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Development of Low-Cost High-Strength Ti-Fe-O-N Alloy Series

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Abstract

Alloy design of low-cost high-strength Ti-Fe-O-N alloy series and their materials properties were described. The alloy series do not contain any expensive elements and have high tensile strength ranging from 700 to 1,000MPa as well as high ductility and excellent hot workability. Their corrosion resistance and weldability are also excellent and the alloy series seem to be suitable for the applications used at temperatures not far from room temperature. On the other hand, some attention should be paid to decrease of strength and change of their properties during long term usage when the alloys are used at intermediate temperature. The Ti-Fe-O-N alloy series are the core alloy series in the newly developed "Super-TIX series" together with the Ti-Fe-Al alloy series and the application of those alloys to various fields are now ongoing.

1. Introduction

When reducing manufacturing cost of alloys by modifying the alloy compositions, the first approach is generally to replace expensive alloying elements with inexpensive ones having similar functions. In the case of titanium alloys, many attempts to replace V or Mo, which are expensive β stabilizing elements contained in the most of the commercial alloys, with inexpensive Fe have been made[1-4]. The author and his colleagues also carried out a similar study and developed new alloys such as Ti-3.5Al-1Fe and Ti-5.5Al-1Fe[4], and some alloys are introduced in the current issue of Nippon Steel Technical Report (No.85). These alloys are, in fact, more inexpensive than conventional alloys which contain expensive β stabilizing elements and also have some heat resistance and other functions peculiar to these compositions, giving them high industrial value.

However, since many of these alloys contain several percent of Al which increases hot deformation resistance and decreases hot workability, there are several drawbacks : the rolling mill power is restricted, a lot of work for removing surface defects is needed, and consequently yield is reduced, etc., resulting in the still high manufacturing cost. Therefore, the next step for reducing the cost of titanium alloys is considered to improve the hot workability. From this point of view, we developed Ti-Fe-O-N alloys not only by using Fe which is an inexpensive β stabilizing element, but also by using interstitial elements O and N as the α stabilizing elements which are inexpensive and are able to increase the strength at temperatures near room temperature without affecting the strength at hot working temperatures, in place of substitutional element Al.

This report introduces the concept of the alloy design and the outline of the development, then describes some characteristics which result from using Fe, O, and N as the alloying elements as well as some precautions. Also, since there are many applications which re-

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quire joining such as welding, the weldability of the alloy series is briefly introduced.

2. Design of Alloy

O and N stabilize and strengthen the α phase like Al. As the added quantity of these elements increases, slip concentrates on a specific slip plane, and so ductility becomes smaller. This so-called planar slip mode is presumed to occur due to the formation of the short range ordered phase of Ti and O or N. For instance, planer slip is observed when the amount of O is 0.3 to 0.4 mass % or more$^{5)}$. Therefore, in terms of the quantity of these interstitial elements to be added to titanium materials, the upper limit of O is 0.4 mass % and that of N is 0.05 mass % even in ASTM grade 4 in which the highest concentrations of O and N are specified in the titanium materials standardized in ASTM.

However, such planar slip is also remarkable with alloys in which 3 to 4 mass % or more Al is added (due to the short range ordering of Ti_3Al [α_2 phase]), and almost all $\alpha + \beta$ type commercial alloys also have such a slip mode$^{5)}$. The reason why these alloys are nevertheless widely used for applications requiring strict specifications such as aircraft is that, despite the planar and heterogeneous slip in individual grains, microstructures are refined to exhibit comparatively uniform deformation as a whole of materials (i.e. the slip distance is shortened), and ductility is secured. Depending to the purpose of use, it is certainly important to control the quantity of O, etc. which helps promote the formation of the short range ordered phase of Ti_3Al (ELI grade)$^{6)}$. It is conventional practice to carry out an appropriate thermo-mechanical processing in addition to dual phasing by adding β stabilizing elements to achieve such refined microstructures.

Based on the above concept, the alloy series have been developed using O and N as the main strengthening elements in place of Al, by adding inexpensive Fe, instead of expensive V or Mo, to cause the β phase to retain, and by appropriately adjusting the amounts of these elements. The excellent hot workability resulted from exclusion of Al is very frequently utilized for reducing production cost as well as for thermo-mechanical processing for refining microstructures.

Fig. 1 shows the tensile strength of the alloys which were studied in the process of developing the alloy series. Every alloy was annealed at 750°C for 1h followed by air cooling after being hot worked in the $\alpha + \beta$ temperature region. [O]eq on the horizontal axis is the oxygen equivalent against tensile strength, and is an expression wherein the strengthening capabilities of O, N, and Fe confirmed by binary titanium alloys were linearly combined with setting the coefficient for O content (designated by [O]) as 1. Although [O]eq was originally evaluated in binary alloys, it was also effective for analyzing the tensile strength of multi-compositional alloys as shown in Fig. 1, thus making it possible to design alloys at a wide range of strengths equivalent to those from ASTM grade 4 to Ti-6Al-4V. On the other hand, ductility was very high and the majority of the alloy compositions enumerated in Fig. 1 showed 20% or more elongation. In the case of highly strengthened materials, however, attention must be paid to the quantity of N and O in order to secure ductility and toughness.

Fig. 2 shows the tensile properties of Ti-Fe-O-N titanium alloys having [O]eq in the range of 0.65 to 0.74. Every specimen was taken from the forged and annealed (750°C, 1h, air cooled) bars of 15 mm in diameter. Alloys other than the two alloys surrounded by the frame in the figures were excellent in both strength and ductility, and their notched tensile strength was also very high. On the other hand, ductility and notched tensile strength of the two alloys within the frame were much lower than those of the other three alloys. The greatest difference between these two groups of alloys is that while the alloys which showed high ductility contained a good balance of O and N, the alloys which showed low ductility did not contain N except at an unavoidable level and were the alloys substantially strengthened only by O. This fact indicates that in order to attain a good balance of

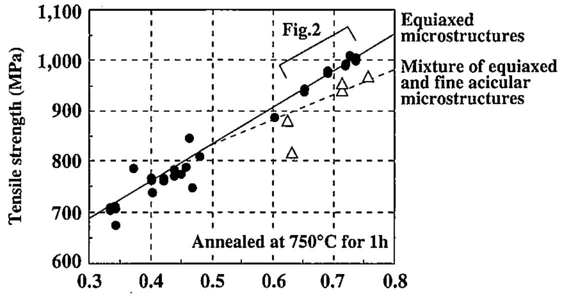
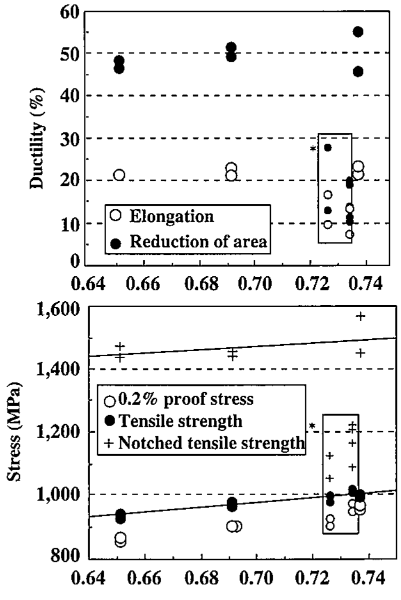


Fig. 1 Effect of oxygen equivalent, [O]eq, on tensile strength of Ti-Fe-O-N titanium alloys



* Marks within the frame show substantial Ti-Fe-O alloys which do not contain N except at an unavoidable level

Fig. 2 Effect of oxygen equivalent, [O]eq, on tensile properties of forged and annealed (750°C, 1h, air cooled) bars of 15 mm in diameter composed of Ti-Fe-O-N titanium alloys

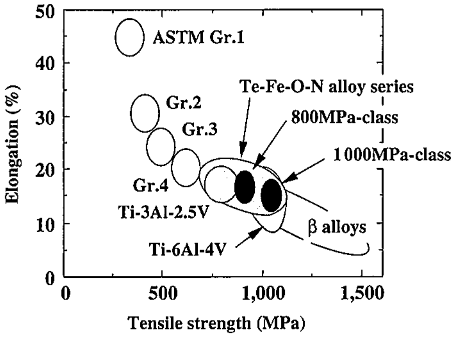


Fig. 3 Relationship between ductility and strength in Ti-Fe-O-N titanium alloy series and conventionally used commercial alloys

strength and ductility, it is important to add both O and N in appropriate quantities.

Fig. 3 is a schematic diagram comparing strength and ductility between the developed alloy series and existing alloys. The developed alloy series can cover a wide range of strengths from ASTM grade 4 to Ti-6Al-4V by adjusting the quantity of Fe, O, and N.

3. Characteristics of material properties of the developed alloy series and limit of application

3.1 Hot workability

The most advantageous features of the developed alloy series are high strength at room temperature and excellent hot workability. **Fig. 4** shows hot workability of Ti-1.5%Fe-0.5%O-0.05%N (tensile strength at room temperature ; approx. 1,000 MPa), Ti-6Al-4V, and ASTM grade 4, evaluated with the Gleeble test. Each specimen was once heated to the β region and air cooled before the tests, and had the acicular microstructure which is believed to show lower hot workability.

Although tensile properties of the developed alloy series at room temperature were similar to those of Ti-6Al-4V, their hot deformation characteristics in the $\alpha + \beta$ temperature region (700 to 950°C) were very different from those of Ti-6Al-4V as shown in Fig. 4: hot deformation stress of the developed alloy was much lower than that of Ti-6Al-4V and was slightly higher than that of ASTM grade 4. Moreover, hot ductility of the developed alloy was much higher than that of Ti-6Al-4V and was almost the same as that of ASTM grade 4 which is a kind of commercially pure titanium. Hence, it was confirmed that the developed alloy series which do not contain Al possess excellent hot workability, as expected.

Because of this excellent hot workability, the decrease in yield resulting from surface defects and/or cracks generated during hot working can be suppressed. In addition, their lower hot deformation resistance makes hot rolling of large ingots or slabs in the $\alpha + \beta$ region possible, which is generally difficult for conventional high-strength titanium alloys. It also becomes possible to manufacture plates having small anisotropy of materials properties by controlling the rolling direction appropriately[7].

3.2 Strength at intermediate temperatures

Although it is the front and back relationship with excellent hot workability, strength of the alloys rapidly decreases with increase of temperature since the developed alloy series do not contain Al which contributes to raising strength in the high temperature region,. **Fig. 5** shows the temperature dependence of strength of a Ti-1.5%Fe-0.5%O-0.05%N annealed plate (12 mm in thickness) in an intermediate temperature region. At room temperature, the annealed plate has strength equivalent to that of Ti-6Al-4V, but its strength was lower than that of Ti-6Al-4V by 200 MPa or more at 200°C. When the developed alloy series are used for applications where such temperature increase may occur, the loss of strength must be taken into account. However, when used at 100°C, the difference of strength between the developed alloy series and Ti-6Al-4V is approximately 100 MPa, and strength equivalent to that of Ti-6Al-4V ELI is maintained.

3.3 Phase stability at intermediate temperatures

In the developed alloy series, Fe, O, and N were added as alloying elements. The diffusivity of these elements is higher than that of other alloying elements such as Mo, V, or Al which are widely used for titanium alloys. In addition, according to the equilibrium phase diagram of Ti and Fe, unlike the conventional $\alpha + \beta$ type titanium

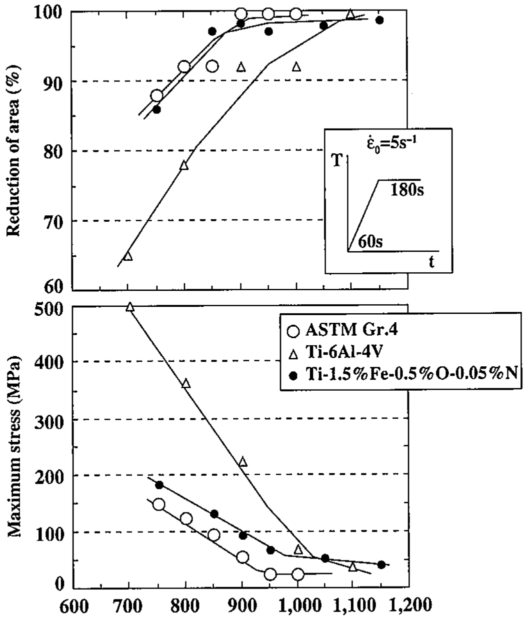
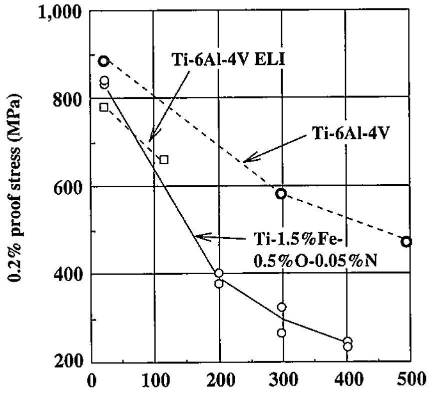
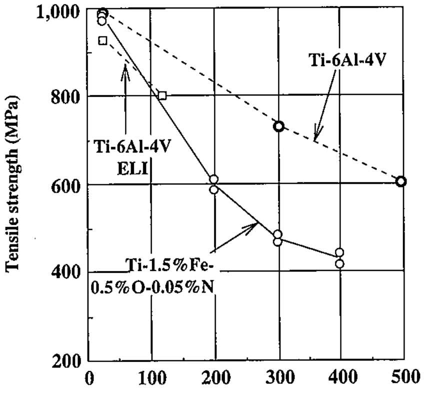


Fig. 4 Hot deformation characteristics of β-annealed Ti-1.5%Fe-0.5%O-0.05% N (Gleeble test)



(a) 0.2% proof stress



(b) Tensile strength

Fig. 5 Temperature dependence of 0.2% proof stress and tensile strength of Ti-1.5% Fe-0.5%O-0.05%N and Ti-6Al-4V hot rolled and annealed plates (12 mm in thickness) alloys, the FeTi phase instead of the β phase is the equilibrium phase at intermediate or lower temperatures including room temperature. Furthermore, when the amount of O and N increases, the ordered phases are likely to be generated. Thus, the phase stability was evaluated by tensile tests at room temperature, etc. using the specimens exposed at temperatures between 150 and 450°C for a long time (up to about 4,000 h).

Fig. 6 shows the effect of long term exposure at intermediate and high temperatures on the strength and ductility of a Ti-1.5%Fe-0.5%O-0.05%N annealed plate having tensile strength level of 1,000 MPa. Although Fe, O, and N were added to the alloy series as alloying elements, almost no change of properties was observed at 200°C or lower, and it was confirmed that the alloy series have fully high stability in a temperature range of 200°C or lower.

On the other hand, at 300 and 350°C, strength increased and ductility decreased with the lapse of exposure time. In particular, in the case of long term exposure at 300°C, the reduction of area, which was 40% or more in the annealed state, lowered to 20% or less. Since the formation of the FeTi phase was not observed in this temperature range, the above mentioned change of tensile properties was considered to be due to the progress of the ordering of O and N with Ti. Meanwhile, exposure at 450°C lowered both strength and ductility. While the formation of FeTi was observed at this temperature, O and N were considered to have dissolved well in titanium matrix at 450°C, so the change of tensile properties was considered to be related to the formation of FeTi.

There is a possibility that the alloy series could be used not only in the annealed state but also in the states of the β annealing and the solution treatment and aging (STA). Then, the formation of FeTi was examined with X-ray diffraction analyses for the specimens exposed at intermediate to high temperatures after the various heat treatments.

Table 1 Exposure time at 450°C for which the formation of FeTi was confirmed for the first time with X-ray diffraction analyses in the β-treated Ti-2%Fe-0.1%O-0.05%N

Cooling rate from the β region Alloy	Water quenching	Air cooling	Furnace cooling
Ti-2%Fe-0.1%O-0.05%N	128h	512h	1,024h

Table 2 Exposure time at 450°C for which the formation of FeTi was confirmed for the first time with X-ray diffraction analyses in Ti-Fe-O-N alloys solution treated in the $\alpha + \beta$ region

Alloys	Solution treatment/water quenching	Annealing
Ti-2%Fe-0.1%O-0.05%N	>64h	>64h
Ti-1.5%Fe-0.5%O-0.05%N	8h	>64h

Table 1 shows the time for which the formation of FeTi was confirmed for the first time with X-ray diffraction analyses when Ti-2%Fe-0.1%O-0.05%N annealed bars (15 mm in diameter) having tensile strength of around 800 MPa were heated to the β region first, then water quenched, air cooled or furnace cooled, and then exposed at 450°C. The slower the cooling rate was, in other words the greater the β phase stability was due to higher Fe concentration in the retained β phase, the more delayed the formation of FeTi was. However, it took 100h or longer to form FeTi even in the water quenched specimens, so the formation of FeTi under usual heat treatment is not a concern.

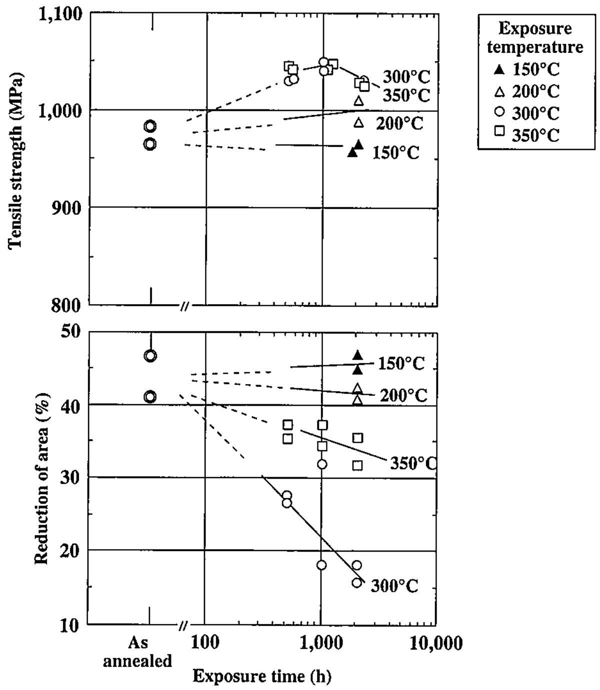


Fig. 6 Effect of long term exposure at intermediate temperatures on tensile properties at room temperature in Ti-1.5%Fe-0.5%O-0.05%N

Table 2 shows the results of the investigation for the FeTi formation at 450°C for two kinds of Ti-Fe-O-N alloys heated in the high $\alpha + \beta$ region and water quenched. Although FeTi was not formed even in 64h of exposure time in Ti-2%Fe-0.1%O-0.05%N in which the concentration of Fe is high, the formation of FeTi was observed only in 8h in Ti-1.5%Fe-0.5%O-0.05%N. This was much shorter than the annealed material in which FeTi was not formed after aging for 64h, and it suggests that Fe concentration (β stability) and martensitic microstructures strongly affect the FeTi formation behavior. However, in the alloy series, high temperature aging for as long as 8h is not necessary, and the formation of FeTi can be easily avoided in an actual heat treatment.

3.4 Corrosion resistance

It is generally believed that, in pure titanium, the increase in content of impurity Fe leads to the reduction in corrosion resistance. Therefore, when the alloy series containing Fe are used in a corrosive environment, it is necessary to correctly grasp the corrosion resistance of the alloy series in advance.

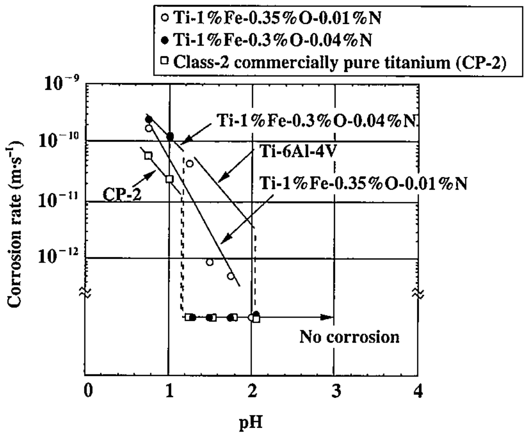


Fig. 7 Corrosion resistance of Ti-Fe-O-N alloy series in boiled 20% NaCl + HCl solutions

Fig. 7 shows the results of measuring the corrosion rates in boiled solutions of 20% NaCl + HCl for 45h. While the de-passivating pH of pure titanium was about 1.0, that of Ti-1.0%Fe-0.35%O-0.01%N which is one of the alloys having tensile strength of around 800 MPa was 1.75, so a slightly lower corrosion resistance was observed. However, it had higher corrosion resistance than Ti-6Al-4V. In Ti-1.0%Fe-0.3%O-0.04%N which contains plenty of N and is also an alloy having a tensile strength of around 800 MPa, de-passivating pH was 1.0 and was almost the same as that of pure titanium, which indicates that the decrease of corrosion resistance due to the addition of Fe could be suppressed by simultaneous addition of N. A similar phenomenon was recognized in Ti-0.5%Fe-0.2%O-0.1%N, etc.[8], but the mechanism has not been clarified yet and should be investigated in future studies.

3.5 Weldability

The 60-degree V-shaped groove was prepared for Ti-1.0%Fe-0.35%O-0.01%N hot rolled and annealed plates of 4.6 mm in thickness, and TIG welding (3 passes including 2 passes from the top surface and 1 pass from the back) was performed using matching filler. The weld metal and HAZ had fine acicular microstructures and hardened (HV250 to 300) a little more than the base metal (HV about 250). Although slight negative Fe segregation was observed along the fusion lines, there was no other segregation nor welding defects, and it was confirmed that the alloy had weldability equivalent to that of commercially pure titanium and Ti-6Al-4V.

Fig. 8 shows tensile properties of weld joints (in the transverse direction to the weld beads). 0.2% proof stress and tensile strength were slightly lower but were within those of the base metal, and did not change even after post weld heat treatment (750°C, 1h, air cooled) was performed. On the other hand, ductility of the as welded joint was comparatively high (7 to 8%), but was greatly enhanced by post weld heat treatment to 20% or higher which is nearly the same level as that of the base metal. It is noted that, in the as welded joint, fracture often occurred in the weld metal, but in the post weld heat treated one, fracture mainly occurred in the base metal.

Fig. 9 shows the results of the Charpy impact tests. Since a JIS No. 4 V notch standard test pieces could not be obtained because of the restriction of the plate thickness, sub-size test pieces of 4.5 mm in thickness were prepared, and two test pieces were fixed together to make a test piece of 9 mm in thickness, which was then tested. The notch position was in the weld metal. As shown in Fig. 8, the Charpy value of the as welded specimens was 40 J·cm^{-2} and was higher than that of the base metal, which was an excellent value for an alloy of this level of strength. However, the Charpy value was further enhanced by post weld heat treatment and reached nearly 60 J·cm^{-2}.

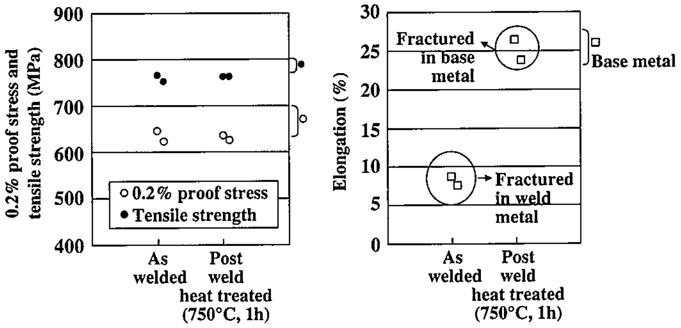


Fig. 8 **Tensile properties of TIG weld joints of Ti-1%Fe-0.35%O-0.01%N plates welded using matching filler**

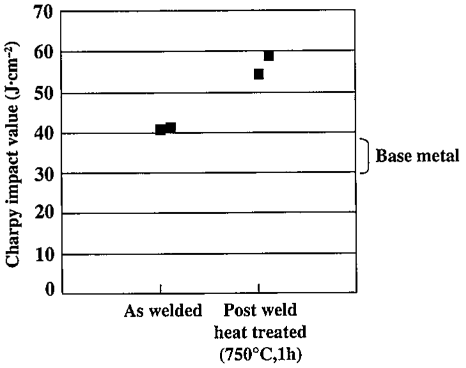


Fig. 9 **Charpy impact toughness of Ti-1%Fe-0.35%O-0.01%N TIG weld metal welded using matching filler**

As has been described above, the developed alloy series can be fully welded as much as the conventional titanium materials, and have excellent properties even in the welded condition. However, far better properties can be obtained by employing post weld heat treatment.

3.6 Other characteristics

In addition to the characteristics introduced so far, the developed alloy series have the following interesting characteristics.

(1) High fatigue properties: Like conventional high-strength titanium alloys, the developed alloy series have high fatigue properties according to the strength level[9].

(2) Superplasticity: Some alloys in the series exhibit superplastic deformation behavior at high temperature[9].

(3) Heat treatability: The developed alloy series contain interstitial elements, O and N, as alloying elements. Alloys containing plenty of interstitial elements have a characteristic that the temperature dependence of volume fraction of the α and β phases is small in the vicinity of the β transus. In other words, even if the temperature during heat treatment changes slightly, the volume fraction does not change so much. It means that strengthening by solution treatment and aging, etc. or the heat treatment to improve anisotropy[7] can be more easily carried out.

4. Conclusions

The alloy design and various material properties of Ti-Fe-O-N high-strength titanium alloy series have been introduced. The alloy series do not contain expensive elements, have high tensile strength ranging from 700 to 1,000 MPa and high ductility at room temperature, and have excellent hot workability equivalent to that of commercially pure titanium. In order to use these alloys to a wide range of applications by fully utilizing these characteristics, it is necessary to understand various phenomena resulting from the unique compositions in advance. It is therefore hoped that the data in this report on the usable range and practical use will be fully used in the future.

The developed Ti-Fe-O-N alloy series introduced so far are positioned, together with Ti-Fe-Al alloy series, in the series of the developed alloys called "Super-TIX series", and a wide range of applications are now under consideration.

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