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Development of Ti-Cu Alloy Sheets for Automobile Exhaust Systems

Hiroaki OTSUKA*　Hideki FUJII
Kazuhiro TAKAHASHI　Kenichi MORI

Abstract

Titanium alloys having excellent performances at elevated temperature and good formability at room temperature for automobile exhaust systems have been developed based on the unique alloy design concept that 1 mass% Cu, together with low oxygen content, was added, and 0.5 mass% Nb was furthermore added in case oxidation resistance at temperatures up to 800°C was necessary. They do not include any conventional alloying elements, such as Al, Si and Sn, which are often added to titanium alloys used at elevated temperatures and lower their formability. In place of them, Cu was added as a solid solution hardening element at high temperature. The oxygen content was lowered together as that in Gr.1 pure titanium(CP) to enjoy the active mechanical twinning at room temperature which is indispensable for excellent formability. The alloy, Ti-1mass%Cu(Super-TIX™10CU), actually has high strength and high fatigue strength (twice as high as those of Gr.2) as well as excellent creep resistance at elevated temperatures. The other alloy, Ti-1mass%Cu-0.5mass%Nb(Super-TIX™10CUNB), has improved oxidation resistance at temperatures up to 800°C with keeping excellent formability equivalent to that of Super-TIX™10CU. Recently a new Ti-Cu alloy which was added some solid solution hardening elements for higher strength at elevated temperature than the former two Ti-Cu alloys has been developed.

1. Introduction

Ti-Cu titanium alloy sheets added with Cu or Cu + Nb have been widely used for automotive exhaust systems under the trade name of Super-TIX™10CU or Super-TIX™10CUNB since 2006 (for motorcycles) and 2009 (for four-wheeled vehicles).[1, 2] The automotive exhaust system is installed near the engine, catalytic converter, and other parts that become extremely high in temperature. Therefore, any titanium alloy used for an automotive exhaust system must have exceptional strength at elevated temperatures and high oxidation resistance. On the other hand, as a material for mass-produced exhaust systems, the titanium alloy must have exceptional formability. Specifically, at room temperature, these alloys require the following characteristics: sufficient elongation, good bendability, stretch-expansion formability, and drawability.

Effective enhancing of strength at elevated temperatures for titanium alloys can be achieved by subjecting them to solid solution strengthening. At room temperature, however, there is a risk that solid solution strengthening could adversely affect the formability of the alloys. In this study, we selected Cu as the solid solution strengthening element (Cu has seldom been used for that purpose), and succeeded in obtaining both high heat resistance (strength at elevated temperatures) and good formability—two properties that are generally incompatible with each other.

This paper describes the design concept for Ti-Cu alloys, their mechanical properties, and heat resistance (especially oxidation resistance) at elevated temperatures. In addition, we shall review the results of a study on creep characteristics (which call for special attention when the alloys are used at elevated temperatures), their formability at room temperature, and recent applications of those titanium alloys. We shall also briefly describe our newly developed Ti-Cu alloy, which has higher strength at elevated temperatures than Super-TIX™10CU or Super-TIX™10CUNB.

2. Designing Ti-Cu Alloys for Automotive Exhaust Systems

Since automotive exhaust systems are installed near the engine,

* Senior Manager, Dr.Eng., Titanium & Technology Div., Titanium & Specialty Stainless Steel Unit
2-6-1 Marunouchi, Chiyoda-ku, Tokyo 100-8071

catalyst converters and other components that operate at elevated temperatures must have excellent strength and high oxidation resistance. Therefore, several titanium alloy sheets have been developed for automotive exhaust systems.[3-5] On the other hand, because many of the exhaust system components have a complex shape due to of their high functions and require complicated forming to impart good design to the finished product (the car's body), they must be able to stand grueling forming conditions. Therefore, the material for an exhaust system must have not only excellent strength at elevated temperatures and high oxidation resistance, but also sufficient workability (formability) at room temperature.

The four major properties that are required of any titanium alloy for automotive exhaust system are as follows:

(1) Sufficient strength at 600˚C and higher temperatures; their strength does not decrease significantly after extensive use.
(2) Decrease in material thickness due to oxidation is negligible at temperatures above 700˚C.
(3) Equal or superior formability (bendability, stretch expansion formability, drawability) at room temperature for JIS Class 2 or ASTM Gr. 2 commercially pure titanium (hereinafter called "Gr. 2").
(4) Deformation of the titanium alloy sheets at temperatures above 600˚C is sufficiently small even when the sheets are subjected to a load lower than their 0.2% proof stress for a long time. In other words, the titanium alloys have good creep resistance.

To increase material strength at elevated temperatures (Item (1)), it is common practice to add Al—a substitutional element capable of solid solution strengthening the α phase noticeably at elevated temperatures—as in the case of Ti-3Al-2.5V. On the other hand, to enhance oxidation resistance at elevated temperatures (Item (2)), adding a small amount of Si is most common. Thus, in designing a titanium alloy that can be used at elevated temperatures, it is common practice to add Al and Si. It should be noted, however, that those elements can also increase the material strength at room temperature. In this case, the good cold formability of commercially pure titanium may be impaired. In particular, because Al causes the stacking fault energy to increase, it may restrain the twin deformation that accounts for the good formability of commercially pure titanium at room temperature, thereby causing cold formability to decline.

With the aim of solving the above problems, we studied the addition of the following elements, including β-stabilizing elements. These include:

- Elements that dissolve in the α phase to some extent, including the metastable state, and display an adequate solid solution strengthening effect at elevated temperature, and
- Elements that do not impair the material formability at room temperature, i.e., elements that do not restrain the twin deformation.

As a result, Cu was found the most suitable.

To verify that Cu does not suppress twin deformation, we introduced tensile strains to a Ti-1Cu alloy and examined the twin deformation of the alloy using Gr. 1 and Gr. 2 as references. The study results showed that under several % of tensile strain, the twin deformation of the Ti-1Cu was nearly the same as that of Gr. 1 and more frequent than that of Gr. 2.[6] The implication is that Ti-Cu alloys have sufficient formability at room temperature as they maintain or even promote the occurrence of twin deformation that plays an important role in securing the desired formability of titanium materials.

The concrete concept of titanium alloy design is as follows:

① Add the substitutional element, Cu, which dissolves in the α phase up to 2.1-mass% in equilibrium state and is easy of oversaturated dissolution (in other words, Ti_2Cu precipitation is sluggish).
② Make the oxygen content comparable to that of JIS Class 1 or Gr. 1, rather than JIS Class 2 or Gr. 2, in order to secure the desired formability at room temperature.
③ As far as possible, minimize the content of Fe—an impurity that is a strong β-stabilizing element—in order to avoid the decrease in dissolution of Cu in the α phase due to the concentration of Cu in the β phase.

Ti-1Cu (Super-TIX™10CU), the basic form of Ti-Cu alloys for automotive exhaust systems, has been developed on the basis of the above design concept. This alloy for exhaust system can be used at high temperatures up to 700˚C. Both excellent strength at elevated temperatures and good formability at room temperature have been achieved by solid solution strengthening of Cu and a reduction of oxygen content to a level comparable to that of Gr. 1.

With respect to oxidation resistance at elevated temperatures in the range 500˚C to 800˚C, Ti-1Cu is equal or slightly superior to commercially pure titanium. At 800˚C, in particular, they are both subject to rapid oxidation. For exhaust systems that demand better oxidation resistance at elevated temperatures around 800˚C, a new titanium alloy added with 0.5-mass% Nb has been developed. Because Nb helps restrain the diffusion of oxygen in the scale of oxidized titanium, it is effective to enhance the oxidation resistance of titanium alloy.[7] In addition, Nb is dissolved in the α phase up to 1.5 to 4.5-mass% (at 500˚C to 800˚C) and does not cause strength at elevated temperatures to decline. Neither does it produce β phase, which reduces the amount of Cu solution in the α phase. Furthermore, Nb does not adversely affect the formability at room temperature.

Thus, Ti-1Cu-0.5Nb (Super-TIX™10CUNB) is a new alloy designed and developed on the premise that it is used for exhaust systems which may rise in temperature up to around 800˚C. For exhaust systems that demand higher strength at elevated temperatures, another new Ti-Cu alloy whose hot strength at 500˚C to 800˚C is about 1.5 times that of Super-TIX™10CU and Super-TIX™10CUNB has been recently developed.

Figure 1 schematically shows the design concept for Ti-Cu alloys. The horizontal axis represents the alloy formability at room temperature and the vertical axis represents the alloy heat resistance (service temperature). The figure shows that the addition of Al, Sn, Si, etc. raises service temperature but causes formability to decrease and that the addition of Cu and Nb permits raising the service tem-

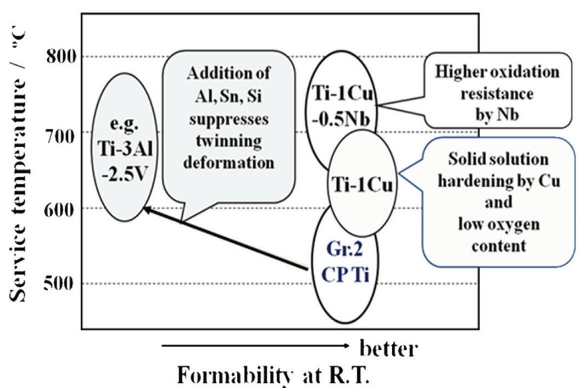

Fig. 1 Image of design concept of Ti-1Cu-(0.5Nb) alloys

perature without influencing the formability. The Ti-Cu alloys that have been developed recently have both excellent strength at elevated temperatures and formability at room temperature.

3. Properties of Developed Alloys

The representative properties of the titanium alloys that were designed based on the above concept are discussed below. Those properties (strength at elevated temperatures, mechanical properties, formability, and creep resistance) were measured using 1-mm-thick Ti-1Cu and Ti-1Cu-0.5Nb sheets prepared by 200 kg vacuum-arc re-melting (VAR), hot-forging, hot-rolling, cold-rolling, and annealing (750˚C, 1 h). As references, pure titanium products (Gr. 1 and Gr. 2), each about 1 mm in thickness, were used.

3.1 High-temperature properties

Figure 2 shows the tensile strength of Ti-1Cu, Ti-1Cu-0.5Nb and Gr. 2 at elevated temperatures of 500 - 700˚C. Due to the solid solution strengthening ability of Cu, Ti-1Cu and Ti-1Cu-0.5Nb have tensile strength approximately twice that of Gr. 2 in the temperature range shown. Furthermore, Ti-1Cu and Ti-1Cu-0.5Nb have approximately the same tensile strength at elevated temperatures. Thus, the addition of 0.5-mass%Nb contributes very little to the strengthening of the Ti-1Cu alloy.

Figure 3 shows the results (S-N curve) of a plane bending fatigue test for Ti-1Cu at 600˚C. Reflecting the higher strength at elevated temperatures of Ti-1Cu as compared to Gr. 2, the fatigue strength of Ti-1Cu after 10^7 cycles (free from failure) was approximately twice that of Gr. 2. The fatigue strength was approximately 60% of the tensile strength measured at 600˚C (Fig. 2). In addition, the fatigue strength of Ti-1Cu measured at 700˚C was twice that of Gr. 2.

Figure 4 shows the weight gain of Ti-1Cu, Ti-1Cu-0.5Nb, Gr. 2 and Ti-3Al-2.5V after heating to 500 - 800˚C in air for 200 hours. Although the weight gain of Ti-3Al-2.5V due to oxidation is somewhat small at 500˚C, all the four titanium alloys are nearly the same in weight gain at temperatures 500 - 700˚C. At 800˚C, however, Ti-1Cu-0.5Nb shows better oxidation resistance than the other three titanium alloys, with the weight gain from oxidation being about 1/7 that of Gr. 2. The scale of oxide formed on the surface of Ti-1Cu-0.5Nb after many hours of exposure to 800˚C can hardly be removed, whereas the oxide scale on the other three titanium alloys comes off easily. **Figure 5** shows a cross section of the surface layer of Gr. 2, Ti-1Cu, and Ti-1Cu-0.5Nb, respectively, after exposure to 800˚C in the air for 100 hours. The oxide scale of Ti-1Cu-0.5Nb is smaller in thickness than that of Gr. 2/Ti-1Cu and does not come off. Thus, the addition of Nb is effective when good oxidation resistance at high temperatures around 800˚C is required.

3.2 Mechanical properties/formability

Table 1 shows the tensile properties of Ti-1Cu-(0.5Nb) and Gr. 1/Gr. 2 alloys that were subjected to final annealing at 750˚C for 1 hour. The elongation of Ti-1Cu-(0.5Nb) in each of the three directions (L: longitudinal, D: diagonal, T: transverse) by far exceeds that of Gr. 2, indicating that Ti-1Cu-(0.5Nb) is highly ductile. Thanks to

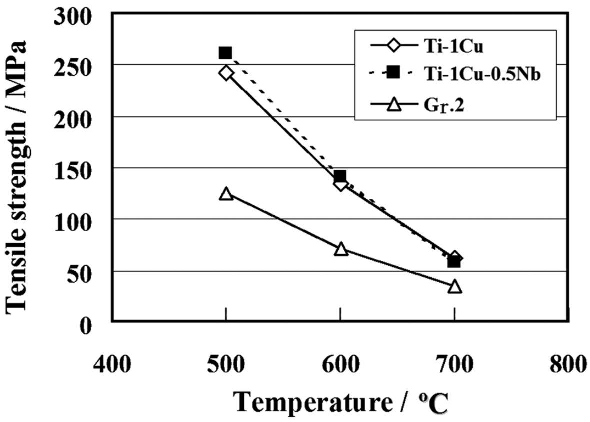

Fig. 2 Tensile strength at elevated temperature of Ti-1Cu, Ti-1Cu-0.5Nb and Gr.2 sheets

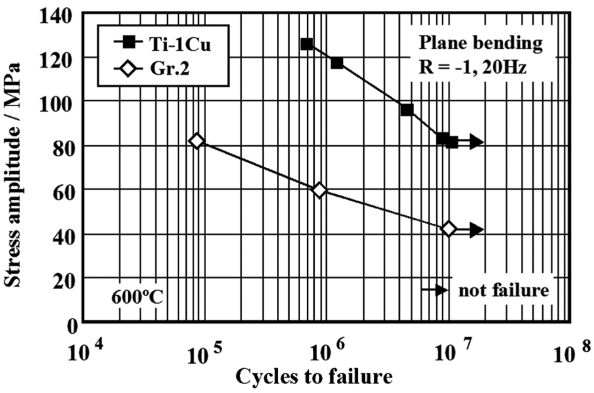

Fig. 3 S-N curves of Ti-1Cu and Gr.2 at 600˚C in air

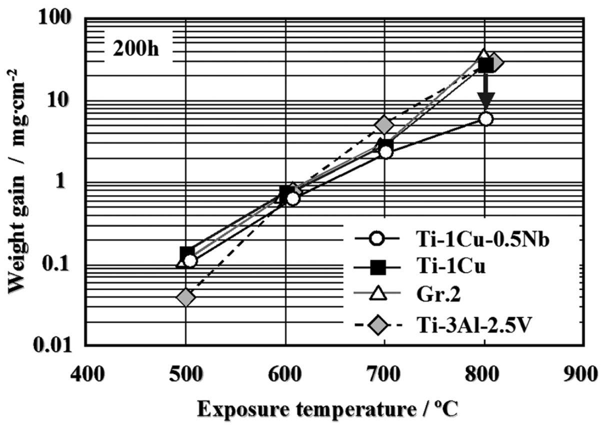

Fig. 4 Oxidation properties at elevated temperature of Ti-1Cu-0.5Nb, Ti-1Cu, Gr.2 and Ti-3Al-2.5V
Specimens were exposed in air.

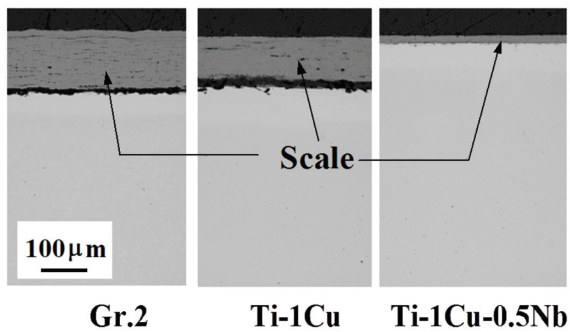

Fig. 5 Cross section of surface layer of Gr.2, Ti-1Cu and Ti-1Cu-0.5Nb after exposure at 800˚C for 100 h in air

the high ductility, a Ti-1Cu-(0.5Nb) sheet 1 mm in thickness can be subjected to completely tight bending work in both L and T directions. When the blank holding force is 5 t, the Erichsen value of Ti-1Cu-(0.5Nb) is 12.5 mm, which is higher than that of Gr. 2 (10.5 mm) and comparable to that of Gr. 1 (13 mm). On the other hand, the Lankford value (r-value) of Ti-1Cu-(Nb) in the L direction is somewhat small (about 1.5). When deep drawing formability is required, a higher r-value in the L direction is necessary. However, it can be obtained by adjusting the final heat treatment conditions. For example, the r-value improves to 2.5 when the alloy is subjected to annealing at 690˚C for 10 h.

Figure 6 shows the changes in r-value and total elongation in L direction of Ti-1Cu when the annealing temperature was varied between 650˚C and 750˚C. The higher the annealing temperature, the larger the total elongation and the smaller the r-value. **Figure 7** shows (0002) pole figures of two Ti-1Cu sheets, one annealed at 670˚C and the other at 690˚C, both having a large r-value, and of a Ti-1Cu sheet annealed at 750˚C and having a comparatively small r-value. As shown in the former pole figures, the integration at the center pole is somewhat more conspicuous.[8, 9] Thus, in the case of the Ti-1Cu alloy, it is possible to control its anisotropy by modifying the crystalline texture formed as a result of Ti_2Cu precipitation, and grain growth using the suitable annealing conditions.

Figure 8 shows an example of a rectangular drawn cup of a 0.5-mm-thick Ti-1Cu sheet annealed at 690˚C. Despite the extremely severe forming condition (corner radius of 1 mm), the sheet that had been given a relatively large r-value under suitable annealing conditions could successfully be formed without any problem.

3.3 Creep resistance

We examined the high-temperature creep properties of Ti-1Cu and JIS Class 2 commercially pure titanium using 1.5-mm-thick cold-rolled and annealed sheets. The test pieces were manufactured in the mill. The test temperature was 650˚C, which was set for convenience as the normal service temperature for exhaust system components. First, a high temperature tensile test was carried out to measure the 0.2% proof stress of each test piece. Then, the appropriate creep stresses were applied. The creep test was carried out in the open air by using test pieces that were identical in shape to those used in the high-temperature tensile test (overall length: 120 mm, gauge length: 35 mm, parallel portion width: 10 mm). Note that on the basis of test piece cross sections observed during the test, the influence of oxidation during the test was assumed to be negligibly small.

The applied stresses used in the creep test were 10, 20 and 40 MPa, which correspond to 14%, 28% and 56% of the 0.2% proof stress of Ti-1Cu at 650˚C, and to 32%, 65% and 129% of the 0.2% proof stress of JIS Class 2 pure titanium at the same temperature. The applied stress of 40 MPa was higher than the 0.2% proof stress of JIS Class 2 commercially pure titanium; however, the test was given priority over testing under the same conditions. Basically, the

Table 1 Tensile properties at room temperature of Ti-1Cu, Ti-1Cu-0.5Nb, Gr.1 and Gr.2 sheets in longitudinal(L), diagonal(D) and transverse(T) directions
Ti-1Cu and Ti-1Cu-0.5Nb were subjected to final annealing at 750˚C for 1 h.

	Direction	0.2%PS (MPa)	Tensile strength (MPa)	Elongation (%)
Ti-1Cu	L	195	408	45.2
	D	230	364	46.9
	T	273	366	36.5
Ti-1Cu-0.5Nb	L	228	433	50.4
	D	252	387	49.5
	T	294	384	37.6
Gr.1 CP-Ti	L	181	313	50.8
	D	205	280	55.1
	T	228	305	39.0
Gr.2 CP-Ti	L	251	383	36.3
	D	260	351	37.6
	T	279	368	32.2

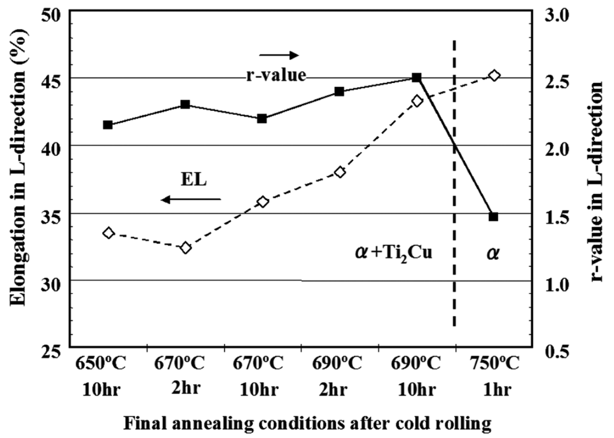

Fig. 6 Influence of final annealing conditions on elongation and r-value in longitudinal direction in Ti-1Cu sheets of 1.5 mm in thickness

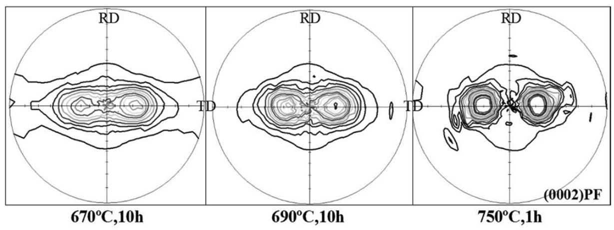

Fig. 7 (0002) pole figures of Ti-1Cu sheets annealed
a) At 670˚C for 10 h, b) At 690˚C for 10 h and c) At 750˚C for 1 h

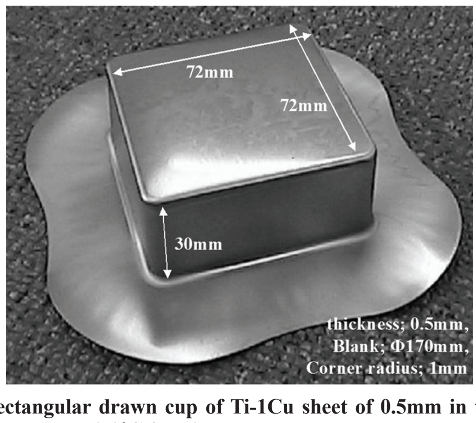

Fig. 8 Rectangular drawn cup of Ti-1Cu sheet of 0.5mm in thickness, annealed at 670˚C for 10 h

creep test was to be continued till each of the test pieces fractured. However, the test was interrupted halfway to collect samples for observation of their microstructures.

Figure 9 shows the relationship between times for the 3% creep deformation and applied stress. A comparison between Ti-1Cu and JIS Class 2 commercially pure titanium shows that under each of the test stresses, the time until 3% creep deformation is longer for Ti-1Cu than for JIS Class 2 commercially pure titanium. This implies that Ti-1Cu has better creep resistance than JIS Class 2 commercially pure titanium at 650˚C.[10)]

Through an observation of the internal structures of the creep test pieces, we considered the reason why Ti-1Cu has superior creep resistance. **Figure 10** (a) shows TEM micrographs of a Ti-1Cu creep test piece to which about 25% strain was introduced under the applied stress of 20 MPa at 650˚C. Dislocations are observed relatively densely within grains, forming a network (subgrain boundaries) locally. This indicates that the creep-deformed Ti-1Cu is of typical recovered structure. Ti_2Cu observed within grains and at grain boundaries (confirmed by energy dispersive X-ray spectroscopy; EDX) was not the compound that had precipitated during creep deformation. It is estimated that the amount of Ti_2Cu precipitation, if any, was very small and that the amount of solid solution Cu remained almost the same throughout the creep test.

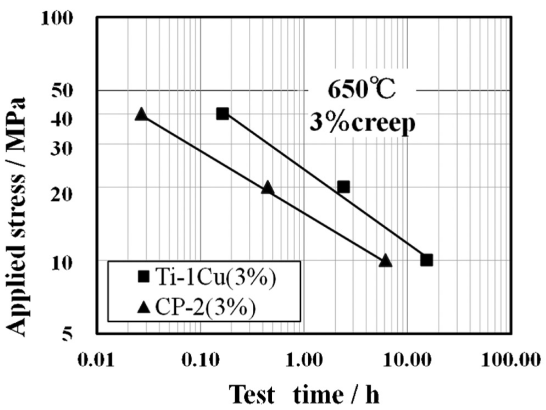

Fig. 9 Relationship between applied stress and time needed to be deformed to 3% creep strain at 650˚C

Figure 10 (b) shows TEM micrographs of pure titanium. Despite the fact that approximately 25% creep strain was also introduced to the commercially pure titanium test piece under a test stress of 20 MPa at 650˚C, subgrain boundaries are observed only slightly, and dislocation density is lower than in Ti-1Cu.

From the above observations, it is considered that in the case of Ti-1Cu, solid solution strengthening by solute Cu and strain hardening by high dislocation density suppress slip deformation. This effect overcomes adverse effects such as grain boundary sliding enhanced by fine grain size, thereby imparting excellent creep resistance to the alloy.

4. Application of Titanium Alloys to Automotive Exhaust Systems

The Ti-1Cu and Ti-1Cu-0.5Nb alloys that have excellent strength at elevated temperature and high oxidation resistance came into existence from the novel alloy design including: Cu addition, low oxygen content, and Nb addition, as per requirements. Under the trade names of Super-TIX™10CU and Super-TIX™10CUNB, these new alloys have already been widely used for automotive exhaust systems. For example, Super-TIX™10CU has since around 2007 been used for those parts of the mufflers of the Suzuki GSX Series (motorcycles) which demand superior heat resistance (**Fig. 11** (a)).

In addition, since 2009, the alloy has been employed for the mufflers of Nissan GTR spec-V and GTR Egoist (from the exhaust pipe to the tail pipe finisher: Fig. 11 (b)). It has helped reduce the vehicle weight dramatically since the titanium muffler is much lighter than the stainless steel muffler.[11)] On the other hand, Super-TIX™10CUNB is used by Akrapovic—Europe's largest maker of exhaust system components—for certain parts of its mufflers for motorcycle (Fig. 11 (c)) and four-wheeled vehicle (Fig. 11 (d), (e)). We consider that the above examples attribute to the fact that the two alloys have not only superior formability at room temperature, but also excellent strength at elevated temperature, high oxidation resistance, and excellent creep resistance.

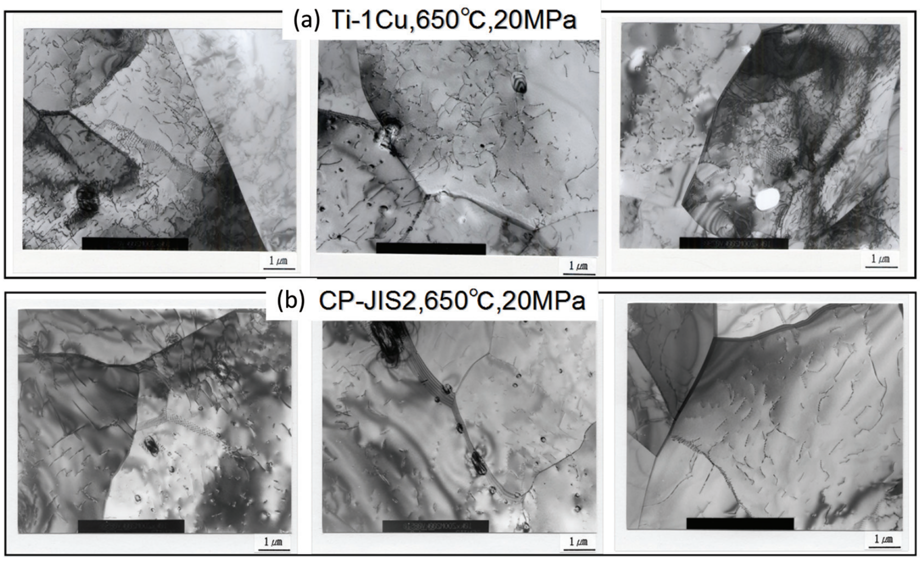

Fig. 10 TEM micrographs of (a) Ti-1Cu and (b) CP Class-2 deformed 25% by the stress of 20 MPa at 650˚C

Fig. 11 Examples of application of Ti-1Cu-(0.5Nb) for motorbike and automobile exhaust systems

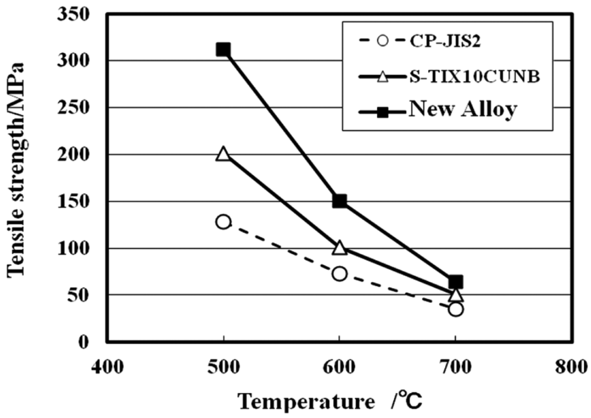

Fig. 12 Tensile strength of the recently developed alloy at elevated temperature compared to the conventional ones

5. Development of New Alloy Having Higher Hot Strength

As has been described above, Ti-1Cu and Ti-1Cu-0.5Nb have already been widely recognized and employed as materials for automotive exhaust systems. However, when they are compared with ferritic stainless steels (e.g., SUS 436J1L) that are more popular materials for exhaust systems, it cannot be said that they have sufficient heat resistance. To increase their popularity of use, it is indispensable to further enhance their heat resistance. Recently, the author (Otsuka) et al. came up with a new alloy: a Ti-Cu-based alloy with an added certain solid solution strengthening element. The tensile strength of the new alloy at high temperatures is shown in **Fig. 12**. In the high-temperature region above 500˚C, the tensile strength of the newly-developed alloy is about 1.5 times that of Ti-1Cu/Ti-1Cu-0.5Nb and about 3 times that of JIS Class 2 commercially pure titanium. In addition, by properly adjusting manufacturing conditions, it is possible to make formability at room temperature of the new alloy comparable to that of JIS Class 2 commercially pure titanium.

6. Conclusion

By selecting Cu as a solid solution strengthening element, Ti-Cu alloys for automotive exhaust systems have been developed. Ti-1Cu (service temperature: 700˚C) and Ti-1Cu-0.5Nb (service temperature: 800˚C) have already been widely used for exhaust system components. In addition, a new Ti-Cu based alloy that has a tensile strength higher than the above two alloys at elevated temperatures up to 800˚C has been developed. Since these alloys feature both excellent heat resistance at elevated temperatures and superior formability (two properties that are generally incompatible with each other), it is expected that the scope of their application as materials for automotive exhaust systems will expand in the future.

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Hiroaki OTSUKA
Senior Manager, Dr.Eng.
Titanium & Technology Div.
Titanium & Specialty Stainless Steel Unit
2-6-1 Marunouchi, Chiyoda-ku, Tokyo 100-8071


Kazuhiro TAKAHASHI
Senior Researcher
Titanium & Specialty Stainless Steel Research Lab.
Steel Research Laboratories


Hideki FUJII
General Manager, Head of Lab., Dr.Eng.
Titanium & Specialty Stainless Steel Research Lab.
Steel Research Laboratories


Kenichi MORI
Senior Researcher
Titanium & Specialty Stainless Steel Research Lab.
Steel Research Laboratories