to contribute much to the expansion of application of aluminum alloys. In order to further promote the growth of aluminum alloys for automobiles in the future, it is important for Nippon Steel and Furukawa-Sky to bring about further technological innovations by taking advantage of the steelmaking technology of Nippon Steel and the aluminum technology of Furukawa-Sky. Furthermore, it is expected that our proposal for multi-material structures that use the right materials (high strength steel, aluminum alloy, etc.) in the right places will help reduce the weight of automobiles.

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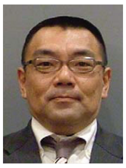
Hideki FUJII
Chief Researcher, Dr.Eng.
Sheet Products Lab.
Steel Research Laboratories
20-1, Shintomi, Futtsu, Chiba 293-8511

Makoto SAGA
Chief Researcher
Sheet Products Lab.
Steel Research Laboratories

Collaborator

Hiroshi SHIMIZU
Manager
Sales Dept. III, Titanium Division

Takashi DOMOTO
Department Manager
Sales Dept. III, Titanium Division



Masafumi KASANO
Manager
Sales Dept. I, Titanium Division

Hiroshi OSAWA
Manager
Planning & General Affairs Dept.
Titanium Division

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

Akihiro MURATA
Senior Manager
Automotive Aluminum Products Dept.
Automotive Flat Products Sales Div.

Youichirou BEKKI
Manager
Research Dept. I
Technical Research Div.
Furukawa-Sky Aluminum Corp.