NIPPON STEEL & SUMITOMO METAL TECHNICAL REPORT No. 106 JULY 2014

Technical Report

UDC 669 . 14 . 018 . 8 - 416 : 669 . 24 - 416 : 669 . 295 - 416

Properties and Uses of Specialty Stainless Steel, Pure Nickel and Commercial Pure Titanium Foil

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Abstract

Nippon Steel & Sumitomo Metal Corporation Naoetsu Works produce the thin strip of specialty stainless steel, pure nickel and commercial pure titanium as a highly functional material, which have been applied in various fields such as automobiles, electronic components, battery materials, and audio equipment, etc. In this paper introduce the outline of manufacturing facilities, and characteristics and applications of thin metal products. In the case of stainless steel thin products, stainless steel surface is modified to improve the mold life of precision press. Thin strip of duplex stainless steel is applied to the flexible tube. Pure nickel foil is applied to negative-electrode material of lithium-ion rechargeable battery. And commercial pure titanium foil is applied to speaker diaphragm, respectively.

1. Introduction

Naoetsu Works, a division of Nippon Steel & Sumitomo Metal Corporation, manufactures various types of high-value-added sheets and foils of stainless steel, pure nickel, nickel alloy, commercial pure titanium and titanium alloy, among others. Their manufacturing capabilities also include precision-rolled stainless steel sheets that must have a high degree of flatness and thickness accuracy. In addition, the Works develops and commercializes high-function materials applying its original technologies, such as grain size control and surface modification. The products of the Works are employed in diverse fields, such as automobiles, electronic parts, battery materials, audio equipment, to name a few. This paper outlines manufacturing equipment at Naoetsu Works and presents typical properties and uses of the sheets and foils of associated products.

2. Sheet Manufacturing Equipment of Naoetsu Works [1-3)]

Naoetsu Works engages itself in the cold rolling of hot-rolled coils to manufacture thin sheets 0.3 mm or less in thickness. Many of the metallic materials handled at the Works have both high deformation resistance and high work hardenability or need high-temperature annealing. When it comes to manufacturing extremely thin sheets, it is difficult to secure a large draft per pass and implement sheet profile control because of roll flattening/contacting caused by an increase in rolling load or to apply annealing to the sheets because of low surface stiffness. Since extremely thin sheets used for precision parts, gaskets, etc. are required to have an exceptionally high degree of thickness accuracy and flatness, they need sophisticated manufacturing technology.

The finish cold rolling of extremely thin sheet is done by a mill dedicated to foil (4CM) or a mill dedicated to precision-rolled product (5CM) shown in **Table 1**. The 4CM is a 12-high-cluster-type mill used mainly to manufacture foils 0.08 mm or less in thickness. The 5CM for mass-producing precision-rolled products is a universal crown (UC) control mill that allows for precise flatness control and large reduction. It uses either large-diameter work rolls (UC-1) or small-diameter work rolls (UC-4) according to the grade, size, and use of steel sheet. When the demand for flatness is very severe, the rolled sheet is subjected to straightening by a tension leveler.

For annealing, either annealing & pickling (AP) equipment or bright annealing (BA) equipment is used. The AP equipment first anneals the rolled sheet in a combustion gas atmosphere and then

Table 1 Specification of cold rolling mill

	4CM	5CM
Mill type	12-hi Cluster type mill	6-hi UC mill
Work roll diameter	25 - 60 mm	UC-1 : 125 - 135 mm UC-4 : 60 - 80 mm
Final thickness	0.01 - 0.5 mm	0.05 - 1.5 mm
Width of the product	Max. 400 mm	Max. 680 mm

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descales it by pickling. It is used for intermediate annealing and finish annealing of relatively thick rolled sheets. The BA equipment uses as its furnace atmosphere a mixture of N_2 and H_2 or Ar gas whose dew point is controlled as low as −40°C or under. In the furnace, the rolled sheet is annealed in a non-oxidizing atmosphere, which permits maintaining the surface condition of as-rolled sheet even after the annealing. Besides, the annealed sheet does not need descaling. For those reasons, the BA equipment is used for intermediate annealing and finish annealing of extremely thin sheets. It is also used as a means of grain size control, strain relieving, surface nitration, etc., which help enhance the performance of thin sheets.

3. Ultrathin Stainless Steel Sheets

3.1 Precision-rolled ultrathin stainless steel sheet

Austenitic stainless steels SUS 304 and SUS 301 can be strengthened by applying cold work hardening, and are widely used in the form of leaf springs and disc springs., etc., which are found in automobiles, electronic devices, various machines and OA/IT equipment, among others. While recent years have seen an ever-increasing supply of inexpensive stainless steels manufactured overseas, Naoetsu Works manufactures ultrathin precision-rolled stainless steel sheets 0.3 mm or less in thickness and ultrathin high-performance stainless steel sheets by applying its original technologies (grain refinement, surface film modification, etc.). Of them, the stainless steel foil for automotive engine gasket and the ultrathin steel sheet for precision working shall be reported in a separate article of the current issue of Nippon Steel & Sumitomo Metal Technical Report.

3.2 Modification of surface film of ultrathin stainless steel sheet

The surface of stainless steel is covered with an extremely thin layer of oxide film (passive film) several nanometers in thickness. It is known that the protective action of the film imparts excellent corrosion resistance to the stainless steel. If stainless steel sheet is extremely small in thickness, the physical properties of its surface film can influence the properties of the sheet.

For miniature bearing parts used in hard disks (**Fig. 1**), SUS 304 BA (annealed steel sheet) 0.08 - 0.2 mm in thickness is applied. These parts are manufactured by superhigh-speed, precision press working hundreds of cycles per minute. With the increase in accuracy and speed of press working, the wear of the dies has become a problem. Under that condition, the surface film of SUS 304 sheet was modified by special surface treatment. As a result, the life of precision press dies could be more than doubled.

To determine the influence of surface film properties on press die life, we measured the hardness of the uppermost layer of sheet using the nanoindentation method.[4] In this method, a diamond microindenter is positioned on the surface of each stainless steel sheet specimen, and very small loads of a few dozen micro-Newtons are sequentially applied to and removed from the indenter.– The depth of indentation by the indenter is then measured. The measurement results are shown in **Fig. 2**. The specimens used are SUS 304 sheets 0.1 mm in thickness. The conventional sheet specimen (a) is an SUS 304 sheet as BA-annealed, and the developed sheet specimen (b) is an SUS 304 sheet subjected to special surface treatment after BA annealing. A comparison between the two specimens reveals that under the same loading condition, the depth of indentation is smaller with specimen (b) than with specimen (a), and that the residual depth of indentation (amount of plastic deformation of the surface film) after removal of the load is also smaller with specimen (b) than with specimen (a). Thus, it can be seen that a thin and hard film has

Fig. 1 Miniature bearing cover (SUS 304 BA)

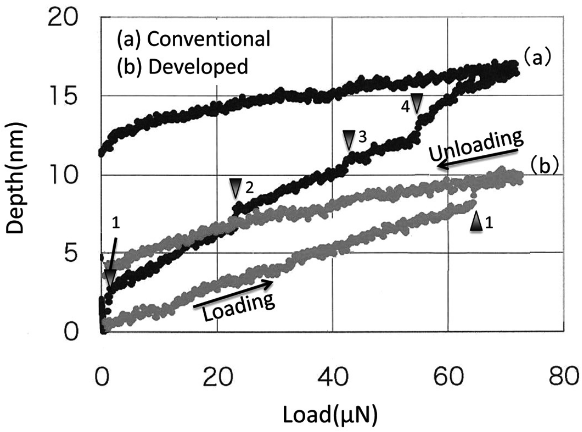

Fig. 2 Nano-indentation measurement

been formed on the surface of specimen (b). On the other hand, specimen (a) shows a number of discontinuous points (indicated by ▼) in the loading process, suggesting that the surface film formed on it during BA annealing is thick and brittle from a nano-level viewpoint.

It is considered that in the case of specimen (a), the wear of dies in precision press working progressed as the surface film of the ultrathin stainless steel sheet was broken through contact with the dies and the adhesion between the exposed base metal and the dies was repeated with a high speed. With specimen (b) having a hard surface film, it is estimated that the breaking of the film mentioned above hardly occurred and hence, the life of the dies was prolonged.

3.3 Ultrathin duplex stainless steel sheets

Austenitic-ferritic duplex stainless steels have excellent strength and corrosion resistance properties, and are used for chemical plants, desalination equipment, offshore structures, etc. Naoetsu Works manufactures plates and sheets of super duplex stainless steel NSSMC-NAR-DP-3W[5] (UNS S39274 "DP-3W") that exhibits superior corrosion resistance in a high-temperature chloride or seawater environment or various kinds of acid environment (sulfuric acid, hydrochloric acid, etc.).

Cold-rolling a duplex stainless steel is difficult using a large draft due to the high strength of the steel. Since the steel is susceptible to 475°C embrittlement or σ embrittlement under high temperatures, and superplasticity[6] at the solution treatment temperature, it is possible that the steel in the form of a coil decreases in width and thickness in the annealing process. Therefore, compared with ordinary stainless steel, the rolling of duplex stainless into thin sheets is extremely difficult. Nevertheless, by optimizing the rolling pass

Table 2 Principal chemical compositions and an example of the mechanical properties

	Principal chemical composition	0.2% proof stress (MPa)	Tensile strength (MPa)	Elongation (%)	Hardness HV1
NSSMC-NAR-DP-3W	25Cr-7Ni-3Mo-2W-0.3N-LC	649	948	26	297
SUS316L	18Cr-12Ni-2.5Mo-LC	208	554	59	134

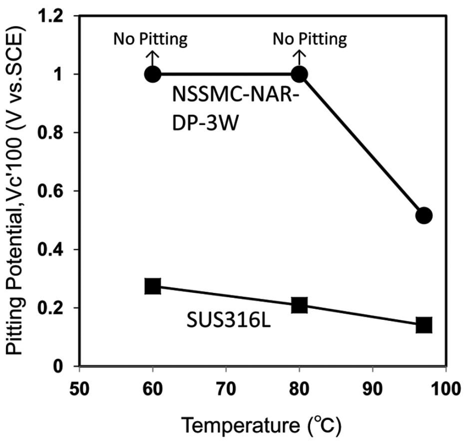

Fig. 3 Pitting potential measurement in artificial sea-water

Fig. 4 Flexible tube of NSSMC-NAR-DP-3W (0.2 mm thickness × 20 mm diameter)

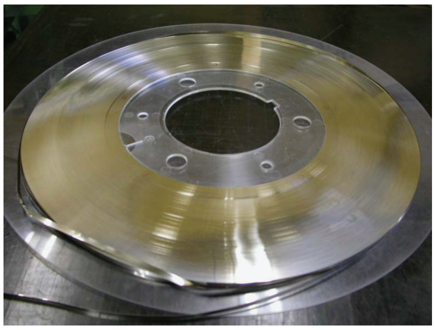

Fig. 5 Pure nickel lead for lithium-ion rechargeable battery

schedule and controlling the temperature and tension in the annealing process, we have made it possible to manufacture ultrathin sheets of DP-3W down to 0.2 mm in thickness.

We compared the performance between DP-3W and ordinary stainless steel SUS316L having good corrosion resistance. **Table 2** shows the representative chemical compositions of DP-3W and SUS 316L and examples of mechanical properties of thin sheets (0.5 mm-thick annealed sheets) of them. **Figure 3** shows their pitting potentials (Vc' 100) measured in high-temperature artificial seawater. DP-3W is superior to SUS316L in both 0.2% proof stress and tensile strength. In addition, DP-3W is free from pitting under high temperatures up to 80°C. Even at 97°C, the pitting potential of DP-3W is better than that of SUS316L, indicating that DP-3W has superior pitting corrosion resistance in high-temperature seawater.

DP-3W sheets (0.7 - 1.0 mm in thickness) have already been put into practical use as materials for the covering of steel pipe piles of offshore structures, the plating jig for manufacturing electronic parts, which is exposed to various types of acid solutions. In addition, a flexible tube made from ultrathin DP-3W sheet (0.2 mm in thickness) (**Fig. 4**) is superior in corrosion resistance, strength, and durability to flexible tubes made from conventional stainless steel sheets (SUS304, SUS316L). Therefore, flexible tubes made from DP-3W sheet are being increasingly applied to water supply piping and joint parts of seawater desalination equipment, etc. By further reducing the thickness of high-strength dual-phase stainless steel, it should also become possible to find new uses thereof, such as a strong yet light structural member.

4. Pure Nickel Foil

4.1 Properties of pure nickel

Since pure nickel has excellent corrosion resistance to caustic soda and other alkali solutions and is capable of withstanding halogen gas and non-oxidizing acids, it is used for various devices, such as reaction towers and tanks and heat exchangers, employed in the soda industry. In addition, because of its low electrical resistance (about 0.7 times that of pure iron), good workability, and good weldability, pure nickel is used for soda electrolytic electrodes, plating electrodes, battery parts, etc. Naoetsu Works manufactures low-carbon pure nickel (JIS H 4551 NW2201) of Ni purity 99.5% and supplies pure nickel plates and sheets for various applications.

4.2 Lithium ion rechargeable batteries

Pure nickel foil manufactured by Nippon Steel & Sumitomo Metal is preferred by many of the leading battery makers as a material for negative electrode leads in lithium ion rechargeable batteries (**Fig. 5**). Comparing secondary batteries, the lithium ion rechargeable battery has the highest energy density and can be made larger in capacity and smaller in size as required. Since the late 1990s, therefore, it has rapidly become widespread as a rechargeable battery for common electronic devices, such as laptops, cell phones, digital cameras, and portable cassette players. Lithium ion rechargeable batteries are separated by shape into three types: cylindrical, square, and laminated. Every lithium ion rechargeable battery is provided with terminals (leads) to supply the energy stored in the battery. Aluminum is used for the positive-electrode lead, and pure nickel is used for the negative-electrode lead. For the leads of small batteries for consumer electronics, metallic foil 0.05 - 0.15 mm in thickness is first precisely slit in several millimeters in width and then cut into narrow strips.

4.3 Technology for manufacturing pure nickel foil for negative-electrode leads

As in the case of stainless steel sheet, Naoetsu Works manufactures pure nickel foil by an integrated process, from electric furnace melting to cold rolling, to ensure high productivity and stable product quality. The integrated manufacturing system also has the advantage of allowing for the centralized management of product quality, yield, and delivery. In addition, through improvements on the pure nickel foil manufacturing technology and R&D on application techniques (welding, slitting, surface properties, etc.) in cooperation with the research laboratories of Nippon Steel & Sumitomo Metal, the Works helps solve technical problems of the customers.

Lithium ion rechargeable batteries must have a high degree of reliability, so strict quality control in all aspects of manufacturing is required. With respect to the material for leads, special importance is attached to its surface quality. Therefore, the Works has an online flaw detection system that records surface defects along the entire coil length to permit tracing the points of defects in narrow strips of the foil after slitting. In the case of a laminated-type battery, the lead is affixed with insulating film on the surface and sealed in a laminate pack. In this case, the surface of pure nickel foil is required to have good wettability so as to ensure sufficient adhesion of the insulating film. Therefore, the rolling rolls that make contact with the material are properly controlled to secure adequate cleanliness of the material surface. In addition, the material is properly packed and stored in an air-conditioned room so as to maintain the required wettability of the material surface. It is expected that demand for pure nickel foil as a material for the negative electrode leads of lithium ion rechargeable batteries will continue to increase proportionally to the demand for smartphones, tablet PCs, etc.

5. Commercial Pure Titanium Foil

5.1 Commercial pure titanium foil as a material for speaker diaphragms

Since titanium is light in weight and has high specific strength and excellent corrosion resistance, it is used in diverse fields, for example aerospace, chemistry, electric power, medicine, and sports. Speaker diaphragms are one of the current uses of commercial pure titanium foils of less than 0.2 mm in thickness.[7-9)]

The speaker diaphragm is an important part that transmits sound waves to atomosphere through the speaker unit. According to the sound range in which they are used, speakers are classified, from the treble to the bass, into tweeter, squawker, woofer, and full range. The tone quality of a speaker is influenced by physical properties (e.g., density, specific rigidity, internal loss) of the diaphragm material.[8-10)] As material density decreases, so the energy level of diaphragm vibration can be decreased. The higher specific rigidity (E/ρ, E: Young's modulus; ρ: density), the lower level of noise produced by crossover vibrations of the diaphragm. On the other hand, increasing internal loss is effective to lower resonance peak of the material and improve the response to diaphragm vibration.

Ordinarily, a sheet of paper, polymer, or metal is used as the material for speaker diaphragms. **Table 3** shows the representative properties of various materials for diaphragm. Generally, metallic materials having a high rigidity are used for tweeters, whereas polymers and paper having a large internal loss are used for squawkers and woofers in the intermediate to low range. Of the metallic materials for speaker diaphragm shown in **Table 4**, titanium is superior in formability to beryllium (high specific rigidity) and magnesium (large internal loss) and is stronger than aluminum (good formability, low cost). Therefore, as a material for speaker diaphragm, titanium is the most widely used, second only to aluminum.

Table 3 Materials of speaker diaphragm [7-9)]

Material	Specific rigidity	Internal loss	Example	Range
Paper	Low	High	Pulp, composite paper, etc.	Full range, woofer, squawker, tweeter
Polymer	Low	High	Polyester, polypropylene, aramid, carbon fiber, etc.	Woofer, squawker
Metal	High	Low	Beryllium, magnesium, aluminum, titanium	Tweeter

Table 4 Characteristics of speaker diaphragm materials [8-10)]

	Density (g/cm^3)	Young's modulus (GPa)	Specific rigidity (cm^2/s^2)	Speed of sound (m/s)	Internal loss
Paper	0.55	2.0	0.36×10^{11}	1,900	0.04
Polymer	0.98	8.7	0.89×10^{11}	2,980	0.05
Beryllium	1.84	287	15.6×10^{11}	12,500	0.005
Magnesium	1.77	41	2.3×10^{11}	4,800	0.01
Aluminum	2.69	74	2.8×10^{11}	5,300	0.002
Titanium	4.51	106	2.4×10^{11}	4,900	0.002

Table 5 Chemical compositions of CP titanium for speaker diaphragm use (mass%)

C	H	O	N	Fe	Ti
0.004	0.0008	0.035	0.004	0.022	Bal.

5.2 Improvement in commercial pure titanium foil formability

The diaphragm of a tweeter has a domed shape. Speaker makers use a press or air blower to form the material into a domed shape. Therefore, good stretchability is required of the diaphragm material. It is generally considered that a commercial pure titanium sheet having larger grains has a larger n-value (work hardenability) and better stretchability. However, for commercial pure titanium foils about tens of μm in thickness, there is a limit to their maximum grain size. Therefore, we optimized the grain size of commercial pure titanium foil to improve its formability.

Tests carried out to optimize grain size used a commercial pure titanium sheet equivalent of JIS Class 1 (**Table 5**) that was cold-rolled into a 25 μm-thick foil.[11-13)] The foil was annealed in a continuous bright annealing furnace with the temperature range between 620°C and 740°C. Foil formability was evaluated by an Erichsen test, and the n-value in the rolling direction was measured by a tensile test.

Figure 6 shows the results of the Erichsen test of the foils whose grain size was controlled by various annealing temperatures. With the increase in grain size up to approximately 80 μm, the stretchability of ordinary titanium sheet improves in proportion to the increase in n-value. When the grain size exceeds 80 μm, the stretchability de-

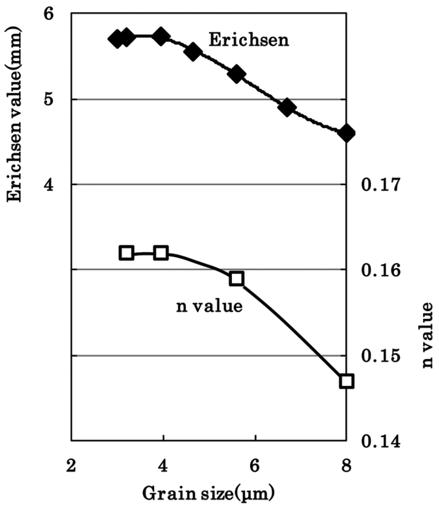

Fig. 6 Effect of grain size on formability [12, 13]

creases as the sheet skin becomes rough.[14] However, in the case of commercaial pure titanium foil 25 μm in thickness, stretchability is the highest and the n-value is the largest when the grain size is about 4 μm. When the grain size was larger, the n-value decreased and stretchability deteriorated. The reason is that with a foil tens of micrometers in thickness, the number of grains in the thickness direction decreases as the grain size increases. Since commercial pure titanium has a hexagonal close-packed structure, its grains have a marked anisotropy. If the sheet has sufficient thickness, the anisotropies will average out. In the case of the foil, however, the number of grains in the thickness direction is so small that the anisotropies do not average out. As a result, the foil is subject to a local deformation, which causes the formability of the foil to deteriorate. Thus, unlike ordinary commercial pure titanium sheets, it is effective to refine the grains of commercial pure titanium foil to enhance formability.

By manufacturing commercial pure titanium foil under the above-described optimum conditions, we obtained a highly formable commercial pure titanium foil for speaker diaphragms. **Figure 7** shows an example of commercial pure titanium foil, and **Fig. 8** shows a speaker diaphragm made from the foil shown in Fig. 7. **Figure 9** shows the frequency response of a 20-mm-diameter speaker diaphragm made from foil manufactured by Nippon Steel & Sumitomo Metal. As shown, we could confirm that the diaphragm offers a good response over a wide frequency range.[11] It is expected that titanium foil for speaker diaphragm will find increasing uses not only in audio equipment but also in car stereos and portable terminals.

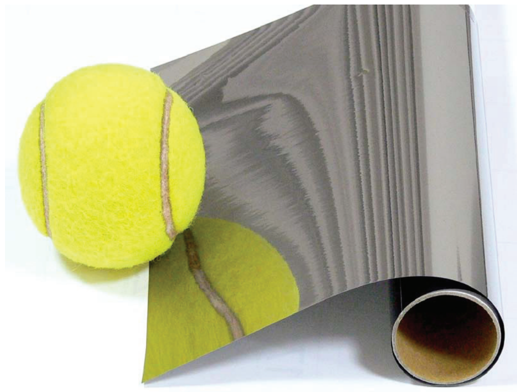

Fig. 7 Commercial pure titanium foil

Fig. 8 Example of speaker diaphragm

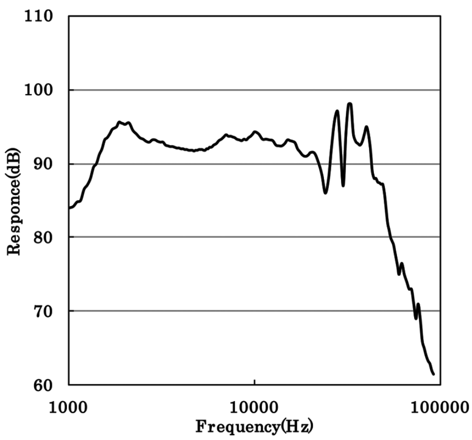

Fig. 9 Frequency response of titanium diaphragm [11]

6. Conclusion

We have outlined sheet manufacturing equipment of Naoetsu Works and explained the typical properties and uses of our ultrathin sheets of specialty stainless steel, pure nickel, and commercial pure titanium. By applying a stainless steel sheet whose surface was modified by special treatment, we could prolong the life of dies for precision press forming. The Works manufactures ultrathin sheets of super duplex stainless steel, DP-3W, down to 0.2 mm in thickness. The DP-3W sheets are being increasingly used for flexible tubes, etc. As a high quality material for the negative-electrode leads of lithium ion rechargeable batteries, our pure nickel foil is employed by many battery makers in Japan and abroad. Commercial pure titanium foil having improved formability is used for speaker diaphragms.

Acknowledgments

We wish to express our heartfelt thanks to Showarasenkan Seisakusho, Co. Ltd. that fabricated samples of flexible tube of NS-SMC-NAR-DP-3W and supplied them to us.

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