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Titanium Alloys Developed by Nippon Steel & Sumitomo Metal Corporation

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Abstract

Titanium alloys as structural materials developed by NSSMC are introduced. Those alloys were developed for aiming at being used in the field of non-aviation industries including automotive parts and utility goods, and actually applied in these fields. The alloys introduced in this article are developed with various alloy design bases; for example, utilization of inexpensive and common alloying elements such as Fe and Cu, and the effective extraction of advantages of conventional alloying elements, such as V and Zr. As a result, all of the alloys have characteristic high-functions. Surrounding technologies needed for actual use such as forming, heat treatment, welding etc. in addition to materials properties in the actual circumstances during the use are fully prepared, and the alloys are as user-friendly as the conventional alloys.

1. Introduction

Thanks to its excellent intrinsic corrosion resistance, commercially pure (CP) titanium has been widely used in the power generation and chemical industries. Recently, in appreciation of its good appearance, and taking advantage of more advanced forming and working practices, the application of titanium has expanded to building construction, civil engineering projects, and general consumer goods. For use in corrosive environments too severe for CP titanium, titanium alloys with a higher corrosion resistance containing small amounts of platinum group elements have been developed and used. High-strength titanium alloys are responsible for many structural members in the aerospace industry, owing to their light weight and high strength, and this field of application is expected to expand even further, to become a huge market.

Making the most of the technical expertise inherited from its two predecessors, Nippon Steel & Sumitomo Metal Corporation has endeavored to expand its markets for CP titanium and titanium alloys, and has earned high appreciation from customer industries.

Pure titanium has excellent corrosion resistance in chloride-containing environments, but crevice corrosion may occur in it when temperatures and chloride concentrations are high, so the use of Ti-Pd alloys containing 0.12 to 0.25% Pd (JIS Classes 11 to 13, ASTM Gr. 7, etc.) is widely recommended in such environments. However, the addition of rare metal elements such as Pd increases the material price significantly, no matter how small the additional element amount may be. For the applications mentioned above, Nippon Steel & Sumitomo Metal has developed more cost-affordable SMIACE™ series alloys (Ti-0.05Pd and Ti-0.05Pd-0.3Co), which contain less Pd but have substantially the same corrosion resistance. These alloys have been included in the ASTM standard system as Grs. 17 and 30, and the company has marketed them exclusively. It obtained a license for TICOREX (Ti-0.5Ni-0.05Ru) containing Ru, the price of which is more stable than that of Pd, and is marketing this alloy under its own brand, principally in the form of thin sheet products. This alloy is also resistant to crevice corrosion in environments characterized by high temperatures and high chloride concentrations; it is also included in the ASTM system as Gr. 13. For more details on these corrosion-resistant titanium alloys marketed exclusively by Nippon Steel & Sumitomo Metal, see another article in the present issue.

The company has also established manufacturing processes to consistently satisfy extremely stringent quality requirements for aerospace materials, and has been supplying bars of Ti-6Al-4V for aircraft engine turbine blades. The company has supplied this alloy even in the form of the springs used during the separation of the stages of H2A/B rockets, which are used to launch satellites. For more details on Nippon Steel & Sumitomo Metal's titanium products for the aerospace industry and the technical developments it has

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achieved in that field, see another article in the present issue.

Until the 1990s, high-strength titanium alloys for structural use were rarely used for automotive parts, consumer products or other general industrial items because of prevailing high prices. In consideration of this situation, and aiming at expanding its market for titanium alloys beyond the aerospace industry, since the mid-1990s the company has focused on developing technologies for reducing material and manufacturing costs, and on establishing methods for working and using the alloys more easily.

A typical example of the fruit of such efforts is the company's development of the Super-TIX™ series alloys.[1-4] These are high-functionality alloys unique to Nippon Steel & Sumitomo Metal. They contain no, or very little, expensive rare metal elements such as V and Mo (which are used widely in other Ti alloys for general applications), but instead include Fe, O, N, Cu and other inexpensive elements. These alloying elements are not very significant in terms of cost, accounting for only 10% or less of total material costs, and, combined with changes in production processes, they give new functionality and new properties to the product alloys, which are now being used for a wide variety of applications, including component parts for motor vehicles and ships, high-speed rotating machines, sporting goods, and self-protection wear. The various β titanium alloys that have been developed contain rare metal elements which are expensive, but their excellent properties more than justify the cost of the added elements,[5] and are widely used for consumer products. This paper presents the unique titanium alloys developed by Nippon Steel & Sumitomo Metal for structural applications.

2. Titanium Alloys Containing Fe

Most high-strength $\alpha + \beta$ titanium alloys contain Al to strengthen the α phase, and also contain prescribed amounts of V, Mo and other β-phase-stabilizing elements to obtain a dual-phase structure for ease of metallographic control, such as obtaining refined microstructures. Since the 1990s, Nippon Steel & Sumitomo Metal has developed various titanium alloys in which all or some of such β-phase-stabilizing elements are replaced with Fe, which is an economical and versatile element that also stabilizes the β phase. **Figure 1** schematically compares the strengths and ductility relationships of these new Fe-containing alloys with conventional ones. Specifically, the strength of the developed alloys ranges from the level of low-alloy materials equivalent to CP titanium, to above the strength of Ti-6Al-4V for general applications.

The Fe-containing alloys that Nippon Steel & Sumitomo Metal has developed are separated into the Ti-Fe-O-N group and the Ti-Fe-Al group. The Ti-Fe-O-N group includes modified CP titanium (mod. CP) and Super-TIX™ 800 (see Fig. 1). To be more exact, mod. CP falls within the category of CP titanium, but owing to its increased Fe content, crystal grain size control is easy, and it is used for motorcycle mufflers and the like. The basic chemistry of Super-TIX™ 800[1, 6, 7] is Ti-1%Fe-0.35%O, and the material has a tensile strength of approximately 800 MPa. Because the alloy does not contain Al (an element that decreases hot workability), its hot workability is as good as that of ASTM Gr. 4 CP titanium, as seen in **Fig. 2**. Taking advantage of this fact, it is rolled into various shapes of products including plates, hot- and cold-rolled sheets, and wire rods. It should be noted, however, that in contrast to their excellent hot workability, the strength of the Ti-Fe-O-N group alloys is inferior to that of Al-added alloys in the middle and high (warm and hot) temperature ranges. The strength of Fe-added alloys decreases with increasing temperature, and this has to be adequately taken into account when considering their use.[1, 6, 7]

The addition amounts of the component elements in Ti-Fe-O-N alloys are not precisely defined one by one, but the total amount of the alloy elements and impurities is defined in terms of oxygen equivalent (Oeq), as given below, in order to allow flexibility in the choice of scrap metal, low-grade sponge titanium, and other raw materials:

$$\mathrm{Oeq} = [\mathrm{O}] + 2.77\,[\mathrm{N}] + 0.085\,([\mathrm{Fe}] + [\mathrm{Ni}] + [\mathrm{Cr}]),$$

where [ ] is the addition amount of each element. The alloys of this group are weldable by TIG welding and other welding methods

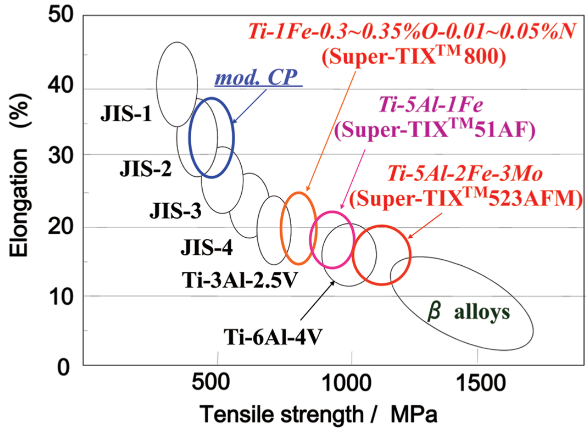

Fig. 1 Relationship between strength and ductility of Fe-added titanium alloys developed by Nippon Steel & Sumitomo Metal (schematic representation)

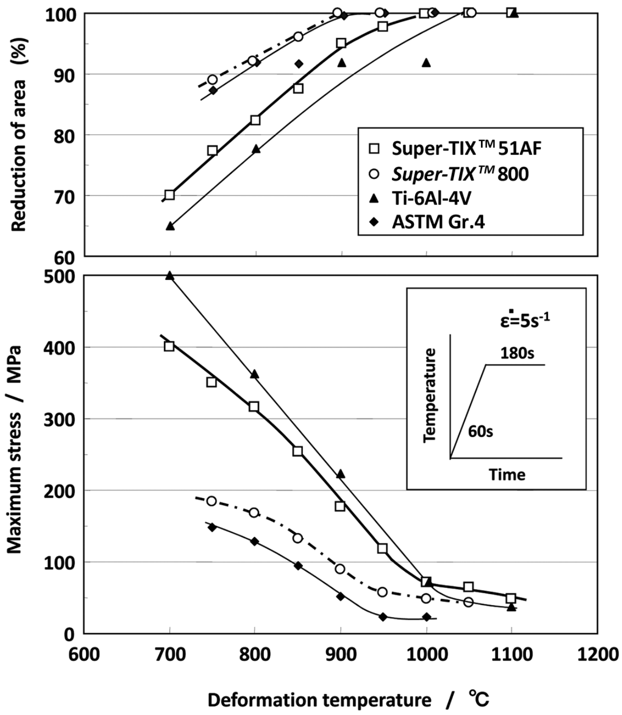

Fig. 2 Hot deformation characteristics (reduction of area (upper) and maximum deformation stress (lower)) of Super-TIX™ 51AF, Super-TIX™ 800, Ti-6Al-4V and ASTM Gr. 4 CP Titanium at Gleeble test (after heat treatment above β transus and slow cooling)

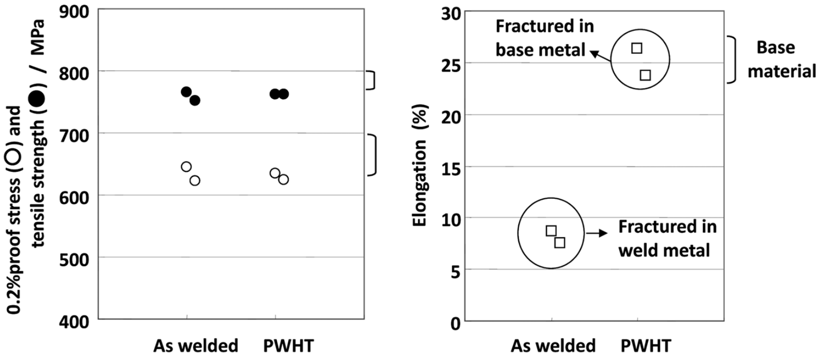

Fig. 3 Tensile properties of TIG weld joints of 5-mm thick Super-TIX™ 800 plates (3-pass welding using matching filler wire) Post-weld heat treatment (PWHT) is effective at raising weld metal ductility.

commonly employed for titanium and its alloys.[7, 8)] It should be noted, however, that, like other high-strength $\alpha + \beta$ titanium alloys, a fine, acicular and brittle martensitic structure is likely to form at the weld joints of these alloys if cooled quickly; as shown in **Fig. 3**, post-weld heat treatment (PWHT) at 700 to 800°C is recommended.[7, 8)]

The company also markets Super-TIX™ 800N (Ti-1%Fe-0.3%O-0.05%N). It contains less O and more N than Super-TIX™ 800, and is used for applications requiring better corrosion resistance[7)] and higher impact toughness than those of the latter. In the manufacture of this alloy, N is not added in the form of TiN, which has a high melting temperature and would be likely to remain as unmelted inclusions. Instead, master alloys of Fe-N (Fe_4N to Fe_3N) are used as the nitrogen source.

Super-TIX™ 51AF and Super-TIX™ 523AFM (Ti-5Al-2Fe-3Mo) fall within the category of the other group, the Ti-Fe-Al alloys.[2, 3, 7)] The chemical compositions of these alloys were defined in consideration of such factors as the effect of the content of Al (an α-phase-strengthening element) and the effect of the content of Fe (a β-phase-strengthening element), on material strength (see **Fig. 4**), possible Fe segregation in large ingots, and the influence of Al on hot workability.[2)] For instance, Super-TIX™ 51AF was developed as an alloy with a base composition of Ti-5Al-1Fe, which has the same strength as that of Ti-6Al-4V ELI (extra low interstitials) or the standard grade of Ti-6Al-4V, and its Al content is 1% less than that of the Ti-6Al-4V alloys, in order to decrease hot deformation resistance (see Fig. 2).

The strength of this alloy group can be controlled precisely by changing the addition amount of O:[2, 7)] when the O content is 0.15% (the standard value), the strength is substantially equal to that of Ti-6Al-4V ELI. But when the O content exceeds 0.2%, the strength goes up to a level comparable to that of the standard grade of Ti-6Al-4V. Thanks to their excellent hot workability and high Young's moduli, the alloys of this group can be hot rolled into round bars and strips in coil. Making the most of their light weight and high strength, they are used for golf clubs and a wide variety of other products.[9)] See another article in the present issue for more details on hot-rolled strips of Super-TIX™ 51AF.

As indicated in Fig. 4, to obtain alloys stronger than Super-TIX™ 51AF it is necessary to increase Al and Fe content. Higher Al content, however, may deteriorate hot workability, marring the advantages of the low-price alloy. In addition, when Fe content exceeds 2%, segregation occurs during solidification, and the casting of large ingots becomes difficult. Super-TIX™ 523AFM (Ti-5Al-2Fe-3Mo) has been developed to solve these problems: Fe addition

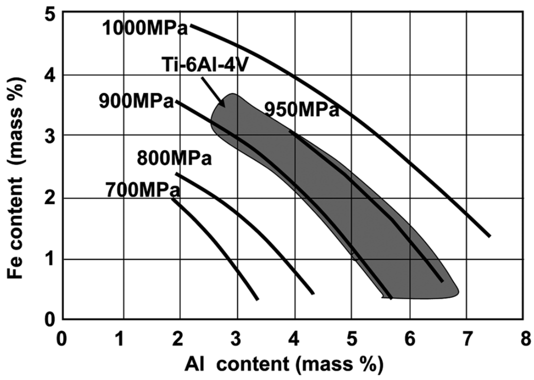

Fig. 4 Effects of Al and Fe contents on tensile strength of Ti-Al-Fe ternary alloys
Specimens were taken from hot-rolled bars containing roughly 0.06 mass% O. Curves in the graph show the same tensile strength depicted by each figure. Strength level of Ti-6Al-4V (including ELI and standard grades) is also shown with dark area.

is limited to 2%, and to increase the β-phase-stabilizing effects, Mo is added by 3%, even though it is an expensive rare-metal element.[3)] Super-TIX™ 523AFM is naturally superior to Ti-6Al-4V in tensile and fatigue strength, and its wire rods are used for the intake valves of motorcycles and automobile engines.[3, 10)]

Super-TIX™ 523AFM strength can be further increased through heat treatment. To improve the alloy's room-temperature workability, it is possible through special heat treatment to lower its 0.2% proof stress (which is roughly 950 MPa in an annealed condition) to as low as around 420 MP. It is also possible, naturally, to increase its strength to the original level through work-hardening or post heat treatment. Another special feature of the alloy is that its Young's modulus, roughly 110 GPa in an annealed condition, can be lowered to approximately 70 GPa, which is comparable to that of β titanium alloys.[11)] Applications for this alloy are being developed, taking advantage of these characteristics. Detailed metallographic analysis has made it clear that characteristics particular to the alloy are due to $\beta \rightarrow \alpha'' \rightarrow \alpha'$ two-stage deformation-induced martensitic transformation.[11)] Characteristic mechanical properties of Super-TIX™ 523AFM are reported in more detail in another article in the present issue.

The equilibrium phase of titanium alloys containing Fe at room to middle temperatures is FeTi, but because this phase forms so slowly, the alloys can basically be regarded as $\alpha + \beta$ alloys. When such Fe-containing alloys are held at 450°C or higher for a long period, therefore, an equilibrium FeTi phase forms, which is likely to cause ductility and toughness to deteriorate.

Photo 1 shows transmission electron microscope (TEM) images of the FeTi phase that formed in the β phase of the specimens of Ti-2.2%Fe-0.1%O-0.05%N and Ti-5Al-2Fe, which were annealed at 750˚C for 1 h, air cooled, and then aged at 450˚C for 1,024 or 2,048 h.[12, 13] Here, the retained β phase is seen to have dissolved into the α phase and the FeTi phase, although these two phases are in equiaxed grains and not the products of eutectoid reactions. It is presumed that the α phase first formed in the retained β phase during aging, and that the Ti and Fe in the β phase, in which Fe was condensed, were then rearranged by an ordering reaction, and as a result the β phase transformed into the FeTi phase.[13] When Ti-Fe-O-N alloys are aged at temperatures lower than the above (for instance, 300 to 350˚C), strength increases and ductility decreases markedly.[12] This was once considered to be due to formation of an ordered phase of Ti and O and another of Ti and N,[12] but since advances in TEM technology, it has been found that an ω phase precipitates in the retained β phase, and a coherent precipitation phase of Fe forms in the α phase during long aging. These factors are now considered responsible for the above-mentioned changes in strength and ductility.[14]

When Ti-Fe-O-N or Ti-Al-Fe alloys are strengthened through solution heat treatment, rapid cooling, and then aging, the FeTi phase appears in a comparatively short aging time (roughly 4 h).[12, 13, 15] The structure of this phase, however, is different from that shown in Photo 1, although the phase precipitates in fine particles (as shown in **Photo 2**) at the boundaries of the martensite phase which forms during rapid cooling after solution heat treatment.[15] On the other hand, in the case of Super-TIX™ 523AFM, to which Mo is added to stabilize the β phase, while the FeTi phase is expected to form at roughly 500˚C according to the phase equilibrium calculation by Thermo-Calc, the phase has not actually been found to form within the usual exposure time at that temperature.[13]

As explained above, while Nippon Steel & Sumitomo Metal's Fe-containing titanium alloys demonstrate properties similar to those of Ti-6Al-4V and the like for general applications, they have various characteristics particular to those obtained with such special alloying elements as O, N and Fe, and care must be taken to ensure appropriate heat treatment conditions and use temperatures. For more details on these alloys, refer to the reference literature given at the end of this paper.

3. Titanium Alloys Containing Cu

In addition to the above-mentioned Fe-containing, high-strength titanium alloys, Nippon Steel & Sumitomo Metal has also developed such Cu-containing alloys as Super-TIX™ 10CU (Ti-1Cu) and Super-TIX™ 10CUNB (Ti-1Cu-0.2Nb), which have cold workability as good as that of CP titanium, as well as high heat resistance.[4, 16, 17] Cold-rolled sheets of these alloys are used for automotive mufflers and exhaust systems. The excellent high-temperature strength of these alloys is due to solid-solution hardening by Cu, which is soluble in the α phase up to a maximum of 2.2 mass%, and due also to good workability at room temperature since the twinning deformation responsible for the excellent workability of CP titanium is not adversely affected by Cu addition; this fact was discovered only recently.[16]

Photo 3 shows optical microstructures of annealed sheet specimens of ASTM Grs. 1 and 2 CP titanium and Ti-1%Cu, after the application of tensile strains of 3, 5.5 and 10.5%.[16] In the Ti-1%Cu specimens, there are as many deformation twins as in the Gr. 1 specimens, or more, even when the strain was low. This indicates that, unlike Al addition, Cu addition does not hinder twinning deformation, or rather, it makes deformation easier to take place. At high

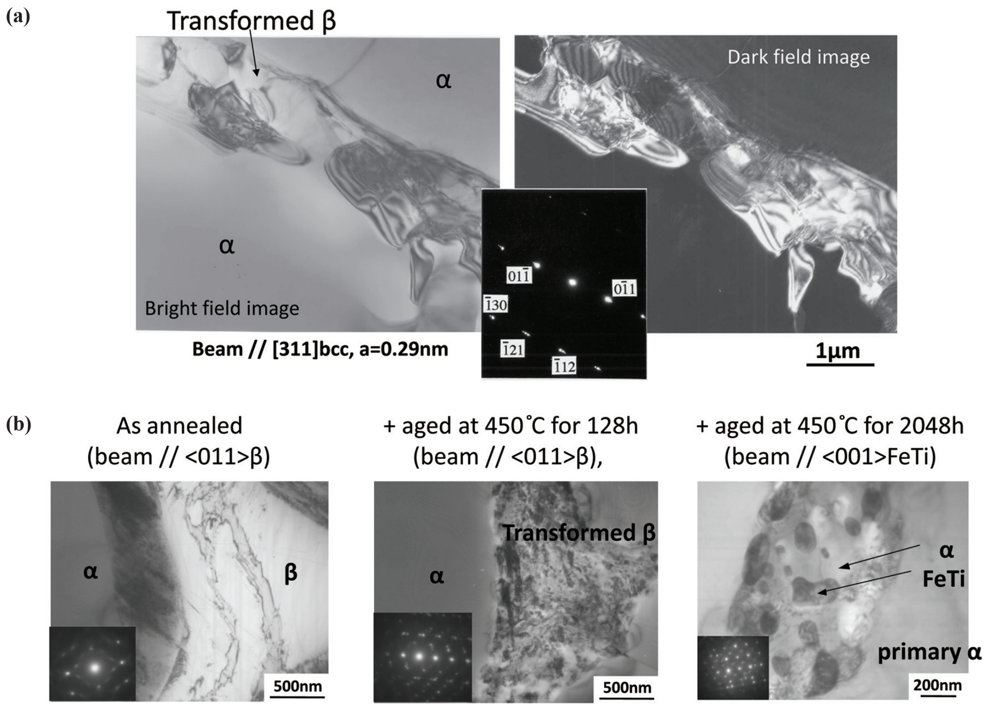

Photo 1 FeTi formation in annealed Fe–added Super-TIX alloys
(a) TEM observations for Ti-2.2%Fe-0.1%O-0.05%N annealed at 750˚C for 1 h, air cooled, and then aged at 450˚C for 1,024 h
(b) TEM observations of Ti-5%Al-1%Fe (Super-TIX™ 51AF) annealed at 750˚C for 1 h, air cooled, and then aged at 450˚C for up to 2,048 h

temperatures, where twinning deformation is unlikely to occur, Cu exhibits a solid-solution hardening ability as high as that of Al or even higher, which means that Cu-containing alloys are, conveniently, excellent in both room-temperature workability and high-temperature strength. In appreciation of this finding and its application to the design of Super-TIX™ 10CU (Ti-1Cu), the company received the Technical Award from the Japan Institute of Metals and Materials for the business year 2010 (ending March 2011).[18)]

For further details on Super-TIX™ 10CU properties, see another article in the present issue. As stated therein, another recently developed alloy contains more solute elements than the Ti-Cu alloys do. At 500˚C or above, this new alloy exhibits a strength roughly one-and-a-half times higher than that of Ti-1Cu or Ti-1Cu-0.5Nb, and three times higher than that of Gr. 2 CP titanium, while maintaining the same room-temperature workability as that of JIS Class 2 or ASTM Gr. 2. In appreciation of this fact, the new alloy has been used for automotive exhaust systems, the working temperature of which is becoming increasingly higher.

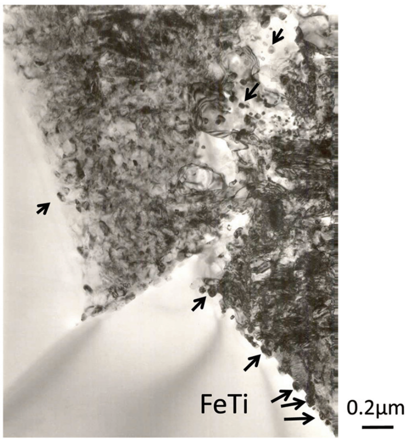

Photo 2 FeTi particles (arrows) in Ti-5%Al-1%Fe (Super-TIX™ 51AF) after solution treatment at 940˚C for 1 h, water quenching, aging at 500˚C for 8 h, and then air cooling

As stated above, instead of only relying on its alloys for aerospace applications, Nippon Steel & Sumitomo Metal has developed various other titanium alloys using economical alloying elements, and has cultivated new applications for them. In appreciation of those applications, especially for automotive parts, the company received the Titanium Application Development Award from the International Titanium Association in 2007.

4. Beta Titanium Alloys

Nippon Steel & Sumitomo Metal produces wire rods of Timetal LCB developed by TIMET, U.S.A., as well as wire rods and sheets of Ti-15V-3Cr-3Sn-3Al for motorcycle suspension springs, eyeglass frames and other products. In addition, the company developed another β titanium alloy SSAT™-2041CF (Ti-20V-4Al-1Sn), which has a smaller deformation resistance at high temperatures and better cold formability than those of such conventional β alloys as Ti-15V-3Cr-3Sn -3Al and Ti-3Al-8V-6Cr-4Mo-4Zr (β - C). This developed alloy is used in products such as high-specification bicycle rear axle gears and ski poles; the ski poles of this alloy were used at the 2008 Winter Olympic Games by virtue of their excellent impact resistance and vibration damping ability. When solution treated, the SSAT™-2041 alloy is softer and has better workability than other β alloys, and after aging treatment, its strength becomes basically as high as that of other β alloys.

Figure 5 compares the cold forging properties of SSAT™-2041 (solution treated at 850˚C) with those of CP titanium and titanium alloys.[5)] Whereas β titanium alloys have the shortcoming of large deformation resistance despite high forming limits, the developed alloy demonstrates cold forming properties as high as those of other β alloys, and lower deformation resistance, which indicates its ex-

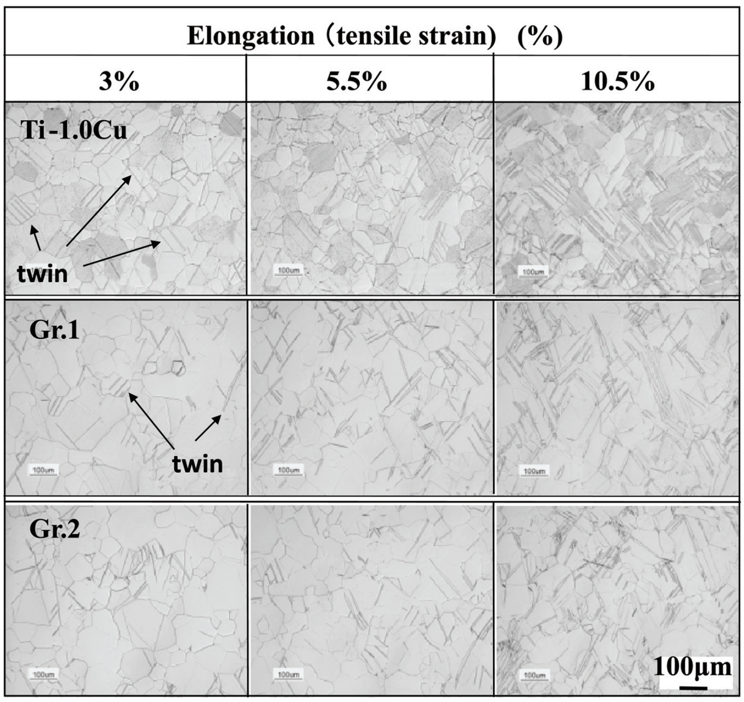

Photo 3 Microstructures of Gr.1, Gr.2 and Ti-1Cu (Super-TIX™ 10CU) tensile deformed by 3, 5.5 and 10.5%

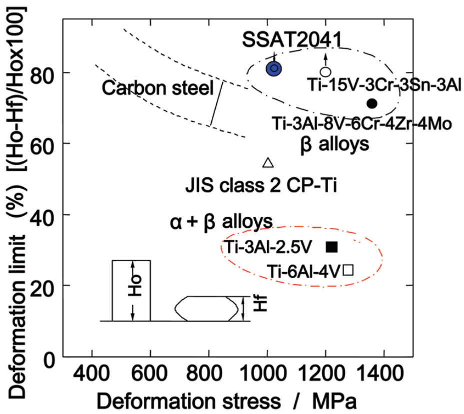

Fig. 5 Cold forgeability of SSAT™-2041(solution treated at 850°C) and other titanium and its alloys

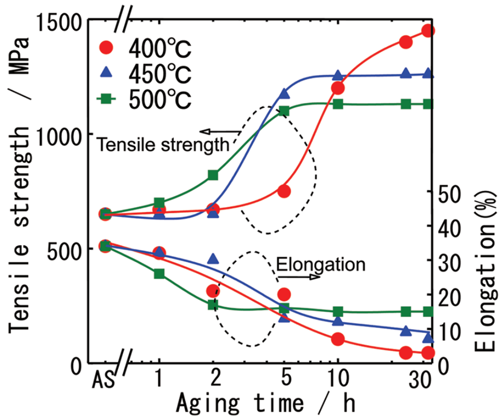

Fig. 6 Aging characteristics of SSAT™-2041(solution treated at 850°C) at 400 - 500°C

cellent workability. In addition, as seen in **Fig. 6**,[19, 20] its tensile strength can be increased to the level of other β alloys (1,200 MPa or higher) by solution treatment at 850°C followed by aging.

5. Other Titanium Alloys

In addition to the alloys presented herein, Nippon Steel & Sumitomo Metal has also developed alloy modifications for different use environments. Besides such modification alloys, SSAT™-10CF (Ti-10Zr) and SSAT™-18CF (Ti-18Zr) have been developed;[21] here, the effects of Zr, which is a common component element of titanium alloys such as V in the SSAT™-2041 mentioned in Section 4, are effectively utilized. These alloys are characterized by their fine crystal grains due to Zr, and exhibit strength, scratch resistance, surface finish properties and formability exceeding those of CP titanium. Thanks to the good biocompatibility of Ti and Zr, they are used for eyeglass frames, watches and other products.

6. Closing Remarks

This paper has presented unique titanium alloys developed by Nippon Steel & Sumitomo Metal for structural applications. Most were developed not for aerospace industries but primarily for applications for automotive parts and consumer goods, and their use for such applications is actually expanding.

During the development stage, the effects of different alloying elements on material properties were identified, and the resulting knowledge was incorporated with microstructure control technologies in thermo-mechanical processing. The company's alloy development capacity, which is based on the fruit of its basic research, is one source of its competitive edge. Nippon Steel & Sumitomo Metal is further solidifying the foundation of its fundamental metallurgical knowledge in order to strengthen its ability to develop higher functionality alloys and manufacturing processes that ensure the intended alloy functionality.

Steps are also being taken to develop new application methods, including the working, forming and joining of new materials, while gathering material data under different use conditions and while preparing guidelines for field use, so that alloys developed by the company can be used as easily as common alloys for general applications.

Nippon Steel & Sumitomo Metal is determined to further contribute to the growth of titanium-producing and consuming industries through application expansion of new alloys, making the most of its competitive edge. Its contributions, primarily in the form of its R&D activities, will enhance material functionality in accordance with fundamental metallurgy, develop new working/forming methods and applications, and acquire information on actual use.

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