Original paper

Dental Materials Journal 19(3) : 294−306, 2000

Development of Ag-Pd-Au-Cu Alloy for Multiple Dental Applications Part 1 Effects of Pd and Cu Contents, and Addition of Ga or Sn on Physical Properties and Bond with Ultra-low Fusing Ceramic

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Received April 15, 2000/Accepted June 12, 2000

Ag-Pd-Au-Cu quaternary alloys consisting of 30-50% Ag, 20-40% Pd, 10-20% Cu and 20% Au (mother alloys) were prepared. Then 5% Sn or 5% Ga was added to the mother alloy compositions, and another two alloy systems (Sn-added alloys and Ga-added alloys) were also prepared. The bond between the prepared alloys and an ultra-low fusing ceramic as well as their physical properties such as the solidus point, liquidus point and the coefficient of thermal expansion were evaluated. The solidus point and liquidus point of the prepared alloys ranged from 802℃ to 1142℃ and from 931℃ to 1223℃, respectively. The coefficient of thermal expansion ranged from 14.6 to 17.1×10^{-6}/℃ for the Sn- and Ga-added alloys. In most cases, the Pd and Cu contents significantly influenced the solidus point, liquidus point and coefficient of thermal expansion. All Sn- and Ga-added alloys showed high area fractions of retained ceramic (92.1-100%), while the mother alloy showed relatively low area fractions (82.3%) with a high standard deviation (20.5%). Based on the evaluated properties, six Sn-added alloys and four Ga-added alloys among the prepared alloys were suitable for the application of the tested ultra-low fusing ceramic.

Key words: Casting alloy, Alloy for metal-ceramics, Silver alloy

INTRODUCTION

Various types of alloys have been introduced into dental practice and effectively used in dental restorations and prostheses. The use of these alloys, however, has been generally limited to several purposes. Type I and II gold alloys have been mainly used for inlays and Type III gold alloy for inlays, crowns and bridges. Silver-based alloys containing 12% Au and 20% Pd have been used for cast inlays, crowns and bridges, but rarely for removable denture frameworks. However, Co-Cr alloys and Type IV gold alloys have mainly been used as removable denture frameworks, but little for cast inlays and crowns. All of the aforementioned alloys are not suitable for application with dental ceramics except some Co-Cr alloys, which are not suitable for cast inlays and crowns without ceramic application.

Recently, new gold alloys claiming multiple dental purposes have been introduced. These gold alloys are claimed by the manufacturers to be suitable for ultra-low fusing with dental ceramics as well as cast inlays, crowns and bridges. The advantage of ceramics is their ultra-low fusing temperature. Some of the marketed products can be fused at around 800℃, which allows the alloys to be cast at relatively low temperature using both gas-air torch and gypsum-bonded investment. According to the manufacturers' catalogues, the tensile strength of these alloys is lower than that of palladium-based alloys (Pd-Cu and Pd-Co alloys) used for conventional low fusing dental ceramics. In addition, although their mechanical properties can be changed with different heat treatments, the range of the change is not as wide as that of Type Ⅳ gold alloys. Therefore, these alloys may not cover various types of dental applications.

In comparison with the new gold alloys, The Ag-Pd-Au-Cu alloys containing 12% Au and 20% Pd have higher strength, which is competitive with that of the palladium-based alloys, and the range of their strength change is wider than that of the new gold alloys[1-3], which indicates a greater potential of these alloys in more applications. One shortcoming of Ag-Pd-Cu alloys is tarnish resistance, but this can be improved with the addition of Au as reported by Moriyama *et al.*[4] In their study, the tarnish resistance of 45Ag-35Pd-20Cu was improved with the addition of 20% gold, although the strength slightly decreased. These findings indicate that Ag-Pd-Au-Cu alloys can be used for multiple dental purposes both with and without ceramics if the alloys bond with ultra-low fusing ceramics. A recent study by Shiozawa *et al.*[5] indicated that a silver-based alloy containing 12% Au and 20% Pd could bond with ultra-low fusing ceramics. Therefore, it is very likely that Ag-Pd-Au-Cu alloys containing high Pd (more than 20%) not only provide a wide range of strength, but can also be used with ultra-low fusing ceramics.

The purpose of the present study was to evaluate the bond between the prepared Ag-Pd-Au-Cu quaternary alloys with different contents of palladium and copper, and an ultra-low fusing ceramic as well as some physical properties such as solidus point, liquidus point and coefficient of thermal expansion.

MATERIALS AND METHODS

Alloy preparation

Nine different Ag-Pd-Au-Cu alloys were prepared in a silica tube (inside diameter: 16 mm) under argon gas atmosphere using an induction melting unit (High Frequency Induction Heating Unit - 10 kW SCR, Tokyo Koshuha-Denkiro Co. Ltd., Tokyo, Japan). These alloys consisted of 20% (mass% except when otherwise indicated) of gold, 20, 30 or 40% of palladium, 10, 15 or 20% of copper, 0.05% iridium and silver as balance as shown in Fig. 1, with alloy numbers from 1 to 9. A preliminary test was conducted to check the bond between prepared alloys and an ultra-low fusing ceramic. In the preliminary test, two specimens of each alloy were evaluated following ISO 9693 : 1991 "Dental ceramic fused to metal restorative materials"[6]. One of the two specimens or both specimens had an approximately 30-50% area fraction of the detached ceramic for all nine alloys, which showed that the quality of the bond was not satisfactory. Based on this finding, either 5% of gallium or 5% of tin was added to each of the nine different alloys aiming at the improvement of the bond.

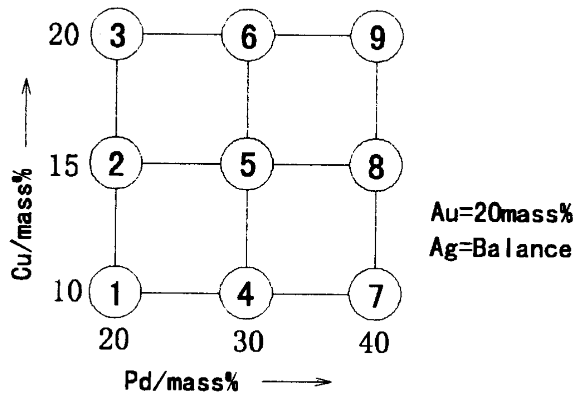


Fig. 1 Compositions of the prepared alloys numbers 1 to 9.

Measurement of solidus and liquidus points

Liquidus point and solidus point were measured for each prepared alloy using a differential thermal analyzer (DT-1500-H, Shinku-Riko, Yokohama, Japan). Approximately 0.5 g of each alloy and α-alumina particles as control were heated to 1300℃ at a heating rate of 10℃/min and then cooled down to 600℃ at the same rate as heating. The thermal change was recorded on a chart. The solidus point and liqiudus point were determined from the start point and the end point of the endothermic change on the recorded chart, respectively. The measurement was made on two samples for each alloy.

Measurement of coefficient of thermal expansion

A rod shape specimen (diameter: 6 mm, length: 20 mm) for the measurement of the coefficient of thermal expansion was prepared using a dental casting procedure. A rod shape pattern was made from an inlay wax (Inlay Wax Medium, GC Corporation, Tokyo, Japan) using a stainless steel die and a casting mold was made from a gypsum-bonded investment (Cristobalite Micro, GC Corporation Tokyo, Japan) which was mixed following the manufacture's instruction. After the casting mold was burned out at 650℃, a prepared alloy was cast into the mold using a centrifugal casting machine (Caster VC500, The Daiei Dental MFG. Co. Ltd. Osaka, Japan). A gas-air torch was used to melt the alloy. The mold was bench-cooled to room temperature and then a cast specimen was taken from the mold. The surface of the specimen was cleaned using an ultrasonic cleaner. Three specimens were prepared for each of the Sn- and Ga-added alloys. For the mother alloys, only one composition (No.5, 35%Ag-30%Pd-20%Au-15%Cu) was evaluated to represent this alloy system. This was based on the preliminary test findings, which showed that the alloys without Sn and Ga had relatively poor bonding with an ultra-low fusing ceramic and the bond was similar among the nine different composite. For this alloy, three cast specimens were also prepared. The thermal expansion of each specimen was measured from 50℃ to 550℃ and was recorded on a chart using a thermal dilatometric apparatus (TMA120, Seiko Instruments Inc., Tokyo, Japan). The coefficient of thermal expansion between 50℃ and 500℃ was determined from the recorded chart.

Evaluation of bond with ultra-low fusing ceramic

The evaluation of the bond with an ultra-low fusing ceramic was carried out following ISO 9693 : 1991 "Dental ceramic fused to metal restorative materials"[6]. A plate shape specimen (thickness: 0.5 mm, width: 5 mm, length: 20 mm) as specified in ISO9693 was prepared for each alloy using a dental casting procedure. The materials and casting procedure were the same as those used for the preparation of the specimen for coefficient of thermal expansion. Six cast specimens were prepared for each of the Sn- and Ga-added alloys. For the mother alloys, only one composition (35%Ag-30%Pd-20%Au-15%Cu) was evaluated for the same reason as for the measurement of coefficient of thermal expansion. For this alloy, six cast specimens were also prepared. The surface of each cast specimen was sandblasted (Micro Blaster II A, The Daiei Dental MFG Co. Ltd. Osaka, Japan) with alumina particles (particle size range: 53-63μm).

An ultra-low fusing ceramic (Deguceram Gold, Degussa AG, Germany, Lot No. 01) was applied to one surface of the cast specimen. The bond powder, opaque and dentin ceramics, which were the basic components of this ceramic system, were sequentially applied to the surface of a cast specimen, and fired at 800℃, 780℃ and 785 ℃, respectively, under vacuum (50 hPa) following the manufacturer's instructions. A ceramic-fused alloy specimen was bent on a 10 mm stainless rod, with the ceramic located at the opposite side of the contacting area, to a 90° angle of the specimen ends, and then straightened. After this procedure, the surface was examined under a scanner connected to a computer and the area fraction of the retained ceramic in the middle third of the specimen was measured using an area computing system (NIH Image Ver. 1.47, National Institute of Health., Bethesda, Maryland, USA)

Data analysis

The measurements for solidus point, liquidus point and coefficient of thermal expansion were statistically analyzed using two-way ANOVA at the 0.05 level of significance where the two main factors were Pd and Cu contents. This analysis was conducted individually for three alloy systems which were the mother alloys, the Sn-added alloys and the Ga-added alloys. Based on the significant terms of factors obtained from two-way ANOVA, a response function, which describes the iso-value curves of each property, was calculated using an orthogonal polynomial. In addition, the difference in solidus point and liquidus point between the three alloy systems was also analyzed using two-way ANOVA and Tukey's interval. A statistical comparison of the coefficient of thermal expansion between the 35%Ag-30%Pd-20%Au-15%Cu mother alloy (No.5) and Sn- or Ga-added alloys was carried out using one-way ANOVA and Tukey's interval.

For the analyses of the area fraction measurements of the retained ceramic, non-parametric tests were applied because a large number of the measurements reached the upper limit (100.0%) and the normality of the population distribution could not be assumed. The Kruskal-Wallis test and the following Dunnett's multiple comparison test were used to determine which of the Sn- or Ga-added alloys were different from the No.5 mother alloy at the 0.05 level of significance. Furthermore, the Friedman test was used to see if there were a significant difference between Sn-added and Ga-added alloys. A significance level of 0.05 was used throughout this study.

RESULTS

Solidus and Liquidus points

Table 1 shows the mean values and standard deviations for the solidus point and liquidus point for the three alloy systems.

The solidus points ranged from 887℃ to 1142℃ for the mother alloy, from 848℃ to 1077℃ for the Sn-added alloy, and 802℃ to 987℃ for the Ga-added alloy. The two-way ANOVA for the three alloy systems showed slightly different results. For the mother alloy the effects of the two main factors were significant but their interaction was not significant. For the Sn- and Ga-added alloys the effects of all three factors

Table 1 Liquidus points and solidus points of the prepared alloys

(℃)

	Solidus point			Liquidus point		
No.	Mother alloy	Sn-added alloy	Ga-added alloy	Mother alloy	Sn-added alloy	Ga-added alloy
1	952 (3.5)	893 (10.6)	861 (2.1)	1065 (0.7)	1024 (1.4)	1007 (2.1)
2	920 (3.5)	857 (6.4)	802 (3.5)	1008 (0.0)	995 (2.1)	978 (3.5)
3	887 (2.1)	849 (0.0)	803 (9.9)	971 (6.4)	975 (4.2)	931 (53.7)
4	1053 (2.8)	967 (5.7)	945 (7.1)	1145 (7.1)	1071 (4.2)	1009 (1.4)
5	1019 (7.8)	920 (1.4)	885 (8.5)	1097 (7.1)	1015 (9.9)	1013 (5.7)
6	988 (5.7)	848 (10.6)	859 (10.6)	1061 (6.4)	988 (37.5)	1014 (11.3)
7	1142 (0.0)	1077 (8.5)	987 (4.2)	1223 (2.1)	1167 (17.7)	1056 (4.9)
8	1107 (7.1)	1043 (2.1)	971 (10.6)	1179 (4.2)	1116 (0.0)	1037 (10.6)
9	1090 (4.9)	1022 (6.4)	959 (11.3)	1156 (3.5)	1111 (16.3)	1068 (17.0)

Standard deviation in parentheses

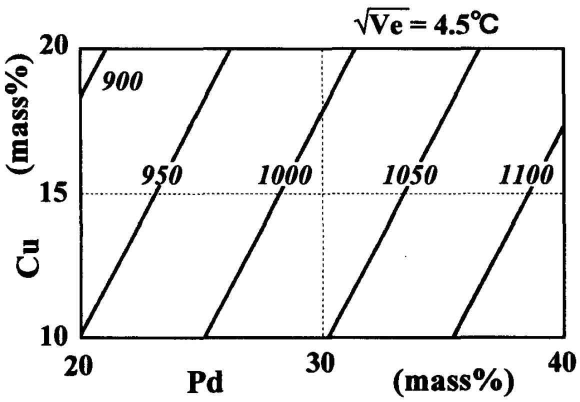


Fig. 2 Iso-solidus curve of the mother alloy.

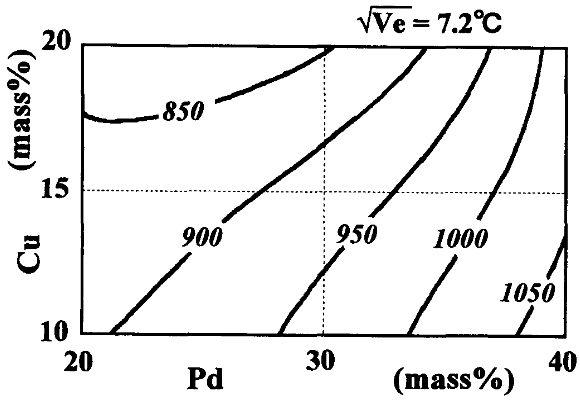


Fig. 3 Iso-solidus curve of the Sn-added alloy.

including the interaction were significant. Figs. 2, 3 and 4 show the iso-solidus point curves obtained from orthogonal polynomials for the three alloy systems. The square root of V seen in each figure of the iso-value curves shows the square root of the mean square of error obtained by the two-way ANOVA. The effects of the Cu and Pd contents on the solidus points were similar among the three alloy systems, the mother alloy, Sn-added alloy and Ga-added alloy. As shown in these figures, the solidus points increased with the increase in Pd content and decreased with the increase in Cu content. The differences in the solidus point among the three alloy systems were analyzed using two-way ANOVA and Tukey's multiple comparison test which showed that the solidus point of the mother alloy was significantly higher than those of the Sn- and Ga-added alloys. Seven Sn-added alloys except Nos.4 and 6 had significantly higher solidus point than the Ga-added alloys at the same Ag-Pd-Au-Cu content.

The liquidus point ranged from 971℃ to 1223℃ for the mother alloy, from 975℃ to 1167℃ for the Sn-added alloy, and 931℃ to 1068℃ for the Ga-added alloy. The two-way ANOVA showed that all three factors including the interaction for the mother alloy, two main factors for the Sn-added alloy and one main factor (Pd con-

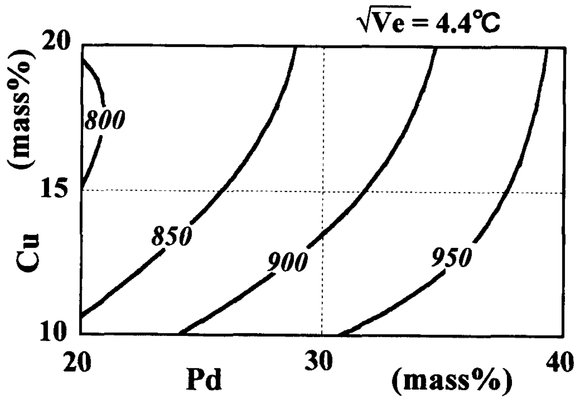


Fig. 4 Iso-solidus curve of the Ga-added alloy.

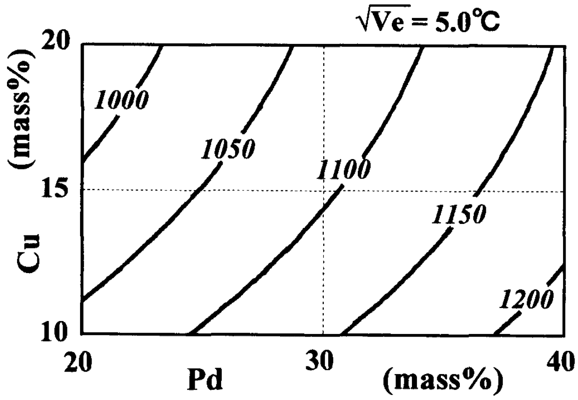


Fig. 5 Iso-liquidus curve of the mother alloy.

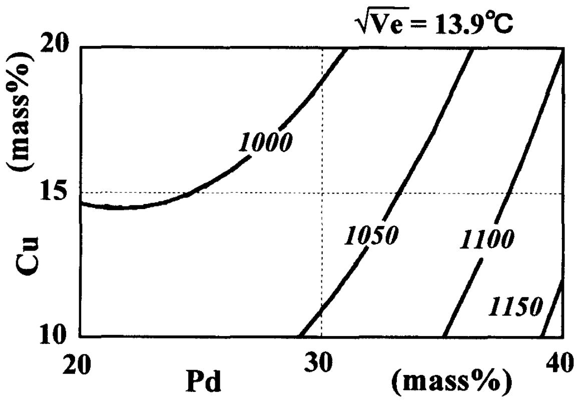


Fig. 6 Iso-liquidus curve of the Sn-added alloy.

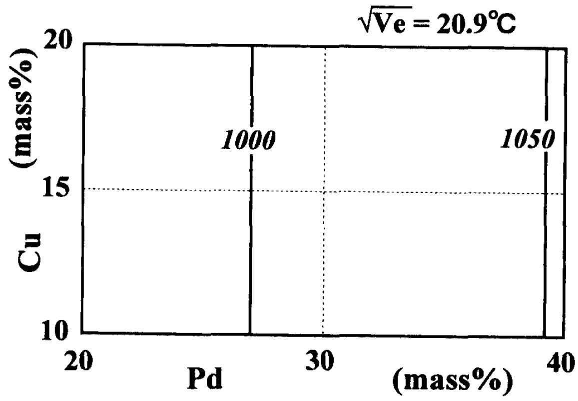


Fig. 7 Iso-liquidus curve of the Ga-added alloy.

tent) for the Ga-added alloy were significant. Figs. 5, 6 and 7 show the iso-liquidus point curves for the three alloys. The effects of Cu and Pd contents on the liquidus point were similar between the mother alloy and Sn-added alloy, and the liquidus points increased with the increase in Pd content and decreased with the increase in Cu content (Figs. 5 and 6). The liquidus point of the Ga-added alloy increased with the increase in Pd content, but the Cu content had no significant effect. The difference in the liquidus points among the three alloy systems were analyzed using two-way ANOVA and Tukey's mutiple comparison test, which showed that the liquidus point of the mother alloy was significantly higher than those of the Sn- and Ga-added alloys. The three Sn-added alloys, that were Nos.4, 7, and 8 alloys, had significantly higher liquidus point than their respective Ga-added alloys with similar Ag, Pd, Au and Cu contents.

Coefficient of thermal expansion

The coefficient of thermal expansion ranged from 14.6 to 17.1×10^{-6}/℃ for the Sn-added alloy and from 14.6 to 16.8×10^{-6}/℃ for Ga-added alloy as shown in Table 2. The two-way ANOVA showed that the effects of the two main factors and their interaction were significant for the Sn-added alloy and the two main factors were significant for the Ga-added alloy. Figs. 8 and 9 show the iso-coefficient curves obtained from orthogonal polynomials for the two alloy systems, the Sn- and Ga-added alloys. The effect of Pd content on the coefficient of thermal expansion was similar between the Sn- and Ga-added alloys and the coefficient decreased as the Pd content increased. The effect of Cu content was slightly different between the two alloy systems. For the Sn-added alloy, the coefficient increased as the Cu content increased at high Pd content (more than 30%). However, the coefficient of the Ga-added alloy increased at the highest content of Cu regardless of the Pd content. The coefficient of the No.5 mother alloy was 15.1×10^{-6}/℃ which was significantly lower than those of the No.5 Sn- and Ga-added alloys, although the differences between the mother alloy and the Sn- and Ga-added alloys were 0.5 and 0.4×10^{-6}/℃, respectively. No significant differ-

Table 2 Coefficient of thermal expansion of prepared alloys

(×10^{-6}/℃)

No.	Sn-added alloy	Ga-added alloy
1	17.1 (0.27)	16.8 (0.07)
2	17.0 (0.15)	16.7 (0.12)
3	17.0 (0.73)	16.8 (0.09)
4	15.5 (0.02)	15.7 (0.05)
5	15.6 (0.06)	15.5 (0.14)
6	15.9 (0.74)	15.8 (0.06)
7	14.6 (0.04)	14.6 (0.04)
8	14.8 (0.12)	14.6 (0.06)
9	15.0 (0.14)	14.9 (0.05)
Mother alloy No.5: 15.1 (0.10)		

Standard deviation in parentheses

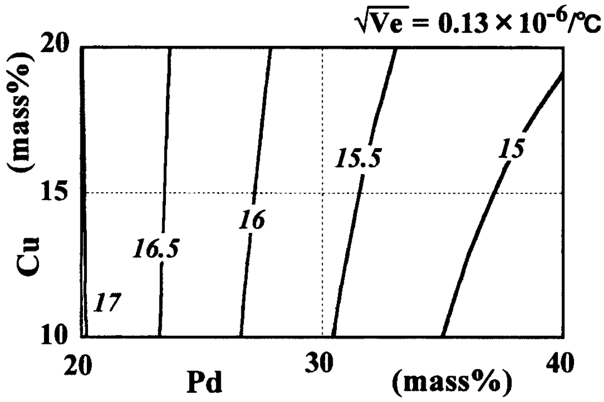


Fig. 8 Iso-coefficient of thermal expansion curve of the Sn-added alloy.

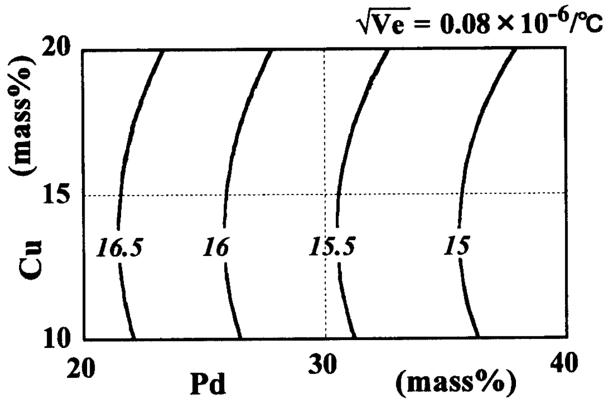


Fig. 9 Iso-coefficient of thermal expansion curve of the Ga-added alloy.

Table 3 Area of retained ceramic

(%)

No.	Sn-added alloy	Ga-added alloy
1	92.1 (17.1)	99.9 (0.1)
2	96.1 (9.6)	100.0 (0.0)
3	99.8 (0.4)	100.0 (0.0)
4	100.0 (0.0)	100.0 (0.0)
5	99.3 (1.7)	99.9 (0.1)
6	99.6 (0.5)	100.0 (0.0)
7	99.8 (0.4)	100.0 (0.0)
8	98.3 (3.8)	100.0 (0.0)
9	99.4 (1.5)	100.0 (0.0)
Mother alloy No.5: 82.3 (20.5)		

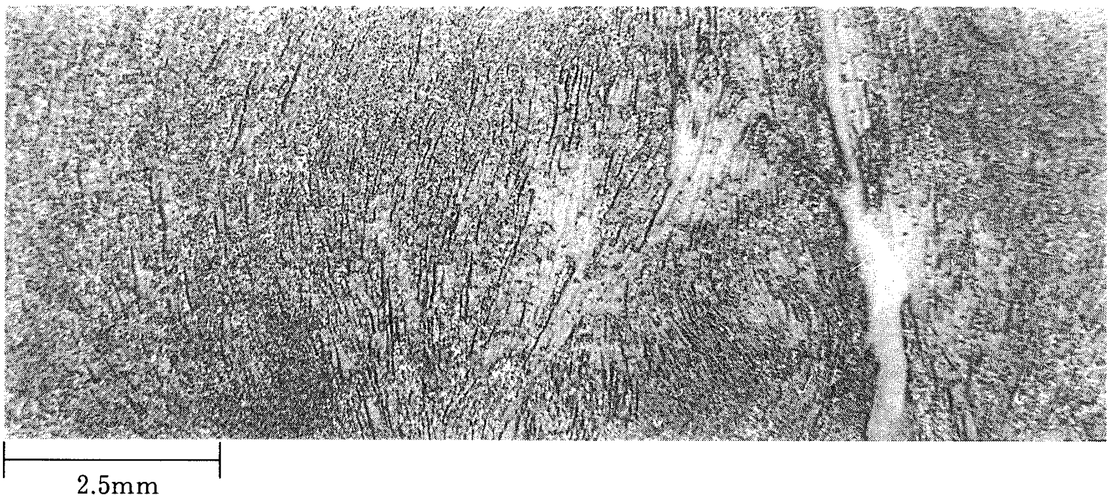
Standard deviation in parenthesis

ence in the coefficient was found between the Sn- and Ga-added alloys with similar Ag, Pd, Au and Cu contents.

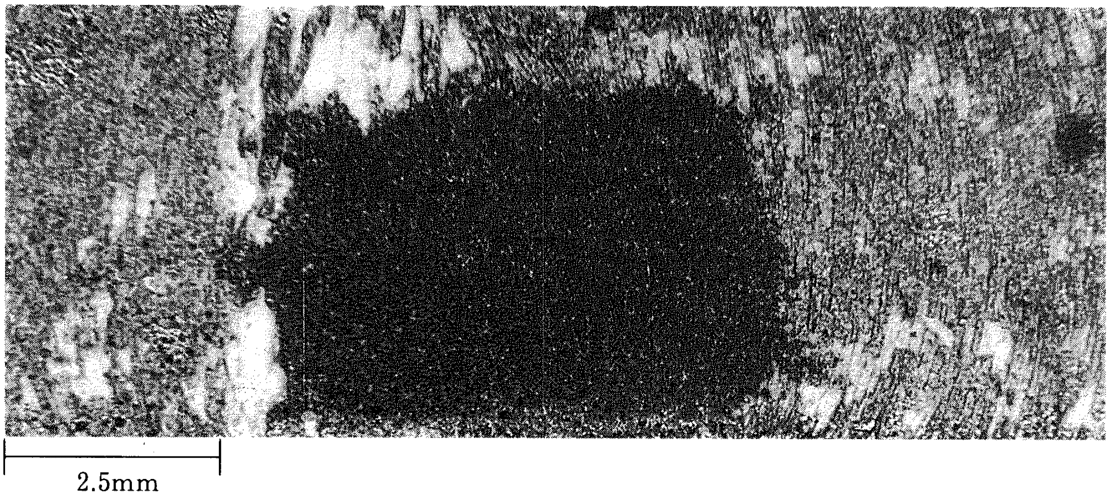
Bond with ultra-low fusing ceramic - Area fraction of the retained ceramic after bending

Table 3 shows the mean values and standard deviations for the area fraction of the retained ceramic after bending. As shown in Table 3, all Sn- and Ga-added alloys showed high area fraction of the retained ceramic (92.1-100.0%), and one of the nine Sn-added alloys and seven of the nine Ga-added alloys had 100.0% retained ceramic with 0% standard deviation. However, the No.5 mother alloy showed a relatively low area fraction (82.3%) with a high standard deviation (20.5%). The surfaces of the specimens with retained ceramic after bending are shown in Fig. 10.

The Kruskal-Wallis test showed that the difference in the area fraction was highly significant among the 19 tested alloys. Statistical differences between the No.5 mother alloy (control) and the Sn- or Ga-added alloys were analyzed using Dunnett's multiple comparison test which showed that the area fraction of the No.5 mother



Ga-added alloys (100% retained ceramic at the middle third of the specimen)



No.5 Mother alloy (45.4% retained ceramic at the middle third of the specimen)

Fig. 10 The surface of the specimens with retained ceramic after bending.

alloy was significantly lower than those of the No.5 Sn- and Ga-added alloys. In addition Nos.4, 7 and 9 Sn-added alloys and Nos.2, 3, 4, 6, 7, 8 and 9 Ga-added alloys had significantly higher area fraction than the No.5 mother alloy. The Friedman test showed that there was a significant difference between the Sn-added and Ga-added alloys.

DISCUSSION

The solidus point of an alloy for metal-ceramic restorations has to be higher than the firing temperature of the ceramics. According to the manufacturer's instruction, the firing temperature of the ultra-low fusing ceramic (Deguceram Gold) is a maximum

800℃. The solidus point of the tested alloys ranged from 887℃ to 1142℃ for the mother alloy, from 848℃ to 1077℃ for the Sn-added alloy, and from 802℃ to 987℃ for the Ga-added alloy. Although the solidus point of all tested alloys was higher than the firing temperature of the ultra-low fusing ceramic, those of the No.2 and No.3 Ga-added alloys were 802℃ and 803℃, respectively. This indicates that the No.2 and No.3 Ga-added alloys may not be applicable for the tested ultra-low fusing ceramic. The solidus point of the other Sn- and Ga-added alloys was at least 48℃ higher than the firing temperature and thus these alloys may withstand the firing of the ultra-low fusing ceramic. Several ultra-low fusing ceramics are now commercially available. Most of these products are fired below 800℃, but one product is fired at 890℃. Therefore, for this product the alloy should have a higher solidus point than 890℃. Among the Sn- and Ga-added alloys, Nos.4, 7, 8 and 9 alloys appear suitable for this product.

The solidus point increased with the increase in Pd content and decreased with the increase in Cu content. The effect of Cu was similar to the findings of Nakamura *et al.*[7] In their study, Pd content was fixed at 20%, and the contents of Au and Cu were varied. Their findings showed that the solidus point of the Ag-Pd-Au-Cu alloy decreased with the increase in Cu content in the range of 5-20% and the 12-20% Au content showed almost no effect. This suggests that the solidus point of the Ag-Pd-Au-Cu quaternary alloy system is mainly dependent upon the composition of the Ag-Pd-Cu ternary system. An Ag-Pd-Cu ternary alloy diagram[8] shows a similar effect of Pd and Cu on the solidus point as observed for the Ag-Pd-Au-Cu quaternary alloy prepared in the present study. Therefore, it is very probable that the solidus point of the Ag-Pd-Au-Cu quaternary alloy is basically determined by the relative content of Ag, Pd and Cu. In addition to the effects of the Pd and Cu contents on solidus point, those on point may also be basically dependent on the Ag-Pd-Cu ternary alloy system. A further study on the microstructure of these alloys is necessary to clarify the relation between the Ag-Pd-Au-Cu quaternary alloy and the Ag-Pd-Cu ternary alloy systems.

The liquidus point of an alloy is one of the essential properties to choose a melting procedure. A gas-air torch could not be used to melt most of the alloys for conventional ceramic application due to their high liquidus point. This is basically related to the high solidus point of the alloy for the firing of conventional dental ceramic at approximately 1000℃ or above. Ultra-low fusing ceramics, however, have allowed the use of a gas-air torch to melt the alloys since the alloys do not need to have high solidus point as required for conventional dental ceramics. The highest liquidus point among all prepared alloys was 1223℃ which may not be applicable for a gas-air torch. This was obtained from the No.7 mother alloy. Among the Sn- and Ga-added alloy systems the highest liquidus point was 1153℃ which was obtained from No.7 Sn-added alloy. This alloy appears somewhat difficult to melt using a gas-air torch, but actually could be melted. All Sn- and Ga-added alloys were melted to prepare a thin cast specimen to apply the ultra-low ceramic using a gas-air torch. No difficulty was experienced with melting or casting any of these alloys including the No. 7 Sn-added alloy. The cast specimens did not have any defects under visual inspection. Therefore, a gas-air torch can be used to melt and cast the alloy with the liquidus point as high as 1153℃.

The coefficient of thermal expansion was measured from 50℃ to 500℃ simulating the glass temperature range (450-535℃) of ultra-low fusing ceramics reported by Ohnuki[9]. The coefficient of thermal expansion of the prepared alloys ranged from 14.6 to 17.0×10^{-6}/℃ for the Sn-added alloy and from 14.6 to 16.8×10^{-6}/℃ for Ga-added alloy. It has been claimed that the coefficient of thermal expansion of a metal-ceramic alloy should be slightly higher than that of a ceramic to induce compressive stress in the ceramic resulting in its reinforcement[10-11]. According to the information disclosed by the manufacturers, the coefficient of ultra-low ceramics is 15.8×10^{-6}/℃ for Duceragold and Duceram Gold, and 15.3-15.9×10^{-6}/℃ for Carrara. In comparison with these values, the coefficients of Nos.7, 8 and 9 Sn- and Ga-added alloys was 15.2×10^{-6}/℃ or less and may not be suitable for use with ultra-low fusing ceramics. The effect of Pd content on the coefficient was similar between the Sn- and Ga-added alloy systems and the coefficient decreased with the increase in Pd content, which may be due to the low coefficient of Pd. For both Sn- and Ga-added alloys, No.1 alloy, with the highest Ag content, showed the highest coefficient among the nine alloys, Nos.1-9. This suggests that Ag, which has the highest coefficient among the four basic components of the prepared alloys, is responsible for the high coefficient of the alloys. The addition of Sn and Ga increased the coefficient of the alloys. This may also be due to their high coefficient. The effect of Cu was slightly different between Sn- and Ga-added alloys. This finding indicates that Sn and Ga have different effects on the coefficient, which may be related to the difference between the produced phases in these two systems. A microstructural study is now being carried out to provide an explanation for this difference.

The area fraction of the retained ceramic was 92-100% for the Sn-added alloys and 99-100% for the Ga-added alloys. In ISO 9693 : 1991 "Dental ceramic fused to metal restorative materials"[6], an area fraction of the retained ceramic greater than 50% is required. The findings obtained from these two alloy systems indicate that both alloy systems exceed the required value and produce a very good bond with the tested ultra-low fusing ceramic. Although the No.5 mother alloy showed a relatively high area fraction (82% in average), the bond was not stable as indicated by the high standard deviation (20.5%). One of the six specimens failed to pass the ISO requirement. In the preliminary test, the No.1 mother alloy (50%Ag-20%Pd-20%Au-10%Cu) was examined and the result was poorer than that from the No.5 mother alloy. This was the reason why Sn or Ga were added to the mother alloy. Shiozawa *et al.*[5] measured the bond strength between an ultra-low-fusing ceramic (Degceram Gold) and a silver-based alloy containing 12% Au, 20% Pd and 20% Cu. They found that the bond strength between these products was higher than that between the same ceramic and a gold-based alloy which was specifically designed for this ceramic. Since they used a different test method and a commercially available alloy containing unknown additives, a direct comparison with the present finding appears difficult. The findings of their study and the present study, however, show that the Ag-Pd-Au-Cu quaternary alloy can be used with ultra-low ceramics.

The effect of the Pd and Cu contents on the area fraction of the retained ceramic was not clear for both the Sn- and Ga-added alloys. This may be due to the high area fraction of all alloys and the different deviations among them. It appears that the lowest Pd and Cu contents result in lower areas fraction, which may be related to the surface texture of this alloy. In contrast to the effects of Pd and Cu, those of Sn and Ga were clearly observed. The area fraction of the No.5 Sn- and Ga-added alloys was significantly higher than that of the No.5 mother alloy, suggesting that the addition of these metals to the Ag-Pd-Au-Cu quaternary alloy appears essential for a good bond with ultra-low fusing ceramics. The Friedman test showed that the Ga-added alloys had significantly more retained ceramics than the Sn-alloys. Two factors are considered necessary for a good quality bond between an alloy and a ceramic. One is the matching of coefficients of thermal expansion between the alloy and the ceramic and the other is the wetting of the fused ceramic to the alloy surface[11]. The result of the coefficient measurements showed that no significant difference was found between Sn- and Ga-added alloys with the same Ag, Pd, Au and Cu contents. Therefore, the wetting of the fused ceramic may be higher for the Ga-added alloy than for the Sn-added alloy. A further study of the surface texture of the alloy may clarify not only the effects of Pd and Cu but also those of Sn and Ga.

Although the area fraction measurement showed that all Sn- and Ga-added alloys had a good bond with the tested ultra-low fusing ceramic, some of the prepared alloys are not suitable for ultra-low fusing ceramics due to their low solidus point or low coefficient of thermal expansion as mentioned above. Based on the finding from the discussions of the solidus point and coefficient of thermal expansion, the following 10 alloys can be chosen as metal-ceramic alloys for the ultra-low ceramic used in this study.

No.1 Sn- and Ga-added alloys
No.2 Sn-added alloy
No.3 Sn-added alloy
No.4 Sn- and Ga-added alloys
No.5 Sn- and Ga-added alloys
No.6 Sn- and Ga-added alloys

These choices are only based on the properties related to the bond with the tested ultra-low fusing ceramic. Therefore, the mechanical properties of these alloys should be evaluated to clarify the most suitable composites not only for the application of the ultra-low ceramics but also for the multiple dental applications.

CONCLUSIONS

Ag-Pd-Au-Cu quaternary alloys consisting of 30-50%Ag, 20-40%Pd, 10-20%Cu and 20%Au (mother alloys) were prepared. Then 5% Sn or 5% Ga was added to the mother alloy compositions, and another two alloy systems (Sn-added alloys and Ga-added alloys) were also prepared. The bond between the prepared alloys and an ultra-low fusing ceramic, as well as their physical properties such as solidus point, liquidus point and the coefficient of thermal expansion were evaluated.

The solidus and liquidus points of the prepared alloys ranged from 802℃ to 1142℃ and from 931℃ to 1223℃, respectively. The solidus points of all three alloy systems increased with the increase in Pd content and decreased with the increase in Cu content. The effects of Pd and Cu contents on the liquidus point were similar to those on the solidus point. The coefficient of thermal expansion ranged from 14.6 to 17.1×10^{-6}/℃ for the Sn- and Ga-added alloys. The coefficient decreased as the Pd content increased for both the Sn- and Ga-added alloys. For the Sn-added alloy, the coefficient increased as the Cu content increased at high Pd content, whereas the coefficient of the Ga-added alloy increased at the highest content of Cu regardless of the Pd content. All the Sn- and Ga-added alloys showed high areas fraction of the retained ceramic (92.1-100%), while the mother alloy showed a relatively low area fraction (82.3%) with a high standard deviation (20.5%).

Based on the evaluated properties, six Sn-added alloys and four Ga-added alloys of the 18 prepared alloys were suitable for use with the tested ultra-low fusing ceramic.

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