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## Mechanical Property and Corrosion Resistance Evaluations of Ti-6Al-7Nb Alloy Brazed with Bulk Metallic Glasses

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Exploitation of metallic glass as new brazing filler for Ti-based biomedical alloy was attempted. Ti-6Al-7Nb was used as a brazed material, and candidates of bulk metallic glass brazing filler were Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub>, Mg<sub>65</sub>Cu<sub>25</sub>Gd<sub>10</sub>, Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> and Pd<sub>40</sub>Cu<sub>30</sub>P<sub>20</sub>Ni<sub>10</sub>. Convergence infrared-ray brazing was conducted for brazing Ti-6Al-7Nb/metallic glass in Ar atmosphere. After brazing, hardness measurement, X-ray tomography, cross-sectional observation, artificial saliva immersion test and tensile test were performed to evaluate brazability, mechanical property and corrosion resistance of the obtained brazing joints.

The results of brazing using these metallic glass fillers show that all the metallic glasses were brazable to Ti-6Al-7Nb except for Mg<sub>65</sub>Cu<sub>25</sub>Gd<sub>10</sub>, Mg<sub>65</sub>Cu<sub>25</sub>Gd<sub>10</sub>, Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub> and their joints collapsed rapidly during immersion test. Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> joint was the best in terms of degradation resistance; however, tensile strength was inferior to the conventional one. Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> filler and Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> filler and their joints did not show any collapse or tarnish during the immersion test. Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint showed the excellent properties in terms of both corrosion resistance and tensile strength, which were superior to a joint brazed using Ti-15Cu-25Ni conventional filler. X-ray tomograph indicates that fracture tends to occur in the vicinity of the brazing interface after tensile test.

The brazed metallic glass fillers were fully crystallized, excluding Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> filler. Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> brazed filler contained maple-leaf like primary dendrite, peritectoid and a few microns interfacial reaction layer in glassy matrix. The results indicated that Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> is promising brazing filler for dental or biomaterial devices. [doi:10.2320/matertrans.MER2007612]

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### 1. Introduction

Pure Ti and Ti alloys are important materials as dental and medical applications due to their excellent physical, mechanical, chemical properties and biocompatibility. Ti-based alloys are commonly used for in load-bearing dental applications such like crown, denture base, orthodontic devices, endosseous implant, and so on. Popular Ti-based alloys for load-bearing medical applications are  $\alpha$  phase and  $\alpha + \beta$  phases such like CP Ti and Ti-6Al-4V or Ti-6Al-7Nb, and Ti-6Al-7Nb is developed for replacement for Ti-6Al-4V. Its chemical, mechanical properties and castability were reported from some researchers.<sup>1-4)</sup> Most recently, new  $\beta$  Ti alloys, which show low elastic modulus close to bone, are developed for artificial joint.

Although Ti-based alloy has excellent chemical and mechanical properties, some other properties, such as its high melting temperature, confine their usage as dental devices. The major problem of processing dental devices using Ti alloys is casting and joining. Nowadays casting process is being improved so that dental technicians can provide a wide variety of dental devices with sufficient quality. Nevertheless joining is necessary process because of Ti's poor conformity for relatively large dental devices or dental bridge made with different type of alloys, however, it is still difficult owing mainly to Ti's high affinity with oxygen and high melting point.

There are two common processes of joining dental Ti and

Ti alloys.<sup>5)</sup> One is laser joining, and another is brazing. Laser joining is developed for dental Ti and Ti alloys and the most convenient way with no or few solder use. On the other hand, laser joining has the following disadvantages: relatively poor dimensional accuracy, deformation and damage of material, and expensive equipment.

The infrared ray (IR) joining is often used for brazing Ti and its alloys as a dental technique because of its easy-to-handle process and lower cost than laser joining. For brazing of Ti in dentistry, Ti-15Cu-25Ni clad wire is often used as well as Ag- or Al-based filler<sup>6)</sup> for engineering use. However, this Ti-based filler has high melting point close to Ni's, and much higher than the other brazing fillers.<sup>7)</sup> In spite of its good wettability and resultant high joint strength, this clad strip material cannot be manufactured as homogeneous foil by conventional rolling owing to brittleness resulting from the alloy intermetallic phases forming upon crystallization of its ingot. In addition, the clad strip melts in three separate stages<sup>8)</sup> and turns into a coarse joint microstructure that has a marked porosity sometimes.<sup>9,10)</sup> Since melting of the clad strip completes above 1173 K, brazing operations should be carried out at temperatures higher than the  $\alpha + \beta$  transformation temperature of Ti and close to the  $\beta$  transus temperature of Ti-based alloys. Brazing at the temperature results in a substantial grain coarsening, loss of ductility and loss of strength of the base metal, besides, corrosion occurs at the interface.<sup>11)</sup> Therefore, the following conditions are required for brazing filler for Ti and Ti-alloys for dental use:

Table 1 Materials used in this study.

Material	State	
Ti-6Al-7Nb	Polycrystal	Brazed metal
Ti-15Cu-25Ni	Polycrystal, clad strip	Brazing filler, control
Cu <sub>60</sub> Hf <sub>25</sub> Ti <sub>15</sub>	BMG	Brazing filler
Pd <sub>40</sub> Cu <sub>30</sub> P <sub>20</sub> Ni <sub>10</sub>	BMG	Brazing filler
Zr <sub>55</sub> Cu <sub>30</sub> Al <sub>10</sub> Ni <sub>5</sub>	BMG	Brazing filler
Mg <sub>65</sub> Cu <sub>25</sub> Gd <sub>10</sub>	BMG	Brazing filler

Highly corrosion resistance, sufficiently high joint strength and ductility, short operation time, sufficiently low melting point which is lower than the  $\alpha + \beta$  transformation temperature of Ti (1158 K) and close to the  $\beta$  transus temperature ( $1283 \pm 15 \text{ K}^{12}$ ), sufficient biocompatibility, low toxicity.

For those reason, some researchers applied bulk metallic glass (BMG) to the brazing filler for Ti and Ti-based alloys.<sup>13,14</sup> Their melting temperature is lower than that of the conventional Ti-Cu-Ni clad strip, and the original BMG has uniformity of microstructure. In addition, many kind of BMG has excellent mechanical properties, corrosion resistance.<sup>15</sup> Some researchers attempted to apply Zr-Ti-Cu based amorphous alloys as brazing filler,<sup>14,16</sup> and they indicated that metallic glass filler has excellent properties for brazing filler.

Therefore, in order to find brazing filler with superior properties to conventional ones, we evaluated different kind of BMGs in terms of corrosion resistance and strength of the joints.

## 2. Experimental Procedures

### 2.1 Materials and brazing

Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub>, Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub>, Mg<sub>65</sub>Cu<sub>25</sub>Gd<sub>10</sub> and Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> metallic glasses (MG) were used for brazing filler. Materials used in this study are summarized in Table 1. Ti-15Cu-25Ni is commercial brazing filler for dental Ti alloys, and Ti-6Al-7Nb is brazed metal, which Ti-6Al-7Nb will be described next paragraph. The reason why these metallic glasses were selected is they have sufficiently low glass transition temperature ( $T_g$ ) and/or melting point ( $T_m$ ), and thus relatively high glass formation ability (GFA). Mg<sub>65</sub>Cu<sub>25</sub>Gd<sub>10</sub> MG was provided as an oval-shaped arc melted ingot, and the others were cast into cylindrical shape with 2–3 mm diameter by arc melting. Those were cut into an appropriate size for brazing, and cleaned with acetone.

Commercial Ti-6Al-7Nb ingot (Ti : Al : Nb = 86.5 : 6.0 : 7.0 mass%) was used for brazed metal. The ingot has forged microstructure consisted with lamellar  $\alpha$  (hcp) +  $\beta$  (bcc) phase as shown in Fig. 1. Brazed surface was mechanically polished by #1500 emery paper and cleaned with acetone before brazing.

A pair of Ti-6Al-7Nb plate for a butt joint were set and fixed separately on the Co-Cr jig as illustrated in Fig. 2(a). To avoid reacting sample with the jig and to obtain rapid cooling rate, the jig held the edge of the plate. Gap opening was at 0.2–0.6 mm, where glassy alloy filler was mounted on. Flux was used only for Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> brazing filler.

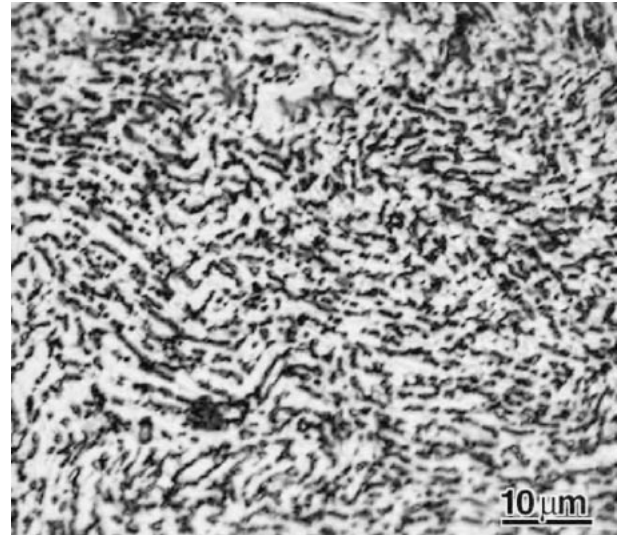


Fig. 1 Typical microstructure of as-provided Ti-6Al-7Nb ingot.

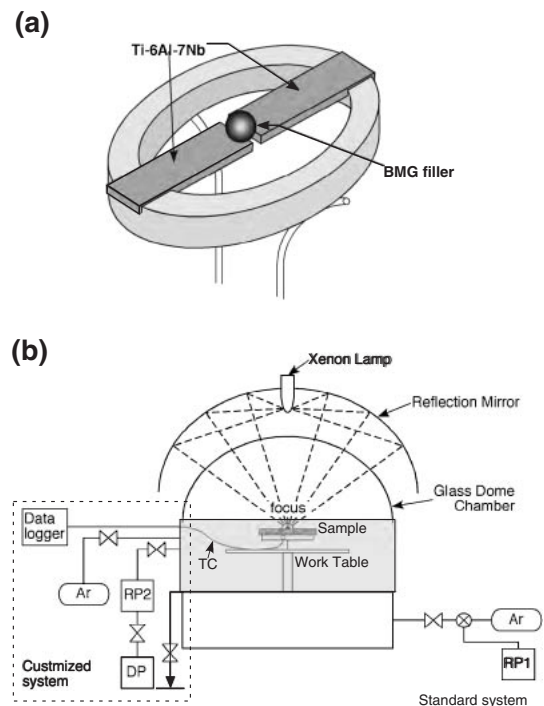


Fig. 2 Schematic illustration of a) brazing stage and b) IR brazing machine. Dotted area and sleeve between glass dome and stage chamber is additional vacuum system added to the original equipment.

According to a literature,<sup>17</sup> K<sub>2</sub>B<sub>4</sub>O<sub>7</sub>(4H<sub>2</sub>O), H<sub>3</sub>BO<sub>3</sub> and K<sub>2</sub>[B<sub>3</sub>O<sub>3</sub>(OH)F<sub>4</sub>] presumably are main composition of the used flux.

Brazing was carried out with preplaced brazing of butt joint in Ar atmosphere after pre-evacuation using customized commercial dental infrared-ray (IR) brazing equipment with halogen lamp. The IR brazing machine is illustrated in Fig. 2(b). Dotted-line surrounding area indicates a customized gas induction and vacuum system with oil diffusion pump, which is equipped in order to obtain enough low pre-evacuation pressure and efficient cooling rate. Pre-evacuation pressure of the customized system was less than  $2 \times 10^{-3} \text{ Pa}$

Table 2 Chemical composition of commercial artificial saliva (Saliveht<sup>®</sup>)<sup>18)</sup> used in this study.

Composition	(mg/L)	Additives and properties
NaCl	42.2	*Additives: Carmellose sodium, D-sorbitol, Sodium benzoate, sorbic acid, carbon dioxide gas (injection gas)
KCl	60.0	
CaCl <sub>2</sub>	7.3	*pH 5.0–6.0
MgCl <sub>2</sub>	2.6	*Specific gravity: 1.010–1.025
K <sub>2</sub> HPO <sub>4</sub>	17.1	*Viscosity: 4–6 mm <sup>2</sup> s <sup>-1</sup> (298 K)

instead of  $1.3 \times 10^2$  Pa of the standard system, and brazing was carried out in Ar atmosphere of  $0.5 \times 10^5$  Pa. Then, Ar gas was induced at the side of the specimen as shown in Fig. 2(b). Brazing temperature was between 800 K and 1100 K, although appropriate brazing temperature varied by melting temperature of filler.

## 2.2 Artificial saliva immersion tests

Artificial saliva immersion test was performed for MG fillers and the joints. These jointed samples were cut by diamond cutting wheel, and the most of Ti-6Al-7Nb plate was removed except for the central part of the joint including overlapped filler. The length of the joint specimen for the test is 2–3 mm.

The MG fillers and butt joint samples were immersed in artificial saliva (Saliveht<sup>®</sup>, Teijin Farma Co. Ltd.) individually, and kept in an incubator at 310 K. Chemical composition of the artificial saliva is shown in Table 2, which is from the instruction manual.<sup>18)</sup> A precision electric scale of which accuracy is  $10^{-4}$  mg was used for the weight loss measurement. To evaluate weight change ( $\delta W = W - W_0$ ),  $\delta W$  was divided by the initial weight of the sample ( $W_0$ ).

## 2.3 Mechanical tests and microstructure observations

Cross section of the bond brazed with Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> and Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> MG filler was observed by SEM-EDS. Brazed joint samples were cut at the center alongside of major axis by diamond low-speed wheel. And then they were polished their surface. X-ray diffraction pattern in brazed metal was measured by micro-area X-ray diffraction machine.

Vickers' hardness ( $H_V$ ) test of cross sectional brazing zone was carried out to estimate O absorption during brazing. The applied load and time is 2.94 N for 10 s. The test was performed to the base metal and weld zone, and to pre- and post-brazing. To compare with mechanical damage, sand-blasted Ti-6Al-7Nb surface was also measured. Average and standard deviation was calculated out of each 5 measurements.

Tensile test was also carried out for the butt joint. Test pieces of Ti-6Al-7Nb were cut from the ingot by the electro-discharge machine, and then polished until #1500 emery paper. The gage length, parallel width, thickness and R are 10.5 mm, 2 mm, 0.8 mm and 2 mm, respectively. Ti-6Al-7Nb plates for tensile test were cut off at the center perpendicular to the gage length and thickness, and brazed as well as immersion test specimen. Tensile test was conducted on an Instron-type machine in ambient temperature and at an initial strain rate is  $1.6 \times 10^{-4}$  s<sup>-1</sup>. After the test, the specimens were observed by X-ray microtomography.

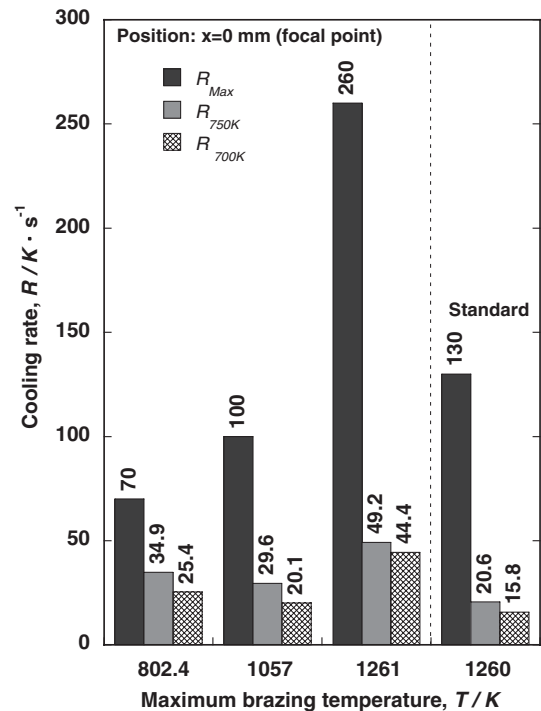


Fig. 3 Measured cooling rate at the maximum temperature ( $R_{Max}$ ), at 750 K ( $R_{750K}$ ) and at 700 K ( $R_{700K}$ ) at focal point of infrared ray. “Standard” data at the right side of dotted line in this figure was obtained from original IR brazing system before customizing.

## 3. Results and Discussion

### 3.1 Brazability and oxidation during brazing process

Since glass formation during solidification is sensitive to cooling rate, cooling rate ( $R$ ) of each brazing temperature at focal point in the system.  $R$  was measured by means of differentiation of continuous cooling time-temperature curves at each temperature. The cooling temperature curve was measured using PR thermocouple placed underneath Ti-6Al-7Nb plate, where is overside of focal point. Three kinds of the cooling rates ( $R$ ) at maximum temperature ( $R_{Max}$ ), at 750 K ( $R_{750K}$ ) and at 700 K ( $R_{700K}$ ) were obtained as shown in Fig. 3.  $T_g$  of Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub> and of Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> is approximately 730 K and 680 K respectively, and according to Nishiyama's research,<sup>19)</sup> nose of crystallization in CCT curve is around 750–700 K in fluxed Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> although  $T_g$  of Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> is approximately 570 K.  $R$  at 1260 K of the standard system was also plotted for reference purposes. Total operating time, which means a period from halogen lamp on to off, was set for about 30 s. In Fig. 3,  $R_{Max}$  decreased rapidly with decreasing the maximum brazing temperature, since temperature decreased logarithmically.

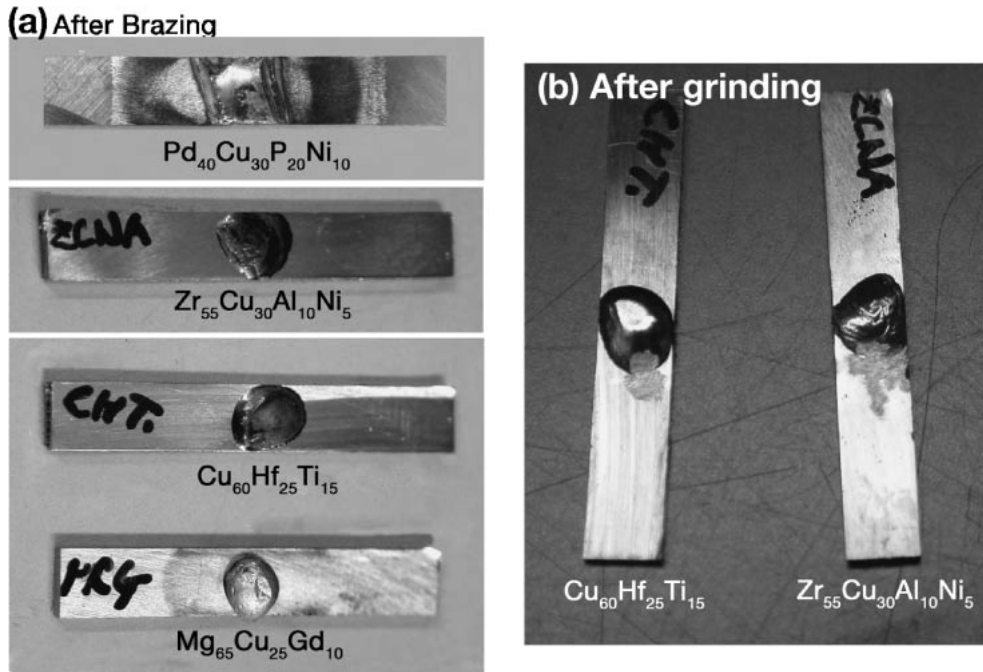


Fig. 4 Photographs of IR irradiated and solidified BMG fillers on Ti-6Al-7Nb plate a) after brazing and b) after grinding and polishing.

mically, thus the  $R_{750\text{K}}$  and  $R_{700\text{K}}$  become much smaller than  $R_{\text{Max}}$ . However,  $R_{\text{Max}}$  of the additional system at 1261 K is more than twice higher than that of the standard system at each temperature. Although  $R$  rapidly decreases, these  $R$ 's are still much larger than critical cooling rate ( $R_c = 0.100 \text{ Ks}^{-19}$ ) of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  at 700–750 K. Thus, they are considered sufficient for obtaining glassy phase of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  filler after brazing.

By virtue of lower pre-evacuation pressure than standard system, all the filler except  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  spread satisfactorily and wetted on the Ti-6Al-7Nb plate. In standard system, Ti-6Al-7Nb/ $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  and Ti-6Al-7Nb/ $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  joint was not able to be obtained, and which is presumably due to their high oxidation sensitivity or supposedly due to vaporization of elements. Thus, oxidation was suppressed enough to obtain wetting by improving vacuum with respect to the  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  BMG brazing filler. Therefore, the higher pre-evacuation level was conducted the more capable of brazing with wide variety of BMG.

Figure 4(a) shows photographs of the solidified metallic glass filler metal melted on Ti-6Al-7Nb plate. Regarding oxidation on the surface,  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ ,  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  and  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  surfaces was tarnished, but coloration of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  filler surface was not perceptible because of using flux. Once tarnished surface was removed by polishing, metallic surface came out as shown in Fig. 4(b). Therefore, surface oxidation during brazing was not severe very much. These fillers and base metals were well jointed at the interface, so that BMG fillers did not tip off from the base metals after post-brazed grinding with coarse carborundum grinding point. The reason why IR brazing did not work to  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  might be severe oxidation or vaporization occurred during heating. Therefore,  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ ,  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  and  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  are brazable by this technique.

### 3.2 Immersion test of the BMG and joint

Time course of weight-change of the BMG alloys and Ti-6Al-7Nb was measured in artificial saliva at 300 K. The obtained time-weight loss curves are as shown in Fig. 5. In this figure, positive value of y-axis indicates weight gain of the sample, and *vice versa*.

From the results of BMG immersion test in Fig. 5(a), Ti-6Al-7Nb and  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  BMG did not show obvious weight change for more than 31.5 Ms (1 year).  $\delta W/W$  of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  decreased gradually at an initial stage of the test, however, the  $\delta W/W$  was saturated within 1.5% reduction of the weight at 10 Ms. It must be noted again that no or less weight change does not necessarily mean excellent corrosion resistance, however, since  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  and  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  did not collapse nor change the surface color during the test, at least these metallic glasses would be capable of application to sustainability in an oral cavity in terms of corrosion resistance. On the other hand, in  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  and  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  were very reactive against artificial saliva. In  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$ , Cu elution and verdigris formation started on the surface in a few days of the immersion test, and  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  was collapsed eventually by 15.5 Ms (6 months). In case of  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ , bubbles came out spontaneously from its surface just after immersion, and the surface started to turn into black. Breakdown of the specimen started just after a few hours of the test, and the specimen was completely collapsed into black particles within a day.

In addition, immersion tests of the brazed butt joint that were also performed as shown in Fig. 5(b). Weight change of Ti-6Al-7Nb was not observed in this study. Therefore, it is indicated that Ti-6Al-7Nb is stable in a similar environment to oral cavity. It should be noted that  $\delta W/W$  of the joint might be smaller than that of BMG itself because the specimens consist of not only BMG filler but also Ti-6Al-7Nb. That is,

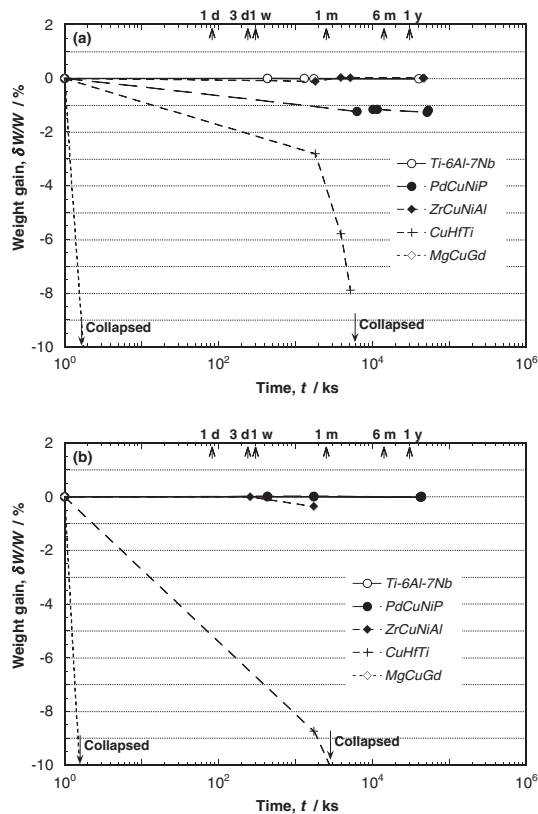


Fig. 5 Time course of weight-change of a)  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ ,  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ ,  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  and  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  BMG alloys and Ti-6Al-7Nb, and b) the  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ ,  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ ,  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$ , and  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  filler part of brazing joint immersed in artificial saliva at 310 K. Positive value means weight gain of the sample.

although contribution of Ti-6Al-7Nb to total weight and surface area need to be taken into account, the obtained weight change can be regarded as that from BMG filler and/or from heat affected zone because of no weight change of Ti-6Al-7Nb base metal.

Interestingly, Ti-6Al-7Nb/ $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  joint did not show any weight change during the test in spite of that  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  itself shows slight weight loss. On the contrary, Ti-6Al-7Nb/ $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  joint showed slight spontaneous weight change from  $2 \times 10^2$  ks to 2 Ms in spite of that  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  BMG itself didn't show any weight change for more than a year. The filler of Ti-6Al-7Nb/ $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  and Ti-6Al-7Nb/ $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  joints collapsed severely as well as the BMG only specimen.

From these results of the butt joint immersion test, when BMG itself has good durability in artificial saliva, a butt joint using the BMG as a brazing-filler also shows good durability although the filler crystallized during solidification process. It was indicated that the BMG fillers after brazing were partially or completely crystallized, and their cross-section microstructures will be shown in the next section.

Corrosion resistance of Zr-Cu-Ni-Al alloys in aqueous solutions tested by electrochemical measurements was reported in several literatures. It was known that Zr-based metallic glass shows excellent corrosion resistance because of forming stable Zr-based passivation film.<sup>20–22</sup> Besides, Al is also a strong passivating element. In addition, Qiu *et al.*

reported  $\text{Zr}_{65}\text{Cu}_{17.5}\text{Ni}_{10}\text{Al}_{7.5}$  exhibits excellent corrosion resistance in artificial body fluid.<sup>20</sup> They indicated that ion release concentration is much lower than SUS316L stainless steel, which was formerly used as a biomaterial. Thus, it is suggested that excellent durability of  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  in this immersion test is probably due to the stable Zr passivation film formation even in static condition. Regarding Ti-6Al-7Nb/ $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  joint, there is a literature indicating that dendritic phase containing Cu in Zr-Cu-Ni-Al-Hf BMG composite caused inferior corrosion resistance due to preferential corrosion at the boundaries between BMG and crystal.<sup>23</sup> In this study, similar preferential corrosion probably occurred at the joint since tested  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  brazing filler of the joint was fully crystallized.

In  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  BMG, good durability was shown and no surface color change was observed in the immersion test, although slight spontaneous weight loss was observed after more than 1-year period. Pd is a noble metal that is used for dental alloys, thus this BMG might be stable against corrosion. Wu *et al.* were reported corrosion behavior of  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  BMG and crystallized alloy.<sup>24</sup> They indicated the BMG exhibited excellent corrosion resistance in aqueous solution because of Pd. In addition, they also indicated corrosion resistance of  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  is improved by means of crystallization due to inert phosphides formation. Therefore, our result of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  BMG and the joint indicates that less weight change of the joint than the BMG was presumably caused by crystallization of the  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  brazing filler.

Alongside of  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  and  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  BMG and joint that showed good durability in immersion test,  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  and  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  showed no durability in this static immersion durability study in artificial saliva. It was reported that corrosion resistance of Cu-Zr-Ti was low in neutral or acidic solution, since Cu weakens Zr-rich passivation film.<sup>25</sup> Our result suggests that Cu, major element of the alloy, prevent stable protective film formation, as well as the results of Cu-Zr-Ti while Hf is also supposed to be effective element in terms of surface protective film formation.<sup>23</sup>

In this study, durability of  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  BMG and its joint was the most inferior to other BMG's. According to literatures about corrosion resistance of Mg-Cu-Ag or Mg-Y-Cu-Ag BMG,<sup>26,27</sup> in Mg-based amorphous, strong alkaline electrolyte with  $\text{pH} \geq 6$  is needed to form stable anodic passivation film. Since artificial saliva used in this study is slightly acidic ( $\text{pH} = 5\text{--}6$ ), surface might not covered with protective film strong enough to prevent collapse.

Therefore, in terms of chemical stability in oral environment, it is suggested that  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  and  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  are likely to be capable for brazing filler for Ti-6Al-7Nb joint.

### 3.3 Joint strength of BMG filler/Ti-6Al-7Nb joint in tension

In terms of joint strength, tensile test of Ti-6Al-7Nb/BMG filler joint was performed. Figure 6 is results of mean tensile stress of the joints tested in this study. Later two results of the Ti-6Al-7Nb/ $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  and Ti-6Al-7Nb/ $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  joints were brazed under less than

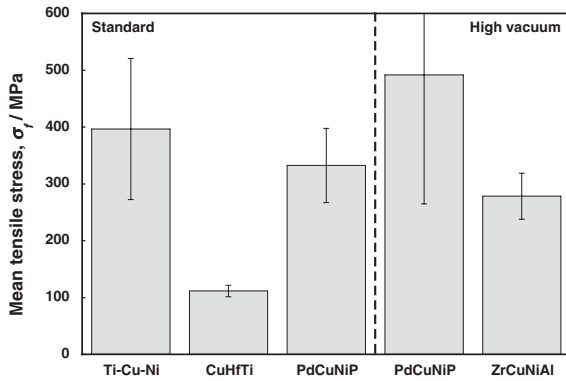


Fig. 6 Mean tensile stress of Ti-6Al-7Nb joint brazed by Ti-25Cu-15Ni clad strip brazing filler,<sup>7)</sup> and Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub>, Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> and Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> BMG filler.

$2 \times 10^{-3}$  Pa pre-evacuation pressure and higher cooling rate. For comparison, first three results of joint strength with conventional Ti-15Cu-25Ni polycrystalline filler reported previously,<sup>7)</sup> Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub> and Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> BMG fillers brazed with worse pre-evacuation pressure and lower cooling rate are plotted in this graph. All the joints exhibited brittle fracture and its tensile strength was lower than that of single phase BMG. Joint strength brazed by Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub> and Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> filler was lower than conventional Ti-15Cu-25Ni filler in standard pre-evacuation pressure. The joint strength Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint brazed in standard system was approximately 8.5% lower than conventional Ti-15Cu-25Ni, and that of Ti-6Al-7Nb/Cu<sub>60</sub>Hf<sub>25</sub>Ti<sub>15</sub> joint was the lowest of all. However, in higher vacuum system, which was mainly applied in this study, Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint exhibited 718.57 MPa in tension at maximum, besides the mean strength was the highest, although standard deviation was larger than other BMG fillers. The mean strength was superior to that of conventional Ti-15Cu-25Ni filler joint and approximately 10% less than that of CP Ti ASTM grade 4 (UTS minimum: 550 MPa<sup>12)</sup>), while Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> filler joint exhibited lower average than conventional Ti-15Cu-25Ni. The scattering of Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint strength might be caused by flux usage at brazing procedures. Regarding an effect of pre-evacuation and cooling rate on the strength of Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint, the joint strength increased 1.5 times higher by increasing those ability.

Summarizing results of mean tensile strengths obtained in this study, Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> is the most promising metallic glass as brazing filler in terms of joint strength. With regard to processing, it is reasonable that higher pre-vacuum obviously improved brazability of BMG filler or its joint strength. This is probably because of preventing surface oxidation, sufficient cooling rate to obtain glassy state, and suppressing fragile interfacial reaction layer formation between Ti-6Al-7Nb and BMG.

It could be suspected that void or porosity was formed at the interface during brazing procedure, and formation of such defects can cause scattering of tensile results or reduction of tensile strength. To confirm existence of internal defect at a brazing joint, brazing interfaces of the specimens after tensile test were investigated by 3D X-ray microtomographs

(resolution: approx. 1  $\mu$ m). Figure 7 shows representative sliced images of fractured tensile specimens of Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> and Ti-6Al-7Nb/Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> after the test. Moiré rings and symmetric pattern is an artifact generated by image reconstruction. Interface between brazing filler (bright area) and base metal (dark area) can be distinguished clearly in Fig. 7. From the image of Fig. 7(a) and (b), Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint, particles and dark blob alongside of brazing interface (e.g., oval around area in b) are observed in the filler, and which was caused by changing chemical composition. Porosity was hardly observed inside the filler, although obvious blowholes were found in surplus filler on the Ti-6Al-7Nb surface, where was considered irrelevant to fracture.

Figure 7(c) and (d) is a diagonal top view of fracture surface and its cross section of Ti-6Al-7Nb/Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub>, respectively. There was a blowhole in the vicinity of an interface in the images of Ti-6Al-7Nb/Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> filler joint, however, obvious porosity or blob was infrequently found at brazing interface as seen in Fig. 7(d). Thus, brazing defect is not likely to be major problem against fracture.

Uneven fracture surface such as Fig. 7(c) indicates that the fracture occurred inside the filler near brazing interface. Optical fracture surface morphology also suggested that cohesive failure occurred around brazing interface. Consequently, it is suggested that joint strength is subject to stress concentration due to difference of modulus or thermal expansion coefficient between Ti-6Al-7Nb and BMG filler.

### 3.4 Cross section of the Ti-6Al-7Nb/BMG brazing joint

Figure 8 shows back scattered electron (BSE) images of a) Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint, b) Ti-6Al-7Nb/Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> joints, and, for comparison, c) Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint brazed in standard (higher pre-evacuation pressure) system. Brazing interface was defined clearly. Grain coarsening in Ti-6Al-7Nb was rarely observed close to the interface.

In Fig. 8(a), smooth matrix appears in the Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> filler in this image, where maple-leaf-shaped primary grains and peritectic surrounding dendrite dispersed in the matrix. In addition, reaction layer is observed clearly at the interface between brazing filler and base metal, and its thickness varies widely in places and in specimens. According to our previous result of chemical composition measured by EPMA,<sup>28)</sup> reaction layer and maple-leaf-shaped grains contains approximately 20 mol% Ti and 0.5 mol% Nb. On the other hand, elements of base metal, Ti, Al and Nb, were very slightly detected (less than 0.08 mol%) in the matrix, and composition of the matrix was close to the BMG itself. Elements of the BMG were hardly detected in the base metal near the brazing interface.

Microstructure of Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> filler in Fig. 8(c) exhibits severe crystallization and inhomogeneous solidification in the filler despite Fig. 8(a) shows relatively homogeneous structure. Segregation, and voids aligned longitudinally were observed in the middle of the filler part. Voids might be generated because of solidification shrinkage. A certain amount of Ti was detected by EPMA at the center area of the filler.

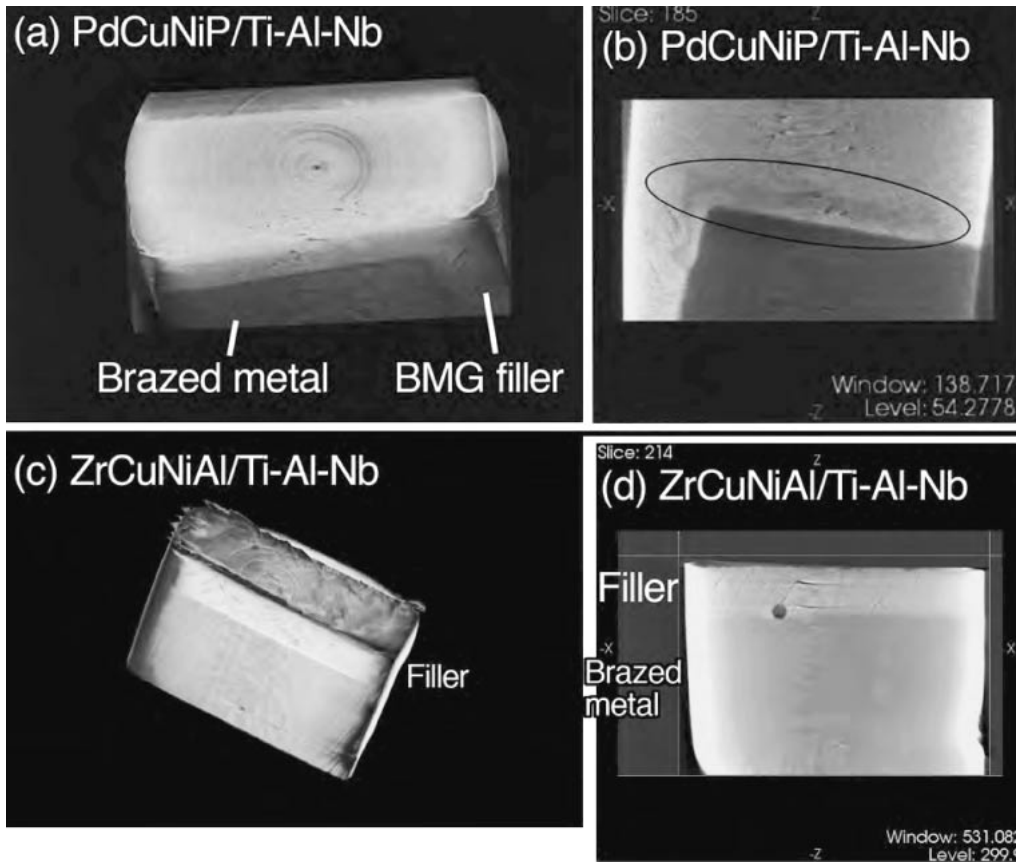


Fig. 7 Computer reconstructed images of a), b) Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> and c), d) Ti-6Al-7Nb/Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> joint measured by 3D X-ray microtomography after tensile test.

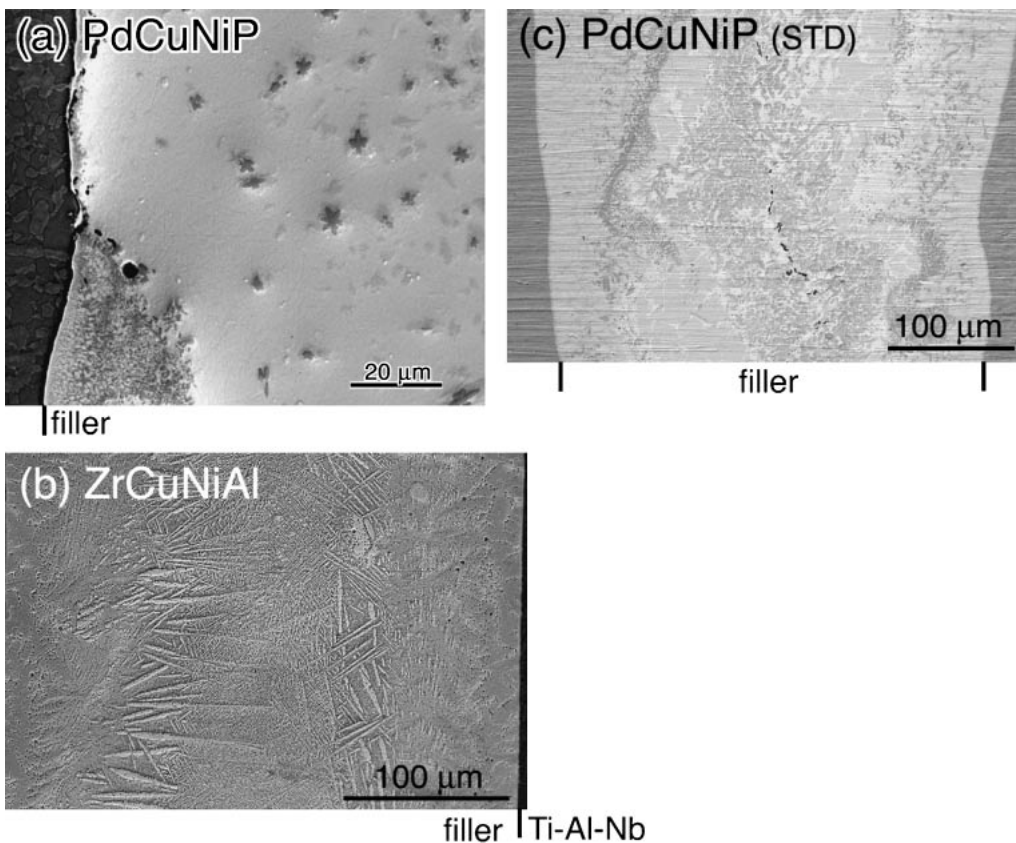


Fig. 8 BSE images of cross section of a) Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> joint, b) Ti-6Al-7Nb/Zr<sub>55</sub>Cu<sub>30</sub>Al<sub>10</sub>Ni<sub>5</sub> joint brazed in modified system, and c) Ti-6Al-7Nb/Pd<sub>40</sub>Cu<sub>30</sub>Ni<sub>10</sub>P<sub>20</sub> brazed standard system.



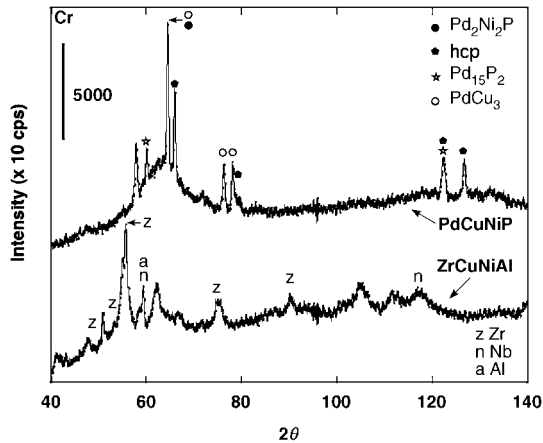


Fig. 9 Microarea X-ray spectra of filler part of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  and  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  brazed filler after brazing.

$\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  filler in Fig. 8(b) had well-grown dendrite microstructure, and Ti content drastically decreased in accordance with the distance from the interface. Approximately 20 mol% of Ti was detected in the filler at the point of 15  $\mu\text{m}$  apart from a base metal, while Ti was no longer detected at the point of 60  $\mu\text{m}$  from the interface.

Microarea X-ray diffraction spectra of the filler part of Ti-6Al-7Nb/ $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  and Ti-6Al-7Nb/ $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  joint are shown in Fig. 9.  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  brazed filler was completely crystallized, and some peaks correspond to Zr hcp peaks. Moderate broad peak of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  brazed filler appearing between 55–75 degrees indicates that the filler matrix is a glassy phase. The filler contains crystalline, which are similar to phases generated during annealing at large undercooling temperature,<sup>29)</sup> such as  $\text{Pd}_2\text{Ni}_2\text{P}$ ,  $\text{Pd}_{15}\text{P}_2$ , and  $\text{PdCu}_3$ . In addition, other unknown peaks were observed. Unit cell of these unknown peaks is likely to be a hexagonal phase, and which presumably correspond to maple-leaf-shape grain since only this phase contains a certain amount of Ti. Synchrotron X-ray studies revealed that there are two types of crystalline in matrix, which have hexagonal and tetragonal unit cells.<sup>28)</sup>

The brazed filler of Ti-6Al-7Nb/ $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  brazed in lower pre-evacuation pressure has a glassy phase, despite brazed filler of Ti-6Al-7Nb/ $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  joint brazed in less clean atmosphere and Ti-6Al-7Nb/ $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  joint was fully crystallized. Generally, not only composition of BMG also various solidification conditions, such as atmosphere, cooling rate, or heating temperature, affect crystallinity of an alloy. From the results of microstructure observations and microarea X-ray diffraction measurements in this study, it is obvious that  $R_c$  of BMG, Ti diffusion into the filler and atmosphere during brazing is the key factors of crystallization of BMG brazing filler.

In terms of elements migration between the filler and the base metal during brazing, dissolution, diffusion or reaction with base metal is the most considerable factor for crystallization of BMG filler. Chemical analysis by EPMA indicates that elements in base metal, especially Ti, diffused into BMG filler even though brazing temperature was lower than melting point of Ti-6Al-7Nb.<sup>12)</sup> Originally,  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$

BMG has excellent glass formation ability (GFA) and this alloy transforms into glassy phase even at the cooling rate of  $0.1 \text{ K s}^{-1}$ ,<sup>19)</sup> and besides, cooling rate applied in this study was sufficiently higher than critical cooling rate ( $R_c$ ). On the other hand, Ti lowered GFA of BMG, so that  $R_c$  around brazing interface would be increased. Therefore, it is suggested that rapid Ti diffusion into BMG and consequently, Ti containing maple-leaf grain was primarily crystallized.

EPMA results of cross section of Ti-6Al-7Nb/ $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  joint revealed that Ti and Nb diffused into the filler at the interface, but not inside the filler. Therefore,  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  filler was completely crystallized after brazing, since GFA of  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  is inferior to that of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ , and besides cooling rate is not sufficient for its glass formation.

Taking into account of all the results obtained in this study,  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  BMG is the most promising metallic glass as a brazing filler for Ti-base dental material in terms of joint strength and durability in artificial saliva, although further investigation is needed to improve its mechanical and corrosion properties.

It is noticeable that both quaternary BMG and Ti-6Al-7Nb brazed filler showed good sustainability against artificial saliva, especially for  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  and its joint. That is, the degradation test results suggest that  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  has a possibility for showing excellent corrosion resistance regardless of crystallinity or phase, although tensile joint strength was not as high as Ti-Cu-Ni commercial brazing alloy. Since cohesion failure was dominant for both  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  filler and  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  filler, reaction at the interface between base metal and the filler is the key to improve their tensile strength. On the contrary, ternary BMG alloys in this study were unlikely to be sustainable for brazing and placing in oral environment.

Even if BMG shows high strength, it is common that its crystal does not necessarily have high strength. As far as our results indicating, it seems to be important for the BMG brazing filler that remaining glassy phase after brazing to obtain excellent joint strength.

#### 4. Summary and Conclusions

Metallic glass brazing filler was used as a brazing filler for Ti-6Al-7Nb, Ti-based dental alloy joining.  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ ,  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$ ,  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$ , and  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  metallic glasses were candidates and were brazed using IR brazing machine in low pre-evacuation pressure. From the results, summary is as follows.

- (1) All the brazed BMG with the exception of  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  successfully brazed with Ti-6Al-7Nb in high pre-evacuation and direct cooling system. Suppression of oxidation during brazing would be a key factor to obtain sufficient wetting with base metal.
- (2) Immersion tests of BMGs and their brazed joints were performed in artificial saliva. Weight change of BMGs and brazing joints using these BMG fillers was measured up to 1 year.  $\text{Cu}_{60}\text{Hf}_{25}\text{Ti}_{15}$  and  $\text{Mg}_{65}\text{Cu}_{25}\text{Gd}_{10}$  collapsed rapidly, on the other hand, weight loss of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$  and  $\text{Zr}_{55}\text{Cu}_{30}\text{Al}_{10}\text{Ni}_5$  showed durability. Weight change of  $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$

and  $Zr_{55}Cu_{30}Al_{10}Ni_5$  was approximately  $-1.5\%$  and almost zero, respectively. Brazing joint using  $Pd_{40}Cu_{30}Ni_{10}P_{20}$  and  $Zr_{55}Cu_{30}Al_{10}Ni_5$  BMG filler exhibits small or no weight change as well as BMG itself.

- (3) Joint strength of brazed Ti-6Al-7Nb with  $Pd_{40}Cu_{30}Ni_{10}P_{20}$  was superior to Ti-15Cu-25Ni conventional brazing filler, and the joint strength was about 10% less than that of CP Ti ASTM grade 4, although maximum strength obtained in this study was about 720 MPa. Better pre-evacuation and higher cooling rate made the joint strength increased. Fracture mainly occurred at inside the filler near the joint interface.
- (4)  $Pd_{40}Cu_{30}Ni_{10}P_{20}$  brazed filler had a glassy phase matrix containing maple-leaf-like primary grains and peritectic that precipitated alongside brazing interface. The maple-leaf-like grains contained Ti. Reaction layer containing elements both filler and base metal formed at the interface.
- (5) In the light of strength and dissolution durability in oral environment,  $Pd_{40}Cu_{30}Ni_{10}P_{20}$  is the most promising candidate for brazing filler for Ti-based dental alloy.

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