Development of Titanium-based Brazing Filler Metals with Low-melting-point

T. Onzawa and T. Iiyama

Abstract

Titanium and titanium alloy are excellent in corrosion resistance and specific intensity, and also in the biocompatibility. On the other hand, the brazing is bonding method of which productivity and reliability are high, when the complicated and precise structure of the thin plate is constructed. However, though conventional titanium-based brazing filler metal was excellent in bond strength and corrosion resistance, it was disadvantageous that metal structure and mechanical property of the base metal deteriorated, since the brazing temperature (about 1000°C) is considerably high. Authors developed new brazing filler metal which added Zr to Ti-Cu (-Ni) alloy which can be brazed at 900°C or less about 15 years ago.

In this paper, the development of more low-melting-point brazing filler metal was tried by the addition of the fourth elements such as Ni, Co, Cr for the Ti-Zr-Cu alloy. As a method for finding the low-melting-point composition, eutectic composition exploration method was used in order to reduce the experiment point.

As the result, several kinds of new brazing filler metal such as 37.5Ti-37.5-Zr-25Cu alloy (melting point : 825°C) and 30Ti-43Zr-25Cu-2Cr alloy (melting point : 825°C) was developed. Then, the brazing joint showed the characteristics which were almost equal to the base metal from the result of obtaining metallic structure and strength of joint of brazing joint. However, the brazing filler metal composition of the melting point of 820°C or less could not be found. Consequentially, it was clarified that the brazing filler metal developed in this study could be practically sufficiently used from results such as metal structure of brazing joint and tensile test of the joint.

Key Words : Brazing, Titanium-based filler metal, Titanium, Titanium alloy, Eutectic alloy.

1. Introduction

Generally, the brazing filler metal of silver and aluminum system is used for the brazing of the titanium. Especially, pure silver and silver filler metal is widely used as a brazing filler metal[1]. However, in case of these brazing filler metal, the strength of joint is low, and the corrosion resistance is also inferior.

Titanium base brazing filler metal using the Ti-Cu-Ni eutectic composition has already been developed [2]. This brazing filler metal has high brazing joint strength comparable with the base material strength and that the corrosion resistance is also good. However, the melting point of this brazing filler metal is high over 900°C, and the workability is also bad.

About 15 years ago, authors developed low-melting-point brazing filler metal of about 850°C[3,4]. When this brazing filler metal is used, the brazing is possible at the low temperature below a-b transformation and b transus temperature of CPTi and Ti-6Al-4V alloy, respectively.

The purpose of this research is to develop brazing filler metal of the melting point which is lower than melting point of titanium brazing filler metal which authors developed[2]. As the experimental method, eutectic composition exploration method described in the after was used in order to reduce the experiment point.

First, the result of studying by eutectic composition exploration method again is reported on low-melting-point Ti-Zr-Cu brazing filler metal which authors have studied before. This brazing filler metal was produced by the rapid solidification processing in the amorphous foil. By using this amorphous brazing filler metal, Ti-6Al-4V alloy and CPTi were respectively brazed. Then, this brazing filler metal practicability was examined by structure observation and strength of joint of the bonded interface.

Subsequently, on the basis of the 37.5Ti-37.5Zr-25Cu alloy in which the melting point is the lowest in Ti-Zr-Cu brazing filler metal, by adding Co, Ni, Cr which is the β stabilization element of Ti, Zr, the low-melting-point region was searched.

T. Onzawa and *T. Iiyama* : Depertment of Mechanical and Control Engineering ,Tokyo Institute of Technology,Tokyo, Japan
E-mail : onzawa@mep.titech.ac.jp

2. Experimental method

2.1 Manufacture and thermal analysis of the brazing filler alloy ingot

The most low-melting-point constituent of filler metal from the binary equilibrium diagram was assumed, and each element was weighed by an electron balance at each composition ratio, and the button ingot (about 20g) was produced using vacuum arc fusion furnace. The remelting of the button ingot was done as a sample for the thermal analysis in vacuum arc fusion furnace. Then, the liquidus temperature measurement of the ingot was carried out by the high frequency heating equipment. The sample was perfectly melted in the graphitic heating crucible. By K thermocouple in the quartz capillary, the cooling curve was measured, until the liquid perfectly solidified. In the time, the reaction of brazing filler metal and crucible in the solidification and melting was also observed. Since it does not supercool, cooling rate was controlled in the every measurement sample.

2.2 The eutectic composition exploration method

As a method for searching the low-melting-point composition, algorithm of eutectic composition exploration method shown in Fig. 1 was used in order to reduce the measuring point number. The specific example is shown in Fig. 2. In solidification process, remained melt (eutectic composition) solidifies finally after the precipitation of primary crystal. This is most the low-melting-point composition.

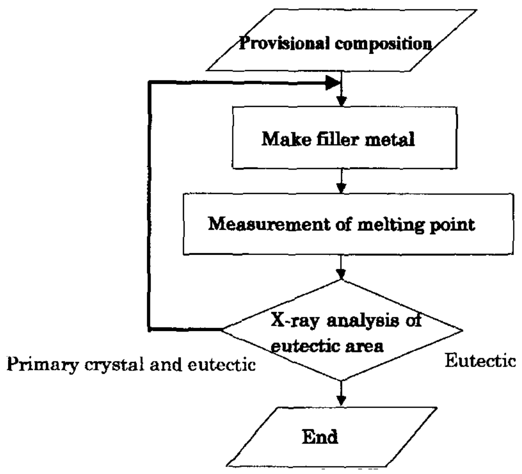


Fig. 1 Algorithm of eutectic composition exploration method

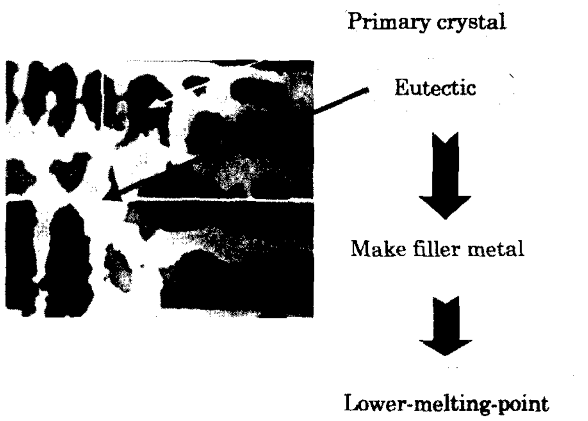


Fig. 2 Example of lower melting point composition

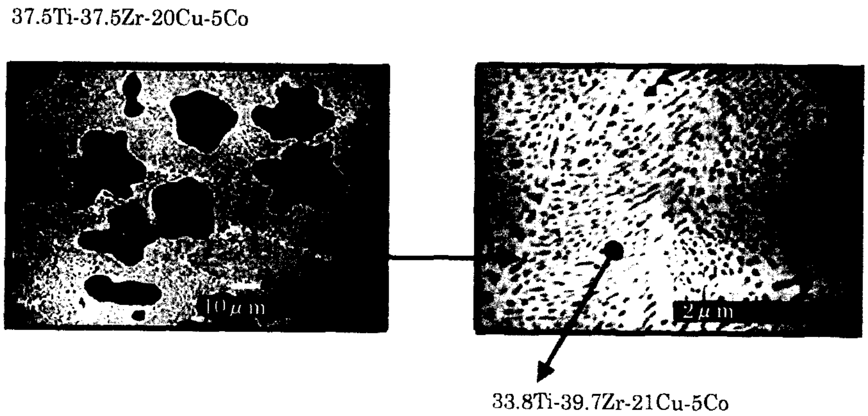


Fig. 3 An enlargement photograph in the eutectic area and the composition

3. Experimental results and discussion

3.1 The result of the Ti-Zr-Cu brazing filler metal melting point measurement

The result of measuring the liquidus temperature in each composition of Ti-Zr-Cu is shown in Fig. 4. From this figure, there is the composition in which the melting point is the lowest on the region of the one-to-one at the ratio of Zr and Ti. And, there is some the low-melting-point composition in 10~15%Ti region.

From the result of the Ti-Zr-Cu filler metal melting point measurement, the 37.5Ti-37.5Zr-25Cu alloy with much content of the titanium was chosen as optimum low-melting-point brazing filler metal. This brazing filler metal became the structure which was very homogeneous from the SEM reflection electron image. And, the wetting is also good, and the liquidus temperature is also low with 825°C.

On the other hand, it was reported that alumina ceramics and CPTi can be bonded using 25Ti-25Zr-50Cu alloy brazing filler metal in comparative low temperature and short time [5]. This 25Ti-25Zr-50Cu brazing filler metal component permeated in the porous graphite crucible, when it was heated over 1000°C. As the result which observed the crucible by cutting off, this brazing filler metal was filled to the inside of the crucible, and very good wettability was shown. From the EDS analysis, the alloy composition which permeated the graphite was 22.8Ti-25.2Zr-52Cu. And, the melting point of this alloy was 820°C from the liquidus temperature measurement.

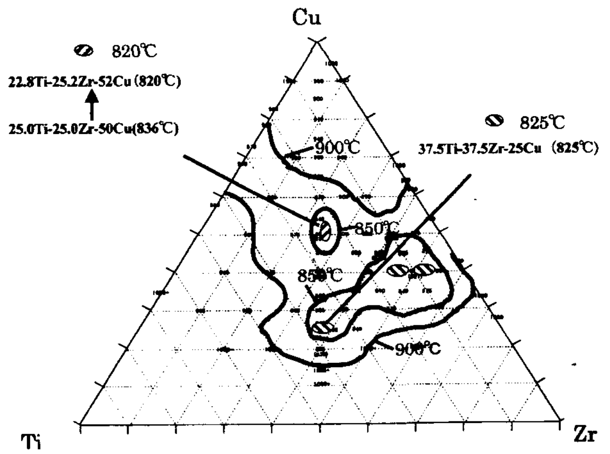


Fig. 4 Ti-Zr-Cu ternary diagram

3.2 Quaternary system brazing filler metal melting point measurement result which added the fourth element to the Ti-Zr-Cu alloy

As selection requirement of fourth additive elements, it were considered that this element has eutectic point on the binary equilibrium diagram for Ti and Zr and that it may improve the brazing filler metal characteristic (corrosion resistance, strength of joint, etc.), even if there is not large melting point depression by the addition of these element. As adding fourth element, Ni, Co and Cr was chosen. It was produced that Cu and fourth additive element would be added in Ti and Zr of the same quantity, and the liquidus temperature was measured.

3.2.1 Ni addition brazing filler metal

Melting point measurement results of Ni addition brazing filler metal is shown in Fig. 5. As the result which did the eutectic composition exploration method in making the start composition to be 42.5Ti-42.5Zr-10Cu-5Ni, primary crystal and eutectic (composition : 30.7Ti-46.4Zr-14.1Cu-8.8Ni) have been formed. By the thermal analysis method, melting point of this eutectic was 825°C as shown in Fig. 5.

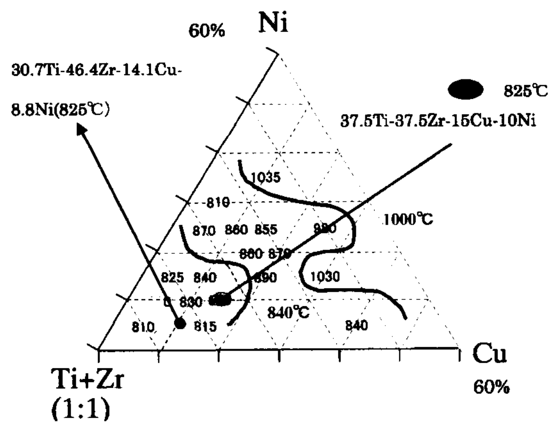


Fig. 5 (Ti+Zr)-Cu-Ni ternary diagram

3.2.2 Co addition brazing filler metal

When Ti and Zr are 1:1 composition, brazing filler metal melting point (818~825°C) of the 37.5Ti-37.5Zr-20Cu-5Co alloy is the lowest,. As a result of eutectic composition exploration method from this brazing filler metal, brazing filler metal of the fine eutectic structure was made without primary crystal. However, the melting point was same only by the change of the composition of Ti and Zr.

Next, different eutectic brazing filler metal of the 43Ti-34.4Zr-9.4Cu-13.2Co composition was produced as a result of eutectic composition exploration method from brazing alloy (M.P.:900°C) which contains Co to 20%. The melting point also dropped to 830°C. However, when the content of Co increased, there was a difficult point that brazing filler metal hardened very much and that the workability becomes bad. Therefore, the bonding test should be carried out using the 5%Co inclusion composition.

3.2.3 Cr addition brazing filler metal.

Cr addition brazing filler metal melting point measurement result is shown in Fig. 6. As a reason of the Cr addition, Cr is the beta phase stabilized type element, and it is also excellent in the corrosion resistance. And, it was considered that Cr might give the good effect at the bond strength.

From Fig. 6, it is effective for the melting point depression, when Cr was added (about 2%) a little. However, it was clarified that the melting point suddenly rose when Cr increases a little. And, when the ratio of Zr and Ti was 1:1, the melting point of brazing alloy did not drop for 830°C or less.

Therefore, melting point (825°C) of the brazing alloy of the 30Ti-43Zr-25Cu-2Cr composition lowered most as the result which did eutectic composition exploration method in making 1010°C (Cr10%) brazing filler metal to be the start point.

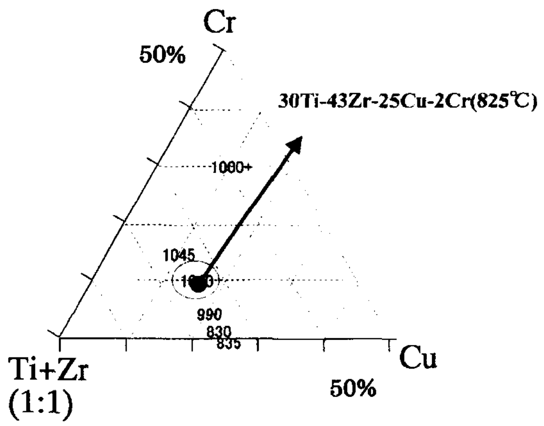


Fig. 6 (Ti+Zr)-Cu-Cr ternary diagram

3.3 Brazing joint tensile strength test

Ribbon (the 50 mm thickness) of eutectic brazing filler metal was produced using the amorphous manufacture equipment. Since manufacture brazing filler metal reacts with the quartz nozzle, the nozzle was produced in the high-density graphite. Alloy composition and melting point of manufacture brazing filler metal are shown in Table 1.

Table 1 Development brazing filler metal

No	Brazing filler metal	Composition (mass %)	M.P. (°C)
1	Ternary A	22.8Ti-25.3Zr-52Cu	820
2	Ternary B	37.5Ti-37.5Zr-25Cu	825
3	Ternary C	25Ti-25Zr-50Cu	836
4	Quaternary (Ni)	37.5Ti-37.5Zr-15Cu-10Ni	825
5	Quaternary (Co)	37.5Ti-37.5Zr-20Cu-5Co	825
6	Quaternary (Cr)	30Ti-43Zr-25Cu-2Cr	825

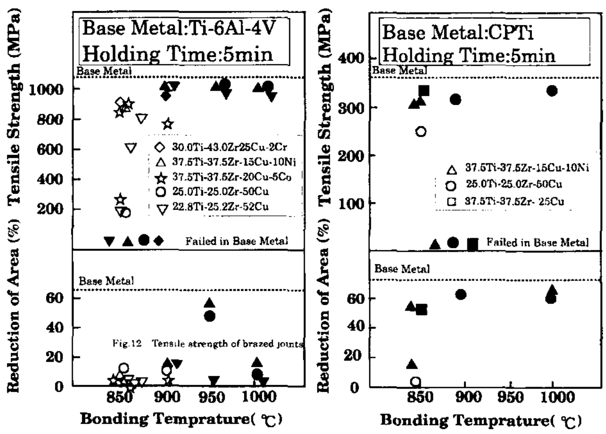
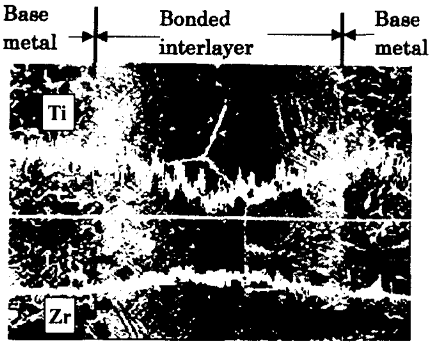


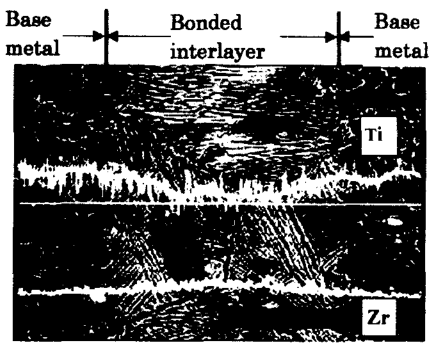
Fig. 7 Tensile strength of brazed joints

Using these brazing filler metal ribbons, butt brazing of Ti-6Al-4V titanium base alloy bar (10mmf) and commercial pure titanium bar was carried out by the induction heating equipment in the vacuum (~10^{-3}Pa). Then, the structure observation of the bonded interface and tensile strength test was carried out. The strength of the brazing joint is shown in Fig. 7. In bonding temperature 900°C and holding time 5 minutes, all brazing joint strength show the strength which be comparable with the base material.

Bonding result of using the 30Ti-43Zr-25Cu-2Cr alloy ribbon of the Cr addition within quaternary composition brazing filler metal is described in detail. In bonding temperature 850°C and holding time 5 minutes, the bond



(a) 30Ti-43Zr-25Cu-2Cr



(b) 37.5Ti-37.5Zr-25Cu

Fig. 8 SEM image of bonding interface

strength which be comparable with the base material strength has been obtained.

The interfacial structure observed by FE-SEM in case of bonding temperature 900°C and holding time 5 minutes is shown at Fig. 8 (a). And, structure photograph of the joint by 37.5Ti-37.5Zr-25Cu ternary system brazing filler metal is shown at Fig. 8 (b).

In ternary compound system brazing filler metal, acicular structure is observed, but in quaternary system brazing filler metal which added Cr, it is not almost observed. As a result of carrying out chemical analysis on central part in the brazing filler metal layer, the element distribution in the interface division becomes the composition which is considerably near for base material.

Newly developed 30Ti-43Zr-25Cu-2Cr alloy seems to be good practical brazing filler metal

4. Conclusion

The results obtained in this study are summarized as follows.

1) In ternary system brazing filler metal, brazing filler metal of the 37.5Ti-37.5Zr-25Cu composition is low-melting-point, and it is the good brazing filler metal from wettings, strength of joint, homogeneity with base material, etc.. It was clarified that 22.8Ti-25.2Zr-52Cu brazing filler metal newly developed from the brazing alloy of the conventional 25Ti-25Zr-50Cu composition by eutectic composition exploration method was low-melting-point (M.P.:820°C) and that it is brazing filler metal of which the wetting is very good.
Therefore, this brazing filler metal can be applied to not only bonding of titanium base alloy but also bonding of ceramics and graphite.
2) For the purpose of brazing filler metal development which was more low-melting-point than ternary compound system brazing filler metal, quaternary system brazing filler metal development which added Ni, Co and Cr was carried out. However, the brazing filler metal development with the melting point which was lower than 820°C was not possible. Therefore, it seems to be the difficulty to develop brazing filler metal of the melting point which is lower than this temperature.

In quaternary system brazing filler metal which added Cr, considerably high strength of joint was obtained in spite of comparatively short holding time.

References

1. R. R. Well : Low Temperature Large-area Brazing of Damage Tolerant Titanium Sturctures, *Welding Journal*, Vol. 54, No. 10 (1975), pp. 348s-356s
2. S. W. Lan : Laminating Brazing Filler Metals for Titanium Assemblies, *Welding Journal*, Vol. 61, No. 10 (1982), pp. 23s-28s
3. T. Onzawa, A. Suzumura and M. W. Ko : Surface Temperature of Ceramic Package and Seam Joining, *Quarterly Journal of the Japan Welding Society*, Vol. 5, No. 2 (1987), pp. 23-28 (in Japanese)
4. T. Onzawa, A. Suzumura and M. W. Ko : Using Low-Melting Point Ti-based Filler Metals, *Welding Journal*, Vol. 69, No. 12 (1990), pp. 462s-468s
5. T. Onzawa, A. Suzumura and M. W. Ko : Brazeability of High Purity Alumina to Titanium Using Ti-Zr Base Filler Metals, *Quarterly Journal of the Japan Welding Society*, Vol. 7, No. 1 (1989), pp. 124-129 (in Japanese)