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Technical Report

Development of Manufacturing Technology of Commercially Pure Titanium Sheets by Titanium Sponge Direct Rolling Process

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Abstract

We have developed the "Titanium Sponge Direct Rolling Method" to improve productivity in the manufacturing process of titanium mill products. This process eliminates the melting and forging steps required in conventional processes. Titanium packages were prepared from titanium briquettes obtained from press-formed titanium sponge. Titanium plates and thin sheet coils produced in the rolling process were evaluated. As a result of the verification phase, it was confirmed that the basic principles of this process were appropriate. In addition, by optimizing the structure and construction method of the package and improving high-quality titanium sponge, we were able to obtain well-shaped, crack-free titanium plates and titanium thin sheet coils with a width of 250 mm from practical size titanium packages. The resulting thin sheet coils have tensile properties and formability comparable to (JIS Class 1) titanium sheets manufactured by the conventional melting process.

1. Introduction

Titanium is a highly corrosion-resistant metal, and the specific strength (strength/density) of titanium alloys is the highest among structural metal materials. By drawing on these advantages, commercially pure titanium is used for components that will come into contact with seawater or corrosive media, such as heat exchangers and offshore structures, and for reaction layers and distilling columns for chemical plants; titanium alloys are also used for parts for jet engines and landing gears in the aviation/space sector.[1–3] In addition, the effective use of these titanium materials improves the fuel economy of automobiles and other types of transportation equipment, which is expected to reduce energy consumption and CO_2 emissions.

However, the annual shipment of titanium mill products in Japan is less than 20000 tons (shipment of titanium mill products in 2019: 16303 tons, according to the Japan Titanium Society[4]). Compared to steel and aluminum, the usage (output) of titanium materials, such as commercially pure titanium and titanium alloys, is smaller and they are rarely used for automobiles and other types of land transportation equipment. It cannot be said that titanium use has spread throughout the world.

The major reason why titanium, the material having these excellent characteristics, has not been widely distributed in the world is its costs. Because titanium's affinity with oxygen is strong, it is difficult to obtain titanium metal by directly deoxidizing titanium ore (titanium oxide) as a raw material. Accordingly, in the Kroll process, which is the representative titanium refining process, the ore is once turned to titanium chlorides ($TiCl_4$) and then reduced with Mg to produce titanium sponge (lump titanium metal having many cavities).[5, 6] In addition, because molten titanium strongly reacts with refractories such as Al_2O_3 and SiO_2, there is no practical container that can maintain such a molten state. Therefore, to melt and cast titanium materials, batch-type special melting and casting processes that consume a large volume of electricity (e.g., vacuum arc melting and electron-beam melting) are used instead of efficient continuous casting, which is used for steel and aluminum. As described above, a very large amount of energy is required to obtain titanium metal, and its manufacturing processes are complicated, involving many steps from raw material to refining (chlorinating and reduction), melting, forging, rolling, and heat treatment. As a result, the lead time is long, the manufacturing cost is high, and CO_2 emissions are also large.

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To promote the use of titanium materials, it is necessary to reduce the costs by improving the productivity of the titanium refining and titanium material manufacturing processes. As technologies to achieve these tasks, the New Energy and Industrial Technology Development Organization in Japan (NEDO) adopted the “Development of innovative low-cost manufacturing processes of titanium thin sheet” as part of “New Innovative Structural Materials Research and Development” and conducted the project under the guidance of the Innovative Structural Materials Association in Japan (ISMA).[7–9] In the project, Toho Titanium Co., Ltd. (ISMA Chigasaki Office) developed two technologies: A high-efficiency manufacturing process technology for producing high-quality titanium sponge to reduce contamination by impure elements in the current titanium sponge manufacturing process (Kroll process); and a new titanium refining technology that turns titanium ore into metal titanium by a new refining technology different from the existing Kroll process. Nippon Steel Corporation (ISMA Futtsu Office) developed a high-efficiency, titanium thin sheet manufacturing technology that directly rolls titanium sponge to obtain titanium thin sheets, aiming at eliminating the melting and forging steps from the current processes. At the same time, we pursue the goal of significantly reducing CO_2 emissions throughout the processes from titanium refining to titanium material manufacturing.

This paper introduces the development of commercially pure titanium sheets by the titanium sponge direct rolling process, focusing on the high-efficiency, titanium thin sheet manufacturing technology developed by Nippon Steel (ISMA Futtsu Office).

2. Concept of the Development

Figure 1 illustrates the fundamental concept of the “development of innovative low-cost manufacturing processes of titanium thin sheet.”[10] The developed high-efficiency titanium thin sheet manufacturing technology, as shown on the right side of Fig. 1, eliminates the titanium material melting and forging steps and manufactures sheets by directly rolling and heat-treating titanium sponge (raw material) (hereinafter, “titanium sponge direct rolling process”). The omission of the melting and forging steps can reduce the lead time and the costs of titanium materials and can also contribute to CO_2 emissions reduction by reducing electricity consumption. Titanium sponge is press-formed into briquettes, and the briquettes are put into titanium boxes made by packing materials (titanium plates) to form titanium packages. Titanium packages are used as materials for hot rolling (slabs). The downstream steps are the same as those in the existing titanium sheet manufacturing processes—titanium sheets are manufactured through hot rolling, oxidized layer removal, cold rolling, and heat treatment. In this rolling, the packing materials of the packages and briquettes inside diffuse and join to turn into one plate.

For the titanium sponge direct rolling process, the melting step is omitted, and thereby it is difficult to evenly disperse elements contained in titanium sponge (such as O and Fe). In addition, a small quantity of $MgCl_2$ remains in titanium sponge manufactured by the Kroll process (hereinafter, “residual $MgCl_2$”) and this residual $MgCl_2$ remains in the sealed packages. Therefore, the titanium sponge used for the titanium sponge direct rolling process is required to be homogeneous and contain a smaller quantity of residual $MgCl_2$. Although the existing Kroll process can manufacture only a small amount of such titanium sponge, its industrial use is not commensurate with the cost. Therefore, a new manufacturing process that would be able to mass-produce homogeneous raw material titanium with less residual $MgCl_2$ at a cost lower than the current cost needed to be developed (left side in Fig. 1). Accordingly, Toho Titanium (ISMA Chigasaki Office) took charge of the two developments: A high-efficiency manufacturing process technology for producing high-quality titanium sponge to improve the existing Kroll process and a new titanium refining technology to develop a new refining process different from the Kroll process.

3. Examination of Basic Properties

In the development of the titanium sponge direct rolling process, titanium sponge materials that were manufactured by the existing Kroll process and contain different levels of impurities were used as raw materials to fabricate titanium sheets on a laboratory scale, and they were evaluated.

3.1 Testing procedure

General-purpose titanium sponge with different compositions manufactured by the existing Kroll process was used to fabricate titanium packages, materials for hot rolling. Considering the ease of handling in testing, they were fabricated with their thickness being 75 mm and their weight 3 to 4 kg (hereinafter, “small packages”). The titanium sponge was press-formed into briquettes, and then they were cut into appropriate sizes. They were put into titanium boxes consisting of titanium plates, and packing materials. The packages were covered with titanium plates (packing materials), the inside was evacuated, and then the packages were sealed. The small packages were heated for hot rolling. The scales on the surfaces were removed, and then the sheets were cold-rolled into sheets with a thickness of 0.5 to 1.0 mm. **Figure 2** shows the fabricating process.[11]

The cold-rolled sheets were heat-treated and JIS 13B half test pieces (length of the parallel section: 30 mm) were sampled from the section near the center in the width direction and at the constant region in the lengthwise direction in such a way that the pulling direction would be the rolling direction. These test pieces were subjected to tensile tests at room temperature at the initial strain rates of

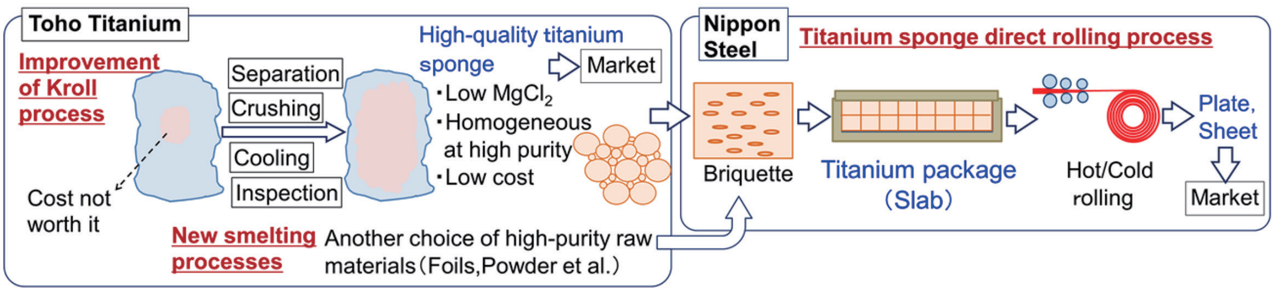

Fig. 1 Fundamental concept of “Development of innovative low-cost manufacturing processes of titanium sheet”[10]

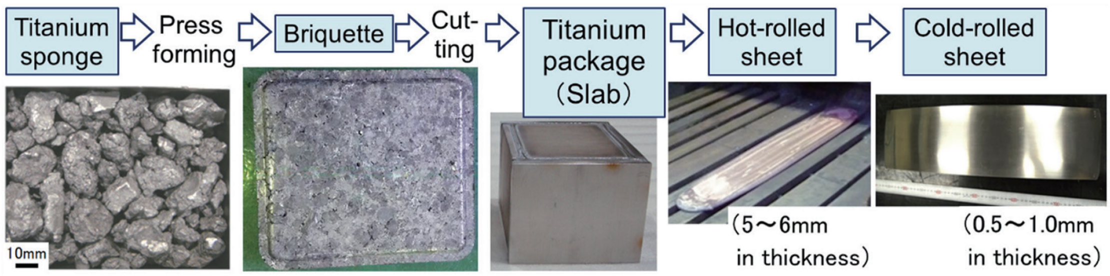

Fig. 2 Fabricating process of titanium cold-rolled sheet in the laboratory, and appearance of trial materials [11]

$6.7 \times 10^{-5} s^{-1}$ (to the yield point) and $5.0 \times 10^{-3} s^{-1}$ (after the yield point).

3.2 Rolling results

The structure of the titanium packages, manufacturing method, and rolling conditions were examined and considered to be appropriate. As a result, defects such as cracks and swelling didn't arise during heating before the hot rolling and during the hot rolling. No cracks arose during the cold rolling as well. Thus, well-shaped hot-rolled sheets and cold-rolled sheets were obtained from the small packages.

3.3 Cavities (pores) and structure

Briquettes that are press-formed titanium sponge have many cavities. The macrostructure of the cross section of the hot-rolled sheet sampled during the hot rolling was observed to see how these cavities would decrease. **Figure 3** shows the results. The packing material and briquette were unified as the rolling proceeded and the gaps between the packing material and briquette and the cavities inside the briquette were pressed. After filling the cross sections of the hot-rolled and cold-rolled sheets with resin and grinding them, close observation of them revealed small holes (pores) that the cavities had turned. Appropriately adjusting the titanium package manufacturing conditions and rolling conditions enabled reduction of the ratio of the area of the pores on the cross section of a cold-rolled sheet to less than 0.2%.

Furthermore, by appropriate annealing of these cold-rolled sheets, the same metal structure (equiaxed α grains) as that of existing titanium sheets manufactured via a melting step was obtained.

3.4 Tensile properties

Cold-rolled and annealed sheets whose ratios of the areas of the pores were less than 0.2% and whose thicknesses were 0.5 to 1.0 mm were subjected to tensile tests. **Figure 4** shows the results.[10] As a comparison, the figure also shows the tensile properties of a cold-rolled and annealed sheet (JIS Class 1) that was fabricated from a slab manufactured via a melting step (hereinafter, the "present material") (◆). For the cold-rolled and annealed sheets fabricated from general-purpose titanium sponge containing residual $MgCl_2$, the average oxygen concentration is rather high and, as their tensile properties, the strength tends to be higher and the ductility tends to be lower compared to the present material. However, the strength-ductility balance is the same as that of the present material for most cases (●). On the other hand, the ductility of some samples is remarkably lower, deviating from this strength-ductility balance. Fractographic study of these test pieces and elementary analysis of their cross sections revealed that $MgCl_2$ had accumulated at part of the fractures. Meanwhile, for the cold-rolled and annealed sheets that were fabricated from high-quality titanium sponge whose quantity of residual $MgCl_2$ was smaller than a certain amount, the average oxygen concentration is low, and thereby their tensile properties showed that the strength tends to be low and the ductility tends to be high; the strength-ductility balance is at the same level as that of the present material and no samples with low ductility were detected (▲).

As just described, it was found that using high-quality titanium sponge whose quantity of residual $MgCl_2$ is less than a certain amount can stably obtain tensile properties at the same levels as those of the present material. Combined with the results in 3.3 above, cold-rolled and annealed sheets fabricated by the titanium sponge direct rolling process are at almost the same level as normal titanium sheets that are manufactured via a melting step.

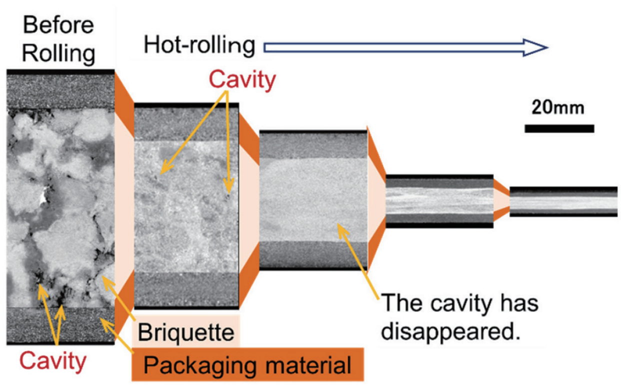

Fig. 3 Structural transition of thickness cross section by hot-rolling

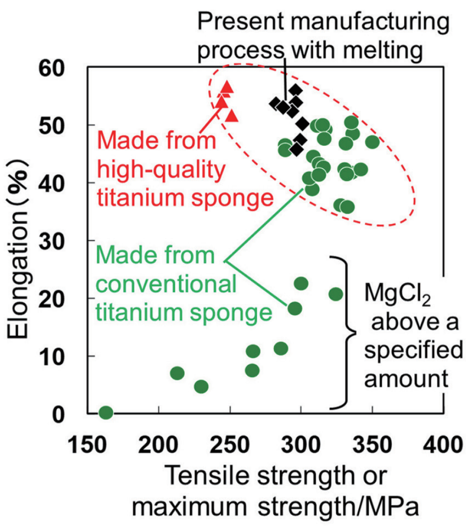

Fig. 4 Tensile properties of final annealed titanium sheets [10]

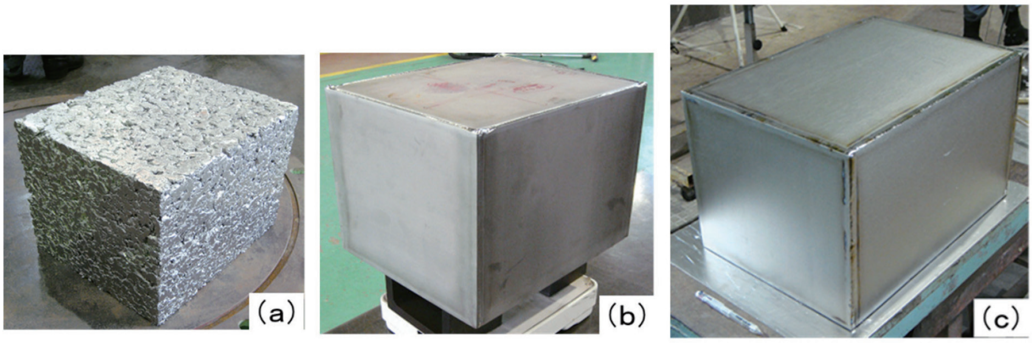

Fig. 5 Appearance of practical size briquette and titanium packages
(a) Rectangular briquette[12], (b) Package[12] (76 kg in weight), (c) Package (156 kg in weight)

4. Fabrication of Sheet Coils Using Large Packages

Based on the aforementioned results of the study of the basic properties, titanium sheet coils were produced from high-quality titanium sponge developed by the ISMA Chigasaki Office (Toho Titanium), through hot rolling tests of titanium packages that were larger size in the laboratory scale. At the same time, issues with their industrial application were extracted and solutions for them were considered.

4.1 Hot rolling tests of large packages

To obtain large packages, briquettes, which were press-formed titanium sponge, were fabricated using rectangular special dies. The thicknesses of the briquettes were 200 mm or more, the practical size. Well-shaped briquettes without edge defects were obtained by optimizing the press-forming conditions (**Fig. 5**(a)[12]).

The size of titanium packages was gradually increased from a small size of 75 mm to medium size of 120 to 180 mm and large size of 220 mm or more as the handling procedure was improved during the tests. One rectangular briquette was put into a 250-mm-thick package (Fig. 5(b)[12]) and two briquettes were put into a 279-mm-thick package (Fig. 5(c)). Thanks to the knowledge acquired through the fabrication of the small- and medium-size packages, even in the fabrication of large packages in the practical size, no major problems occurred.

The fabricated large packages were heated to a designated temperature for hot rolling to fabricate plates with a thickness of 15 to 40 mm. As the size of titanium packages was increased, large cracks that had not been seen on the small packages sometimes arose during the hot rolling. To solve this problem, the briquette packing procedure, the structure of titanium packages, and the construction procedure were improved. As a result, even for large packages with a thickness of 220 to 279 mm, conditions that don't generate cracks during the hot rolling were found. This finding made it possible to obtain well-shaped plates with a thickness of 15 to 40 mm (**Fig. 6**[12, 13]).

As described above, the production of large packages with the practical thickness ($\geq$ 200 mm) was successfully achieved without major problems by applying appropriate fabrication conditions. Although increasing the size of packages and putting multiple briquettes into one package generated various types of cracks during the hot rolling at first, such cracks could be controlled finally by improving the package structure, construction procedure, and briquette packing procedure.

4.2 Fabrication of sheet coils

Some of the plates fabricated by hot rolling the large packages

Fig. 6 Appearance of trial titanium plate made by hot rolling from large titanium package
(a) 15 mm thick plate[13], (b) 40 mm thick plate[12]

Fig. 7 Appearance of cold-rolled titanium coils made in the laboratory

were additionally hot-rolled into sheets with a thickness of 5 to 6 mm. After they were cut into sizes so as to fit within the specification range of a cold rolling mill on the laboratory scale, the scales on the surfaces of the steel sheets were removed, and the sheets were cold-rolled. At this time, no major cracks and defects that would hinder the rolling arose. Thus, well-shaped titanium sheet coils with a thickness of 0.5 mm and a width of 255 mm were obtained (**Fig. 7**).

For each of these titanium sheets with a thickness of 0.5 mm (hereinafter, "developed titanium sheets"), the ratio of the area of the pores was less than 0.2%. The tensile strength-ductility balance of the developed titanium sheets made of high-quality titanium sponge was the same as that of the present JIS Class 1 materials.

To evaluate the formability of these developed titanium sheets, punch stretch forming and deep drawing tests were performed, and they were compared to the present materials and evaluated. As for the punch stretch forming, an Erichsen test was performed according to JIS Z 2247 B. A 90-mm-square test piece was used and graphite grease was applied to the section that would come into contact with the punch. The Ericksen values (projection height) of these developed titanium sheets were 12.6 to 13.8 mm and they are larger than those of the present materials (11.9 to 12.2 mm). This may be

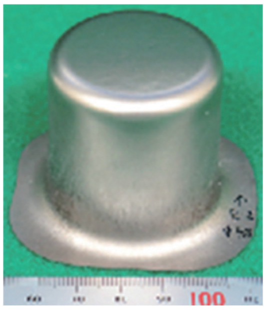

Fig. 8 Appearance of developed titanium sheet after deep drawing test

because the ductility of these developed titanium sheets used for the tests is approximately 51% at the total elongation, which is larger than that of the present materials (48%).

As for deep drawing, a φ-40-mm cylindrical deep drawing test was performed. The diameter of the test pieces was 92 to 100 mm, and a polyethylene sheet was used for lubrication. **Figure 8** shows an example of a deep-drawn test piece. The limiting drawing ratios (LDR = D/d, D: drawable maximum diameter of a test piece, d: punch diameter (40 mm)) of the developed titanium sheets were 2.2 to 2.3, which are at the same level as that of the present materials (2.2).

As seen above, from the sheets that were fabricated by hot rolling the large packages, titanium sheet coils with a thickness of 0.5 mm and width of 255 mm, whose ratio of the area of the pores was less than 0.2%, were successfully fabricated. In addition, using higher-quality titanium sponge as a raw material realized titanium sheets with the same tensile property (strength-ductility balance) and formability as those of the present materials.

5. Various Types of Commercially Pure Titanium Sheets

Generally, increasing the contents of O, Fe, and impurities (e.g., N and C) in commercially pure titanium will increase the tensile strength and proof stress and decrease the elongation. The JIS standard (JIS H 4600) specifies four types: Soft JIS Class 1 sheets (O ≤ 0.15 mass%, Fe ≤ 0.20 mass%) to high-strength JIS Class 4 sheets (O ≤ 0.40 mass%, Fe ≤ 0.50 mass%).[14]

As described above, in this development, it was found that using high-quality titanium sponge as raw material makes it possible to obtain soft and high-ductility titanium sheets similar to the present materials (JIS Class 1 sheets manufactured via a melting step). Although soft JIS Class 1 sheets excel in formability, the strength may be insufficient for some usages. Also for this development, higher-strength commercially pure titanium is expected to be produced (e.g., equivalent to JIS Class 2 and Class 3).

To obtain higher-strength sheets that are the same or similar to JIS Class 2 and Class 3, high-quality titanium sponge with different oxygen contents was used as the raw materials to fabricate eight small packages (with a thickness of 75 mm). These small packages were hot-rolled and cold-rolled in the same way as 3.1 above to produce cold-rolled and annealed sheets with a thickness of 0.5 mm. Analysis of these cold-rolled and annealed sheets shows that the oxygen concentration is 0.04 to 0.34 mass%. The cold-rolled and annealed sheets were heat-treated, and then two to five JIS 13B half test pieces (length of the parallel section: 30 mm) were sampled from each sheet in such a way that the pulling direction would be the rolling direction. They were subjected to tensile tests at room temperature at the initial strain rates of $5.0 \times 10^{-5}\,s^{-1}$ (to the yield points) and $2.0 \times 10^{-3}\,s^{-1}$ (after the yield points).

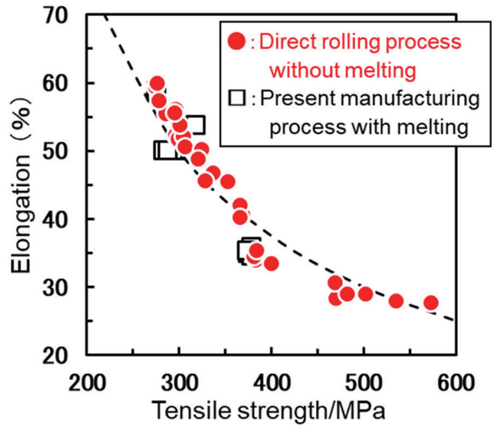

Fig. 9 Tensile properties of final annealed titanium sheets made from titanium sponges with varying oxygen concentrations

Figure 9 shows the tensile test results. The tensile properties of the obtained sheets vary: The tensile strength is 270 to 570 MPa and the total elongation is 28 to 60%. They are equivalent to JIS Class 1 to Class 3. As is the case with general commercially pure titanium, the higher the tensile strength (TS), the lower the total elongation (EL). However, the strength-ductility balance (TS × EL) is almost constant.

Thus, this development has revealed that adjusting the contents of oxygen and other elements in raw material titanium sponge enables fabricating sheets with various tensile properties.

6. Conclusion

In order to improve the productivity of the titanium mill product manufacturing processes, the titanium sponge direct rolling process, in which the melting and forging steps are omitted, has been developed. Titanium sponge was press-formed into briquettes and they were put into titanium boxes made of packing materials (titanium sheets) to form titanium packages. The titanium packages were hot-rolled and cold-rolled to fabricate titanium sheets and then the sheets were evaluated.

1) General-purpose titanium sponge of different qualities was used as the raw materials to fabricate small packages and they were rolled into sheets. The obtained sheets were evaluated. By optimizing the manufacturing and rolling conditions of the small packages and using high-quality titanium sponge whose quantity of residual $MgCl_2$ was less than a certain level, the sheets having almost no pores (ratio of the area < 0.2%) and having the same tensile properties as those of the present materials manufactured via a melting step were successfully produced. This result verifies the basic concept of this development.
2) As the package size was increased, major cracks, which had not been seen on the small packages, arose during the hot rolling. The briquette packing procedure, the structure of titanium packages, and the construction procedure were improved. As a result, even for large packages with a thickness of 220 to 279 mm, conditions that don't generate cracks were found. This finding has made it possible to obtain well-shaped plates with a thickness of 15 to 40 mm.
3) By hot-rolling and cold-rolling some of these plates, titanium

sheet coils having almost no pores (ratio of the area < 0.2%) with a thickness of 0.5 mm and a width of approximately 250 mm were successfully produced. In addition, using high-quality titanium sponge enabled the production of titanium sheets having the same tensile properties and formability as those of general JIS Class 1 sheets manufactured via a melting step.

4) It was confirmed that also in this development, titanium sheets with tensile properties equivalent to those of JIS Class 1 to Class 3 sheets can be fabricated by using high-quality titanium sponge with different oxygen contents.

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References

1) Yamade, Y., Kitagawa, H., Koike, O.: Journal of Japan Institute of Light Metals. 67 (4), 126 (2017)
2) Tokita, M., Sasage, M., Takechi, T.: Shinnittetsu Sumikin Giho. (396), 9 (2013)
3) Compiled by the Japan Titanium Society: Series of Metal Materials for Manufacturing Sites—Titanium. 1st edition. Tokyo, Kogyo Chosakai Publishing Co., Ltd., 2007, p. 15
4) Japan Titanium Society: Titanium. 68 (2), 194 (2020)
5) Compiled by the Japan Titanium Society: Titanium Processing Technologies. 1st edition. Tokyo, Nikkan Kogyo Shimbun, Ltd., 2003, p. 2
6) Takeda, O., Okabe, T.: Journal of Japan Institute of Light Metals. 67 (6), 257 (2017)
7) Material Technology and Nanotechnology Department, NEDO: Research and evaluation committee "New Innovative Structural Materials Research and Development" (interim evaluation) subcommittee, material 7-1-1 "New Innovative Structural Materials Research and Development" original project register [disclosure] III-2.4.2-1, Kawasaki, 2020-8, NEDO
8) Fujii, H., Okui, T.: Journal of Society of Automotive Engineers of Japan. 72 (11), 28 (2018)
9) Fujii, H., Okui, T.: Journal of Japan Institute of Light Metals. 69 (1), 68 (2019)
10) Innovative Structural Materials Association: ISMA REPORT. No. 8, 2 (2017)
11) Innovative Structural Materials Association: ISMA REPORT. No. 10, 4 (2018)
12) Futtsu Office, Innovative Structural Materials Association: Posters for the FY2020 result briefing session for "New Innovative Structural Materials Research and Development," Tokyo, January 2021, p. 42
13) Futtsu Office, Innovative Structural Materials Association: Programs and posters for the FY2018 result briefing session for "New Innovative Structural Materials Research and Development," Tokyo, January 2019, p. 16
14) Compiled by the Japanese Standards Association: JIS Handbook 3—Non-Ferrous Metals and Metallurgy. 1st edition. Tokyo, Japanese Standards Association, 2016, p. 1070

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