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Technical Report

Development of V Free Ti-Al-Fe Based Titanium Alloy Strip Products

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Abstract

To expand the application of α+β type titanium alloys, cold strip products using Super-TIX™51AF (Ti-5Al-1Fe) and hot strip products using Super-TIX™20AFG (Ti-2Al-0.2Fe) were developed. The high strength α+β type titanium alloy Ti-5Al-1Fe has higher workability at room temperature than Ti-6Al-4V, and its cold-rolled strip can be manufactured. Also, it has excellent properties, such as high formability at room and high temperature. Ti-2Al-0.2Fe is a titanium alloy with high glossiness and abradability developed for watch parts, and provides high specularity and workability with adequate control of the chemical composition and microstructure. All the properties required for watch parts in the hot rolled sheets of Ti-2Al-0.2Fe manufactured at a production mill have been improved significantly compared to the hot rolled sheet of pure titanium.

1. Introduction

Titanium alloys represented by Ti-6 mass%Al-4 mass%V have been widely used for aircraft applications as materials having high-specific strength and high corrosion resistance.[1] In addition to these characteristics, since titanium alloys have excellent aesthetic quality and biocompatibility, they have been widely used for automotive parts, such as mufflers and connecting rods, as well as for consumer goods, such as golfing gear, watches, and glasses in recent years. Because titanium alloys are used for these various applications, titanium alloys that are specific for each application have been developed.

V, which is often used as an alloying element for titanium alloys, is expensive and approximately 95% of the raw materials are disproportionally found in China, Russia, and South Africa. Therefore, in recent years, there has been concern about country risks, generating demand for V-free titanium alloys. Nippon Steel Corporation has developed various types of V-free titanium alloys using low-priced general-purpose elements, such as Al, Fe, Cu, O, and N.[2] This paper introduces the development of cold-rolled strips from Nippon Steel's proprietary high-strength $\alpha+\beta$ type titanium alloy Super-TIX™51AF (Ti-5 mass%Al-1 mass%Fe), and the development of hot-rolled strips from Super-TIX™20AFG (Ti-2 mass%Al-0.2 mass%Fe) with high glossiness and high abradability developed for watch parts.

2. Development of Cold-rolled Strips from Super-TIX™51AF

Manufacturing strips from high-strength $\alpha+\beta$ type titanium alloys containing much Al, which are typified by Ti-6Al-4V, is difficult due to their large rolling reaction force, frequent edge crack occurrence, poor unwinding property due to their high-strength and small Young's modulus, and other reasons. Consequently, such high-strength $\alpha+\beta$ type titanium alloy sheets are usually manufactured by the sheet rolling method or pack rolling method. In the pack rolling method, several titanium sheets are laminated and enclosed with steel materials (packing), and hot-rolled while warm. However, this method has some problems, such as low productivity and poor thickness accuracy.[3] If hot-rolling and cold-rolling mills can be utilized to manufacture strips for unidirectional hot-rolled sheets and cold-rolled sheets, these problems will be solved. Therefore, much research has been conducted.[3–5] Nippon Steel has succeeded in manufacturing Ti-5Al-1Fe hot-rolled strips (with a thickness of approximately 4 mm). On the other hand, almost no cold-rolled strips have been manufactured from Ti-6Al-4V or other high-strength $\alpha+\beta$ type titanium alloys on the industrial scale. One reason is their poor cold-rollability. Titanium with its hexagonal close packed (hcp) structure deforms due to both slip and twinning deformation.[6] However, in titanium alloys containing Al, twinning deformation does not tend to occur, and slip deformation tends to become dominant.

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When the content of Al is high, the critical resolved shear stress (CRSS) of a+c slip becomes very high.[7] Therefore, deformation in the c-axis direction of hcp does not occur much, worsening the workability.

Nippon Steel has developed Ti-5Al-1Fe as a high-strength $\alpha+\beta$ type titanium alloy. For the alloy, expensive V and Mo are not used as β stabilizing elements and Fe, which is a low-priced general-purpose element, is used.[2, 8] Ti-5Al-1Fe has high strength comparable to that of Ti-6Al-4V Extra Low Interstitials (ELI).[1] In addition, its excellent hot-rollability and large Young's modulus are utilized to mass-produce round bars and hot-rolled strips, which are used for connecting rods and golf clubs.[2, 3] Furthermore, Al content of Ti-5Al-1Fe is less than that of Ti-6Al-4V, and thereby it has excellent workability at high temperatures and also at room temperature. Due to these characteristics, the manufacture of cold-rolled strips is expected. This section introduces the properties of cold-rolled Ti-5Al-1Fe strips manufactured using production mills.

2.1 Manufacturing of cold-rolled strips using production mills

We manufactured cold-rolled strips with a thickness of 0.4 mm using a hot-rolling mill (Setouchi Works, Hirohata Area) and a cold-rolling mill (East Nippon Works, Naoetsu Area). **Photo 1** shows the appearance of a cold-rolled Ti-5Al-1Fe strip manufactured using the production mills. **Figure 1** shows the microstructure image of the cold-rolled and annealed strip taken with an optical microscope. The fine equiaxed microstructure was formed in the cold-rolled strip manufactured using the production mills.

2.2 Mechanical properties and formability at room temperature

Table 1 shows the tensile properties of a 0.4-mm-thick cold-rolled Ti-5Al-1Fe strip in the L direction (longitudinal direction of the strip). As the tensile properties of the cold-rolled strip, the strength-elongation balance is equivalent to that of Ti-6Al-4V ELI. In addition, no crack on the surface occurred in bending at 105 degrees, which is required for aircraft applications. To further investigate the formability at room temperature, three-point bending and deep-drawing tests were performed.

Figure 2 shows the maximum bending angles of a 0.4-mm-thick cold-rolled Ti-5Al-1Fe strip in the three-point bending test (punch R: 0.4 mm, clearance: 2 mm, pushing speed: 10 mm/min). **Photo 2** shows the appearance of the test piece after the three-point bending test. Here, the maximum bending angle means the angle at which a crack was formed on the surface during the bending. For the cold-rolled Ti-5Al-1Fe strip, the bendability is excellent in both the L direction and T direction (traverse direction of the strip), and for the T direction, in particular, even when the strip was bent to the testing limit (120 degrees), no crack was formed. On the other hand, a crack on the surface formed on the Ti-6Al-4V sheet (commercial material) at 80 to 90 degrees for both the L and T directions.

Photo 3 shows the appearance of a cold-rolled Ti-5Al-1Fe strip after the deep-drawing test (test piece diameter: 80 mm, punch diameter: 40 mm, blank holder force: 2.8 tons, lubrication with NAFLON™ sheet). For the cold-rolled Ti-5Al-1Fe strip, no crack was formed at the shoulder sections and deep drawing at room tempera-

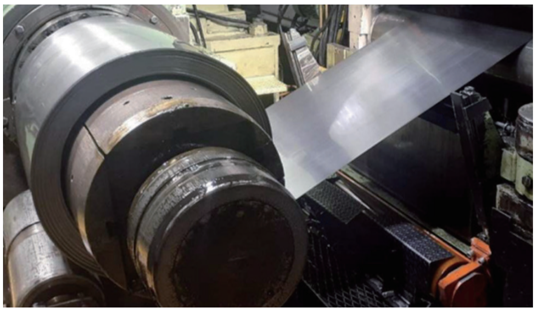

Photo 1 Appearance of cold-rolled Ti-5Al-1Fe strip manufactured at production mill

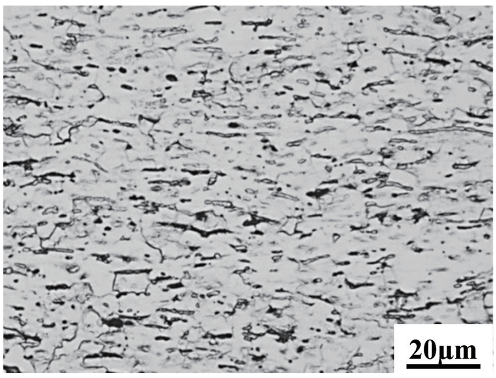

Fig. 1 Microstructure of cold-rolled Ti-5Al-1Fe strip manufactured at production mill

Table 1 Mechanical properties of cold-rolled Ti-5Al-1Fe strip with a thickness of 0.4 mm

0.2%PS (MPa)	TS (MPa)	T-El (%)	Bending (105°)
770	929	14.7	OK

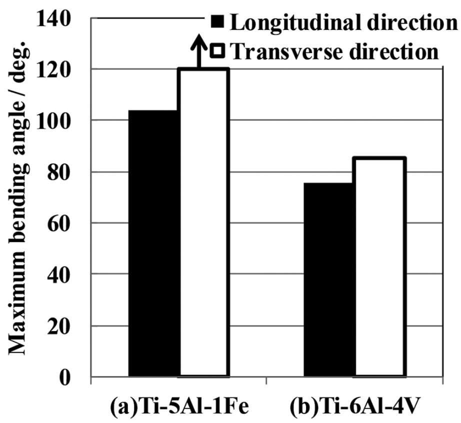

Fig. 2 Maximum bending angles in three-point bending test of (a) Ti-5Al-1Fe strip and (b) Ti-6Al-4V sheet with a thickness of 0.4 mm

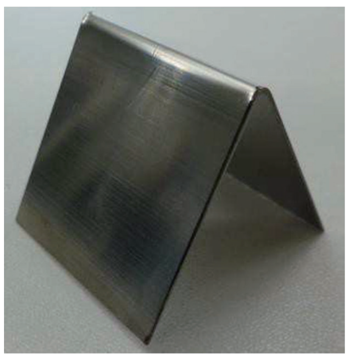

Photo 2 Cold-rolled Ti-5Al-1Fe strip with a thickness of 0.4 mm after three-point bending test

ture was possible. Thus, the formability of cold-rolled Ti-5Al-1Fe strips at room temperature is excellent.

2.3 High-temperature tensile test

Figure 3 shows the elongation when a high-temperature tensile test was performed in the L direction in the atmosphere at 700 and 800°C and at the strain rates of 1×10^{-4} to 1×10^{-2}/s (gauge length: 35 mm, stroke control). In the high-temperature tensile test, 1-mm-thick cold-rolled and annealed sheets that were manufactured using the same method as those manufactured at the production mill were used as test samples. At 700°C and at the strain rate of 1×10^{-2}/s, the elongation is less than 100%; while, in the other cases, it is 100% or more. At 800°C and at 1×10^{-3}/s, the elongation is approximately 200%. The elongation is smaller at the strain rate of 1×10^{-4}/s and this may be because the lower the strain rate is, the larger the influence of oxidation by the atmosphere. Therefore, it is estimated that if there had been no influence by oxidation, the elongation would have been 200% or larger.

Table 2 shows the m-values. While the m-value at 700°C and at the high strain rate is smaller than 0.3, it is 0.3 or larger at 700°C and at the low strain rate, and also at 800°C. In the state of superplasticity, the elongation is roughly 200% or larger and the m-value is 0.3 or larger. Therefore, the table shows that the cold-rolled Ti-5Al-1Fe sheet shows superplasticity at 800°C or higher.

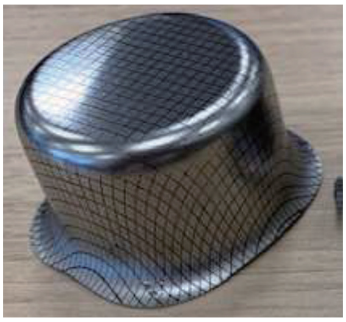

Photo 3 Cold-rolled Ti-5Al-1Fe strip with a thickness of 0.4 mm after deep drawing test

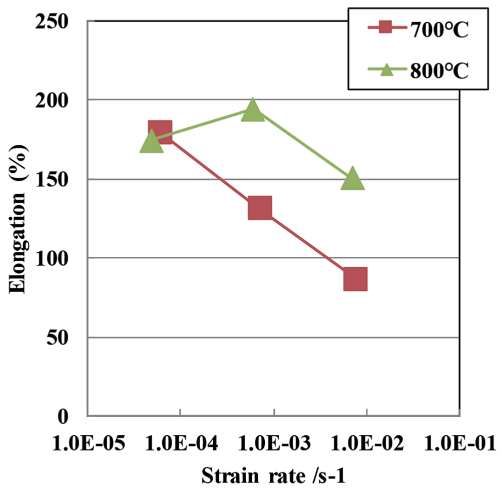

Fig. 3 Change in elongation of cold-rolled Ti-5Al-1Fe sheet (1 mm thick) in relation to strain rate at high-temperature tensile test

Table 2 m-value of cold-rolled Ti-5Al-1Fe sheet at flow strain of 0.2

	Strain rate (10^{-2}–10^{-3}/s)	Strain rate (10^{-3}–10^{-4}/s)
700°C	0.28	0.31
800°C	0.31	0.35

In general, for Ti-6Al-4V, superplasticity occurs at the strain rate of approximately 1×10^{-4}/s and at around 900°C, at which the fractions of the α and β phases become almost equal.[9, 10] It has also been reported that superplasticity occurs even at 800°C in fine equiaxed microstructure.[11] Because the fraction of the β phase in Ti-5Al-1Fe is smaller than that in Ti-6Al-4V at these temperatures, superplasticity properties hardly occur. It can be considered that superplasticity occurred at 800°C, at which the fraction of the β phase was small, because the fine equiaxed microstructure was formed in the cold-rolled sheet (Fig. 1). These results indicate that cold-rolled Ti-5Al-1Fe strips can be formed into severe shapes requiring superplasticity properties.

From the results above, cold-rolled Ti-5Al-1Fe strips can be manufactured using production mills and their formability at both room and high temperature is exceptional, having excellent properties. Therefore, far wider applications are expected in the future by drawing on these characteristics.

3. Development of Super-TIX™20AFG with High Glossiness and High Abradability

As described in Chapter 1, using its light weight, high corrosion resistance, and high biocompatibility, titanium is used for accessories, such as watch cases and watchbands. Stainless steel is another metal material used for watch parts besides titanium. **Table 3** shows the properties required for watch parts in titanium and stainless steel. Titanium has many advantages over stainless steel: low density, high corrosion resistance to seawater, high biocompatibility, and excellent radio reception characteristics (relative permeability close to 1). Meanwhile, the disadvantage is the inferiority of its specularity after mirror polishing. Nippon Steel has developed titanium alloy Super-TIX™20AFG (Ti-2Al-0.2Fe) in cooperation with CASIO Computer Co., Ltd. under TranTixxii™—a brand for titanium alloys with excellent aesthetic quality. The developed titanium alloy has the advantages of titanium with improved specularity. This chapter introduces various properties of Ti-2Al-0.2Fe hot-rolled strips along with an example application.

3.1 Chemical composition of Super-TIX™20AFG

Ti-2Al-0.2Fe is a titanium alloy produced by adding approximately 2 mass% of Al and a minute quantity of Fe to titanium. The specularity after mirror polishing depends on the roughness after the polishing, and the higher the hardness is, the smaller the projections and depressions after polishing and the higher the specularity. However, the higher the hardness is, the poorer the stamping formability and boring workability. Therefore, alloys for parts that will be stamped (e.g., watch parts) need to satisfy high hardness and excellent formability and boring workability at the same time. For Ti-

Table 3 Properties required for watch parts in titanium and stainless steel

Properties	Titanium	Stainless steel
Density	<u>smaller</u>	larger
Glossiness (specularity)	lower	<u>higher</u>
Specific permeability (the closer it is to 1, the better)	<u>around 1.0001</u>	α SUS: 1 000 γ SUS: 1.003–7
Biocompatibility	<u>higher</u>	lower

2Al-0.2Fe, Al was selected as a solid solution strengthening element to retard the decrease in the hardness due to heat generation by polishing. Compared to titanium alloys having the same level of strength, the specularity of Ti-2Al-0.2Fe is higher. In addition, adding a small amount of Fe brings about formation of the β phase. And the β phase works as pinning particles in annealing, which can retard the growth of α phase grains. Due to this, fine equiaxed α microstructure can be formed after annealing, which can improve the specularity.

3.2 Microstructure of a hot-rolled and annealed strip

Figure 4 shows the microstructure of a hot-rolled and annealed strip manufactured at the production mill. Although Ti-2Al-0.2Fe was hot-rolled by heat treatment in the two-phase (α+β) region, mostly the single α phase was hot-rolled because the quantity of Fe, which was a β stabilizing element, was very small at 0.2 mass%. Therefore, when the hot-rolled strip was annealed, recrystallization occurred and the fine equiaxed microstructure with an average crystal grain diameter of 10 μm or smaller can be formed. In addition, the ultra-fine β phase is homogeneously distributed at the grain boundaries and inner α grains. The specularity of this microstructure is superior to acicular structure that is obtained by annealing at the β single phase region. Thus, in addition to the optimization of the chemical composition described in 3.1, controlling the hot-rolling and annealing conditions produces microstructure that is suitable for mirror polishing, which can realize excellent specularity.

3.3 Various properties of hot-rolled and annealed sheets

Table 4 shows the properties required for watches in Ti-2Al-0.2Fe, JIS Class 2 pure titanium, and SUS304. The term "distinctness of image (DOI)" is an index indicating the clearness of images. **Photo 4** shows that the letters on the test sample with higher DOI are clearer. The DOI of Ti-2Al-0.2Fe is higher by approximately 50% or more compared to pure titanium, which shows the specularity has been remarkably improved. The density of Ti-2Al-0.2Fe is also lower by approximately 1% than that of pure titanium and lower by 40% or more than that of SUS304. Regarding the relative permeability and electric resistivity that affect the radio reception characteristics, the relative permeability of Ti-2Al-0.2Fe is the same as that of pure titanium, while the electric resistivity is more than double that of pure titanium. Furthermore, the Vickers hardness is higher by approximately 70% than that of pure titanium. The corrosion of Ti-2Al-0.2Fe by seawater and ion elution is at the same level as those of pure titanium and excellent compared to SUS304. Thus, Ti-2Al-0.2Fe is a titanium alloy all of whose properties required for watch parts have been improved.

Ti-2Al-0.2Fe is a titanium alloy which has both high specularity and workability for watch parts by the control of the chemical composition and microstructure. All the properties required for watch parts in hot-rolled Ti-2Al-0.2Fe sheets manufactured at the production mill have been greatly increased compared to pure titanium.

3.4 Actual example application

Photo 5 shows CASIO Computer's G-SHOCK "GMW-B5000 TR-9," for which Super-TIX™20AFG was adopted. As for titanium

(a)
(b)

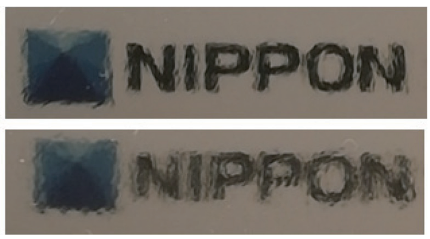

Photo 4 Mirror-polished titanium with (a) high DOI and (b) low DOI

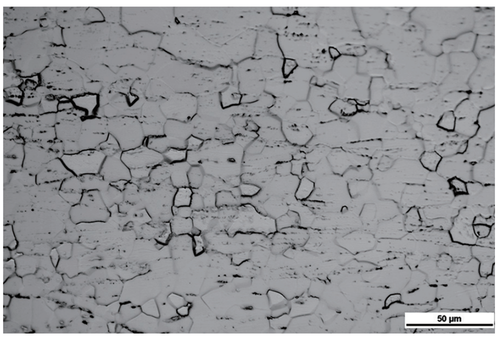

Fig. 4 Microstructure of hot-rolled Ti-2Al-0.2Fe strip manufactured at production mill

Photo 5 G-SHOCK made of Super-TIX™20AFG "GMW-B5000TR-9", provided by CASIO Computer Co., Ltd.

Table 4 Properties required for watch parts in Ti-2Al-0.2Fe, JIS Class 2 commercially pure titanium, and SUS304

Properties	Unit		Ti-2Al-0.2Fe	CP titanium	SUS304
Specularity (DOI)	%	The higher it is, the higher the mirror surface	84	55	–
Density	g/cc	The smaller it is, the lighter	4.47	4.51	7.93
Radio reception characteristics (specific permeability)	–	The closer it is to 1, the better	1.0002	1.0002	1.004
Radio reception characteristics (specific resistance)	$\mu\Omega$·cm	The higher it is, the better	95	45	72
Vickers hardness	HV1.0	The higher it is, the harder	203	120	170
Corrosion resistance for seawater	–	–	○	○	×

materials, which have been difficult to mirror-finish so far, the adoption of this alloy for GMW-B5000TR-9 enabled the same level of mirror-finish as that on stainless-steel materials. GMW-B5000TR-9 uses fully mirror-finished top plates for its bezel and band for the first time as a G-SHOCK titanium model. In addition, this specularity created a new expression that showcased the beauty of ion plating (IP), which enabled adopting multi-color IP for the first time as a G-SHOCK metal model. As described above, Super-TIX™20AFG is a titanium alloy that contributes to excellent specularity and surface design that is greatly secured with the specularity. Further expansion of applications in the future is expected.

4. Conclusion

This paper, aiming at expanding applications of $\alpha+\beta$ type titanium alloys, introduced the production of cold-rolled strips from high-strength $\alpha+\beta$ alloy Super-TIX™51AF (Ti-5Al-1Fe) and also introduced the development of Super-TIX™20AFG (Ti-2Al-0.2Fe) with high glossiness and high abradability. Firstly, cold-rolled Ti-5Al-1Fe strips could be manufactured using production mills. The fine equiaxed microstructure which is similar to that of Ti-6Al-4V sheets manufactured by pack rolling is formed in the cold-rolled Ti-5Al-1Fe strips. The bendability and deep drawability at room temperature are also excellent, and superplasticity occurs at high temperatures. Thus, the cold-rolled Ti-5Al-1Fe strips have formability at both room and high temperature. Utilizing these characteristics will further expand applications.

Secondly, Ti-2Al-0.2Fe is a titanium alloy with high specularity developed for watch parts. It has a great combination of specularity and workability, which is realized by controlling the chemical composition and microstructure. For Ti-2Al-0.2Fe hot-rolled sheets manufactured at a production mill, all the properties required for watch parts were remarkably improved compared to pure titanium. This alloy has been adopted for CASIO Computer's G-SHOCK "GMW-B5000TR-9," contributing to the realization of fully mirror-finished top plates, which was difficult for conventional titanium.

Acknowledgments

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