Kobe Steel's Original Titanium Alloys Developed in the Past 20 Years

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In the past 20 years, Kobe Steel has developed and commercialized various titanium alloys. AKOT is a corrosion-resistant alloy, in which Cr has the important role of enriching Pd and Ru on the corroded surface. Ti-1.2ASN is a heat-resistant alloy that can be used at temperatures up to 800℃, in which oxidation resistance has been improved by the addition of Al and Si, and grain growth is inhibited by silicide. Ti-9 is a quasi Ti-6Al-4V alloy that is as coilable as CP-titanium. Its Al content has been suppressed to 4.5% to enhance cold rollability, and Si has been added to ensure the ductility of welds. KS EL-F is a quasi Ti-6Al-4V and is as hot-forgeable as CP-titanium, in which C is exploited to achieve high strength at temperatures up to approximately 500℃ and to reduce flow stress during hot-forging.

Introduction

Titanium has come to be widely known as a lightweight, non-corroding metal; however, there are cases where the metal corrodes in severely corrosive environments. Basically, metallic titanium is obtained by reducing titanium oxide and can easily be oxidized and become brittle when exposed to the atmosphere. Thus, some environments are difficult for simple commercially-pure (CP) titanium to withstand. Alloy Ti-6Al-4V is a typical titanium alloy commonly used for aircraft parts; however, it suffers from poor hot/cold workability, which often results in low productivity.

In the past 20 years, Kobe Steel has developed various original titanium materials for solving these problems, while as much as possible avoiding an increase in cost, in the hope that titanium would be used in a wider range of environments. This paper outlines these titanium materials.

1. Anti-crevice-corrosion alloy： AKOT

Crevice corrosion occurs easily in severe environments, such as a highly concentrated chloride environment at elevated temperatures. Alloys including Ti-0.15Pd have been developed to resist such crevice corrosion.[1)] Since platinum group elements are very expensive, many researchers have focused on reducing the additive amount of platinum group elements as much as possible.[2)-4)] Under such circumstances, Kobe Steel developed Ti-0.4Ni-0.015Pd-0.025Ru-0.14Cr, named AKOT.[5)]

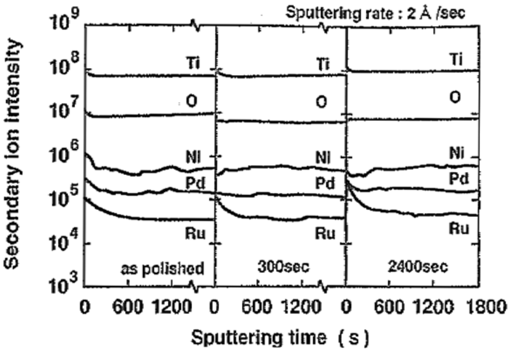

Fig. 1 SIMS depth profiles of Ti-0.41Ni-0.01Pd-0.02Ru alloy immersed in boiling 10 mass% hydrochloric acid solution

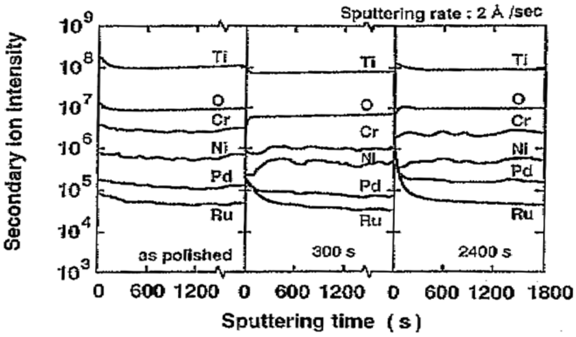

Fig. 2 SIMS depth profiles of additive elements in Ti-0.41Ni-0.01Pd-0.02Ru-0.14Cr alloy immersed in boiling 10 mass% hydrochloric acid solution

Figs. 1 and **2** are the results of secondary ion-microprobe mass spectrometry (SIMS) performed on Ti-0.41Ni-0.01Pd-0.02Ru alloy and Ti-0.41Ni-0.01Pd-0.02Ru-0.14Cr alloy, respectively, showing the concentration depth profiles of the additive elements in the alloys, which were immersed in 10mass% boiling hydrochloric acid solution for 0s (as polished), 300s and 2,400s. In both alloys, the platinum group elements, Pd and Ru, are enriched near the surface, and this enrichment tends to become more pronounced with the addition of Cr. On the basis of this knowledge, the additive amounts of Ni, Pd and Ru were optimized to develop AKOT. AKOT has been used in severe atmospheres, such as that found in soda electrolysis.

2. Titanium alloys, Ti-1.5Al, Ti-1.2ASN and Ti-0.9SA, for mufflers

CP titanium has been used for motorcycle mufflers since the early 1990s. Kobe Steel was ahead of the rest of the world in starting to develop high-temperature resistant alloys for mufflers in order to widen the applicability of titanium materials and commercialized Ti-1.5Al[6] in the year 2000. A motorcycle muffler cools down in the air more easily than does a muffler for four-wheel vehicles. Hence, the company continued developing muffler alloys that can withstand even higher temperatures. The major challenge in developing a temperature resistant muffler material is to prevent embrittlement due to oxidation and grain coarsening at elevated temperatures. Trying to solve this problem with a minimal addition of alloying elements presents another challenge, since a large amount of added elements deteriorates the formability indispensable to this application.

Against this backdrop, Kobe Steel continued a study on the minor addition of Al and Si on the basis of the fact that the oxidation of Ti-1.5Al is more suppressed than that of CP titanium and that Si forms silicide that suppresses grain growth, as described later. As a result, the company developed Ti-1.2ASN, a muffler alloy that can be used at temperatures up to 800℃.[7] The alloy was adopted in the Toyota Supercar, Lexus LFA, in 2010. Furthermore, attempts have been made to expand the application, not only to supercars, but also to a wide variety of vehicles. Expensive Nb, which was used in Ti-1.2ASN, was eliminated, and the amounts of additive elements were adjusted to improve the formability by lowering the annihilation temperature of silicide such that the formation of silicide can be controlled during annealing in a continuous annealing/pickling line. This effort resulted in the development of Ti-0.9SA.[8]

Fig. 3 compares the thickness reduction and grain size of CP titanium, Ti-1.5Al, and Ti-1.2ASN after exposure to air at 800℃ for 200 hours. The CP titanium exhibits a significant thickness reduction due to the exfoliation of oxidation scale with more pronounced coarsening of crystal grains, whereas Ti-1.5Al exhibits suppression in both the formation of oxidation scale and crystal grain growth. Furthermore, Ti-1.2ASN exhibits almost no thickness reduction with the grain coarsening being effectively suppressed thanks to the presence of silicide. **Fig. 4** compares CP titanium with Ti-1.2ASN in the state of oxidation scale after the above described exposure to high-temperature air. The CP titanium exhibits thickly formed oxidation scale with a number of voids, whereas the oxidation scale formed on Ti-1.2ASN is dense and thin. The reason is considered to be as follows: as shown in **Fig. 5**, the electron-probe micro analyzer (EPMA) images taken from beneath the oxidation scales after the exposure to high-temperature air shows Al and Si, despite being minor additive elements, enriched on the metal surface, preventing Ti from diffusing to the surface.

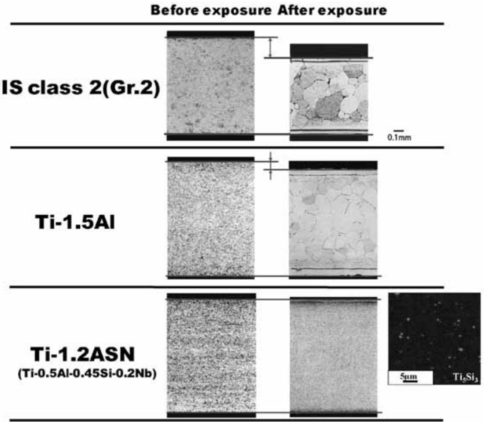

Fig. 3 Comparisons of wall thinning and grain growth behavior in JIS class 2, Ti-1.5Al and Ti-1.2ASN materials after exposure at 800℃ for 200 hours in air

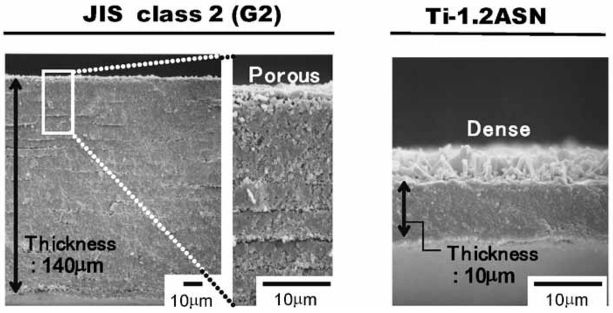

Fig. 4 Comparison of oxidation scale in JIS class 2 CP-Ti and Ti-1.2ASN after exposure at 800℃ for 200 hours in air

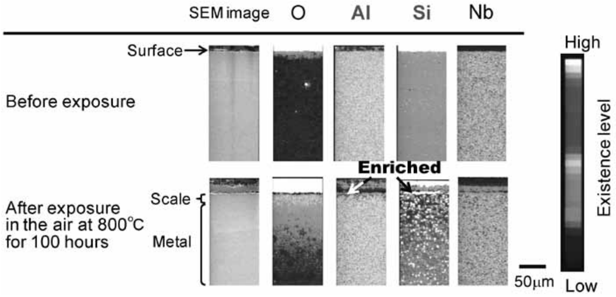

Fig. 5 EPMA mappings of Ti-1.2ASN after exposure at 800℃ for 200 hours in air

3. Alloys compensating for the weakness of Ti-6Al-4V alloy: Ti-9, KSEL-F and Ti-531C

As described in the introduction, titanium alloy is represented by Ti-6Al- 4V alloy, whose workability is rather poor under either hot or cold working. Due to this, when, for example, a thin sheet is manufactured, a rolling method called pack-rolling is adopted. In this method, a rolling stock with a certain degree of thickness is completely surrounded by steel sheets so as to maintain the temperature during rolling. This rolling technique requires a complicated process that is one of the major factors increasing the cost. In order to overcome this problem, Kobe Steel has developed an alloy equivalent of Ti-6Al-4V, Ti-9, which can be coil-rolled as in the case of CP titanium.[9), 10)] In addition, poor hot-workability results in cracking during hot-forging, leading to an increase in the number of forging steps. To cope with this issue, Kobe Steel has developed another Ti- 6Al- 4V equivalent alloy, KS EL-F,[11)] which is just as forgeable as CP titanium, and also developed Ti-531C,[12)] whose composition has been adjusted to improve the machinability of KS EL-F.

Fig. 6 shows the tensile properties of a coil of Ti-9. Although anisotropy in strength due to unidirectional rolling is observed, an elongation of 7-8% or greater has been obtained even in the T direction, which exhibits higher strength. Ti-9 has a composition of Ti-4.5Al-2Mo-1.6V-0.5Fe-0.3Si-0.03C, in which the amount of Al is kept at 4.5% to secure cold-rollability. Other elements have also been optimized in view of the strength and post-welding characteristics.

Fig. 7 compares KS EL-F（Ti-4.5Al-4Cr-0.5Fe-0.2C) with Ti-6Al-4V alloy in tensile strength at ambient to elevated temperatures. KS EL-F has a reduced amount of Al, an element that increases high-temperature strength, with an increased amount of C to compensate for the decrement in strength. This alloy exploits the fact that C, an interstitial element, contributes to solid-solution strengthening in a relatively low temperature range, however, this solid-solution strengthening effect is decreased significantly at the elevated temperatures at which hot forging is performed. A large amount of C is added in the vicinity of the solid-solubility limit in the β phase, while other additive elements are selected from low cost options whenever possible. As shown in Fig. 7, the strength is at a level similar to that of Ti-6Al-4V up to approximately 500℃; however, the strength decreases significantly at temperatures of 700℃ or higher, offering excellent hot workability. KS EL-F can be hot-forged into a part with a shape such as that shown in **Fig. 8** in a single heating cycle.

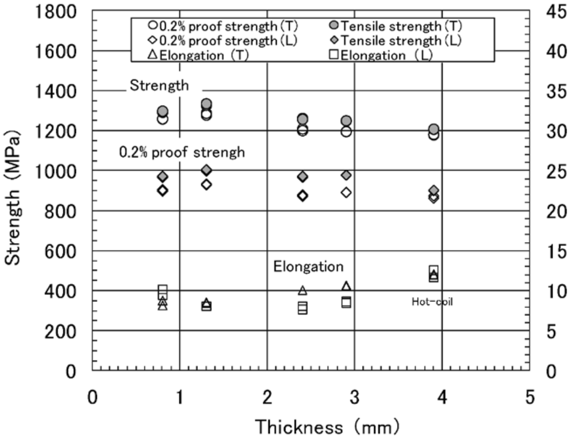

Fig. 6 Tensile properties of first strip of Ti-9

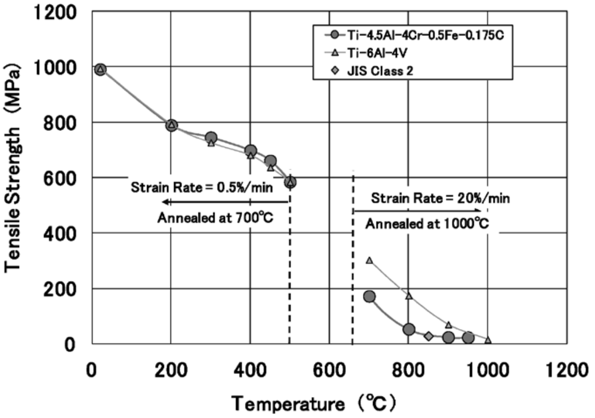

Fig. 7 Temperature dependence of tensile strength of KS EL-F

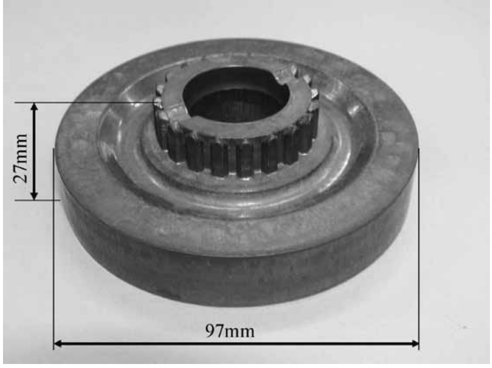

Fig. 8 Gear part forged from 45 mm diameter and 66 mm length billet of KS EL-F in mass production line for steel (SCM415) in single heat process

There may be TiC found in KS EL-F, due to production hysteresis. Although it has been confirmed that TiC does not inhibit mechanical properties, including fatigue strength, an increased amount of TiC has been demonstrated to decrease machinability as shown in **Fig. 9**. The effect of the amount of Cr and Fe on the solid solubility limit of C in β phase was therefore calculated as shown in **Table 1**. Two compositions, F-1 and F-2, in which a part of Cr is replaced by Fe, were selected and compared with KS EL-F and Ti-6Al-4V in terms of machinability. As a result, F-1 and F-2 have been demonstrated to exhibit machinability superior to that of KS EL-F, as shown in **Fig.10**. On the basis of these results, the composition was finalized as Ti-4.5Al-2.5Cr-1.25Fe-0.1C (Ti-531C.)

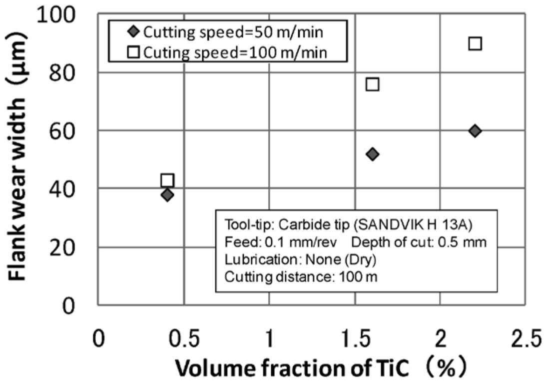

Fig. 9 Influence of TiC volume fraction on flank wear width of cutting tool tip

Table 1 Alloy compositions and their calculated solubility limits of C into β phase

(mass%)

Alloy	Al	Cr	Fe	C	Solubility limit of C
KS EL-F	4.5	4	0.5	0.15	0.14
F-1	4.5	2.5	1.25	0.15	Not calculated
F-2	4.5	1	2	0.15	0.198

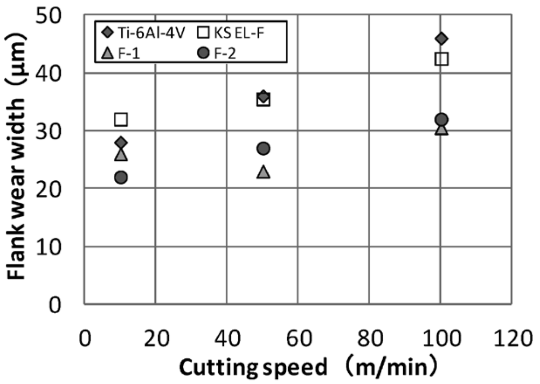

Fig.10 Comparison of flank wear width of cutting tool tip in F-1, F-2, KS EL-F and Ti-6Al-4V

Conclusions

Some of the titanium materials that Kobe Steel originally developed in the last 20 years have been outlined in terms of technical points, including the concept of alloy development. These alloys were developed with the aims of expanding the applicability of titanium materials and satisfying customers. Kobe Steel will strive to develop titanium materials that adequately meet the needs of customers by further enhancing the technologies of the titanium materials developed thus far and by expanding the field of view, including the technologies of multi-material utilization.

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