Mechanism of Distortion of Precious Alloy Restoration at High Temperatures

(Part 2) Effect of Addition of Fe, In and Sn on the Deflection at High Temperatures

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Iron, indium and/or tin were added to two mother alloys, 90Au-10Pd and 80Au-20Pt, and 10 kinds of alloys were prepared from each mother alloy. The total amount of the additional elements was 0.75 wt%. The deflection at high temperatures (the final deflection after the specimen was heated until 1050°C) and the deflection-beginning temperature (the temperature at which 20 μ m deflection occurred) were measured, and the effect of the additional elements on these two properties was examined.

The deflection decreased by addition of Fe, In and/or Sn in both alloy system. The deflection-beginning temperature increased by addition of the elements. These results showed that the mechanical properties at high temperatures were improved by addition of Fe, In and/or Sn. The deflection at high temperatures and the deflection-beginning temperature were negatively correlated. Indium appears to increase the deflection in both alloy systems.

Key words: Deflection, Additional elements, PFM alloys

INTRODUCTION

The distortion of the cast core during the firing process is sometimes caused by the weight of the cast itself, especially at high temperatures¹⁻⁵). This phenomenon, called sag, was measured for the Au-Pt-Pd alloy system in the previous study⁶), and the sag behavior was found to be a good index to evaluate the alloys for porcelain fusing. In the previous study, nine kinds of Au-Pt-Pd alloys were prepared and the deflection and the deflection-beginning temperature were determined.

A small amount of some metals are added to commercial gold alloys for porcelain fusing to increase the mechanical and/or bonding strength. Iron, indium and tin are mainly used as the additional elements in gold alloys for porcelain fusing. The effect of these elements on the bonding strength⁷) and the thermal expansion coefficients⁸) was examined in detail. The effect of these elements on the deformation of a casting core was examined by the measurement of the thermal expansion hysteresis⁹). It was concluded that an increase of indium content or decrease of tin content increased the thermal expansion hysteresis and that iron was not effective for the hysteresis. A large thermal expansion hysteresis results in a large deformation of the casting.

It is interesting to examine the effect of addition of these elements on the sag behavior. Among nine Au-Pt-Pd alloys used in the previous study, two alloys, 90Au-10Pd alloy and 80Au-20Pt alloy, are binary. The other seven alloys are ternary, and they have inter-

mediate compositions between the two binary compositions. To examine the effect of the additional elements on the deflection at high temperatures, it would be better to add these elements to the binary alloys rather than to the ternary alloys. Fortunately, the 90Au-10Pd alloy showed the minimum deflection at high temperatures, and the 80Au-20Pt alloy showed the maximum one. In this study, these two alloys were selected as the mother alloys, and iron, indium and/or tin were added to these two binary alloys. The sag behavior was examined, and the effect of Fe, In and Sn on the deflection at high temperatures and the deflection-beginning temperature were observed.

MATERIALS AND METHODS

Two kinds of alloys, 90Au-10Pd and 80Au-20Pt, were used as the mother alloys. Iron, indium and/or tin were added to each mother alloy, and 10 kinds of alloys were prepared as shown in Fig. 1. The total amount of additional elements was 0.75%. Each mother alloy was rolled to about 0.3 mm thickness and was divided into 10 parts. Powdered iron, indium and/or tin were weighed and they were wrapped by the rolled mother alloy. They were forged and melted in fused quartz tube by induction furnace in argon gas atmosphere. After melting, each alloy was kept at 1350°C for 20 minutes for homogenization and was quenched in water. Each alloy was rolled and cut into small pieces for the convenience of casting. The specimens for the measurement of the deflection were cast by the same method as described in Part 1. The size of the specimens was 32 mm × 5 mm × 0.5 mm. They were heated at 1050°C for 10 minutes for homogenization. The same instrument was used for the deflection measurement as described in Part 1. The method to determine the deflection-beginning temperature was changed in this study, because some chart papers that showed very small deflection made it difficult to determine the linear portion for extrapolation. Instead the temperature at which the deflection became 20 μ m was defined as the deflection-beginning temperature.

Figure 1 Composition arrangement of additional elements. Compositions of the mother alloys are 90Au-10Pd and 80Au-20Pt.

RESULTS

The results of the deflection at high temperatures and the deflection-beginning temperature are shown in Table 1. The mean values are plotted in Fig. 2 (a) and (b). The

Table 1 The Deflection and the Deflection-Beginning Temperature

Alloy No.	Additional Elements (Wt%)			90Au-10Pd Alloy System				80Au-20Pt Alloy System			
	In	Sn	Fe	Deflection (μm)		Temperature ($^{\circ}\text{C}$)		Deflection (μm)		Temperature ($^{\circ}\text{C}$)	
1	0	0	0.75	184	175	809	823	540	560	715	674
2	0.25	0	0.50	191	232	824	813	630	592	733	717
3	0	0.25	0.50	134	196	903	833	549	542	713	726
4	0.50	0	0.25	152	281	876	829	548	575	794	760
5	0.25	0.25	0.25	204	234	824	834	549	600	675	679
6	0	0.50	0.25	140	180	894	815	524	534	699	735
7	0.75	0	0	220	262	812	778	600	531	688	712
8	0.50	0.25	0	178	188	859	877	452	521	763	755
9	0.25	0.50	0	144	208	821	819	430	448	798	807
10	0	0.75	0	168	209	824	817	508	580	755	729

Figure 2 Concentration dependence.

(a) Deflection at high temperatures

(b) Deflection-beginning temperature

90Au-10Pd alloy system showed lower deflection than the 80Au-20Pt alloy system. On the other hand, the deflection-beginning temperature of the 90Au-10Pd alloy system was higher than that of the 80Au-20Pt alloy system. When the data were plotted in the order of the alloy number shown in Fig. 1, they could be grouped by iron concentration. In each group, the effect of the contents of additional elements was very complex in both (a) and (b). However, both alloys, 90Au-10Pd and 80Au-20Pt, showed the same concentration dependence in both alloy systems. The alloy that deflected larger showed the lower deflection-beginning temperature. The values of the mother alloys, which were redefined from the chart paper according to the new method described in the previous section, are also shown in the same figure. The deflection at high temperatures became smaller and the deflection-beginning temperature higher by addition of the elements in both alloy systems.

To understand the effect of the additional elements, equi-deflection contours and equi-deflection-beginning temperature contours were examined (Figs. 3 and 4). In the 90Au-10Pd alloy system, the effect of indium content appeared to be strong. The mean maximum value, 241 μm , was obtained in 0.75In vertex (No. 7). The minimum value was observed in two area, 0%In and 0%Fe sides of the triangle. The 80Au-20Pt alloy system showed different contour patterns. Both maximum and minimum values were obtained in the alloys that contain 0.25% indium. Iron appeared more effective than indium in this case.

The equi-deflection-beginning temperature contours of both alloy systems were very complex. The 90Au-10Pd alloy system had two areas of the maximum temperature. The 80Au-20Pt alloy system had two areas of the minimum temperature. No. 7 alloy, 0.75In, showed minimum or very low deflection -beginning temperature.

In both alloy systems, the relationship between the deflection and the deflection-beginning temperature was examined (Fig. 5). Both alloy systems showed a negative linear correlation. This means that the alloy that showed the larger deflection began to deflect

Figure 3 Equi-deflection contours (μm) drawn on the composition arrangement chart.

(a) 90Au-10Pd alloy system

(b) 80Au-20Pt alloy system

Figure 4 Equi-deflection-beginning temperature contours (°C) drawn on the composition arrangement chart.

(a) 90Au-10Pd alloy system (b) 80Au-20Pt alloy system

Figure 5 The relationship between the deflection-beginning temperature (x) and the deflection (y).

Regression line: $y = 1127.04 - 0.801x$ (80Au-20Pt alloy system),
 $y = 830.09 - 0.762x$ (90Au-10Pd alloy system)
Correlation coefficient: -0.616 (80Au-20Pt alloy system),
 -0.615 (90Au-10Pd alloy system)

at lower temperature. In 90Au-10Pd alloy system, the distribution ranges of both the deflection and the deflection-beginning temperature were smaller than those of the 80Au-20Pt alloy system.

DISCUSSION

The method to determine the deflection-beginning temperature was changed in this study. In the previous study, the linear portion of the deflection curve was extrapolated to its zero point, and the temperature corresponding to the extrapolated point was defined as the deflection-beginning temperature. The final value of the deflection curve on every chart paper ranged from 264 to 664 μm , so it was easy to find the linear portion for extrapolation to the zero point. In this case, the 90Au-10Pd alloy system showed a maximum value of 260 μm , so it was difficult to find a linear portion for extrapolation. Further, when the sensitivity of the detector amplifier was changed, the deflection-beginning temperature varied, indicating that the temperature can not be reliably determined. Therefore, another method had to be devised. The temperatures at which 10, 20, 30 and 40 μm deflections occurred on the recorded chart papers were selected, and the usefulness and the reliability of the values were compared. The deflection of 10 μm was too small to accurately obtain the temperature in some chart papers, and 40 μm was too large for the chart papers that recorded small deflection. The temperature at which 20 μm deflection was observed was the most reliable. Thus this temperature was defined as the deflection-beginning temperature in this study, and the relation between the two definitions was examined. The corresponding values are plotted in Fig. 6. The correlation coefficient was 0.899, indicating that the tendency of the concentration dependence of the deflection-beginning temperature and the arrangement of the equi-deflection-beginning temperature contours discussed in the previous paper are unchangeable even if the values are replaced by those of the new definition.

The equi-deflection contours of both alloy systems show that the effect of the additional alloys is very complex. One of the ways to see the effect of each additional element is the one way analysis of variance in which the number of subjects per group varies. For example, No. 1 alloy contains 0.75% Fe, Nos. 2 and 3: 0.50% Fe, Nos. 4, 5 and 6: 0.25%,

Figure 6 The relationship between the two methods of defining the deflection-beginning temperature.

x: the temperature at which 20 μm deflection occurs.

y: the deflection derived by the extrapolation.

and the rest contains no Fe. If Fe content is used as the factor of the one way analysis of variance, the effect of Fe content can be evaluated. In this method, if the data are grouped according to Fe content, the effect of other elements is averaged. In the 80Au-20Pt alloy system, the effect of Sn content became effective with 95% confidence. Other elements were not effective. In the 90Au-10Pd alloy system, no element was effective. In case of the deflection-beginning temperature, no element was effective in either system. Though the statistical analysis showed the ineffectiveness of the additional elements, the deflection ranged from 430 to 630 μm , for example, in the 80Au-20Pt alloy system. This means the combined effect of the additional elements is more important, than the effect of individual elements.

The values of the mother alloys due to the new definition are shown in both Figs. 2 and 5. The additional elements decreased the deflection and increased the deflection-beginning temperature. This means that the additional elements decreased the possibility of a deformation of the castings during the firing procedure.

Kojima¹⁰⁾ studied the effect of Fe, In and Sn on the deflection at high temperatures by use of 85Au-5Pt-10Pd mother alloy. The result is shown in Fig. 7. The total amount of the additional elements was 1 wt%, compared to 0.75 wt% in this study, but, there are some characteristic features to be noted. The composition of his mother alloy corresponds to that of No. 6 alloy in the previous study. The deflection at high temperatures in the previous study was 271 μm , and his result was 263 μm . Though the two experimental conditions were slightly different, almost equal values were obtained. By addition of Fe, In and/or Sn, the deflection decreased, and its values were distributed from 115 to 245 μm , mostly being less than 180 μm . The deflection of the 90Au-10Pd alloy in the previous study was 268 μm , and it decreased between 140 to 262 μm by addition of Fe, In and/or Sn (Table 1). The effect of the additional elements in the ternary alloy

Figure 7 Equi-deflection contours (μm) drawn on the composition arrangement chart (ref. 10).
Total of Fe, In and Sn is 1.0%. Composition of mother alloy is 85Au-5Pt-10Pd.

system may be larger than that of the binary alloy system. The next point to be noted is that the arrangement of the equi-deflection contours is very different, not the mixture of the arrangements of 80Au-20Pt alloy and 90Au-10Pd alloy contours. Kojima¹⁰⁾ found that the deflection decreased toward the vertex of Fe 1%, and increased toward In 1% and Sn 1% vertexes. There are two maximum areas, contrary to the present result. Only common finding is that indium decreases the deflection to some extent, sometimes to the minimum value. The alloys that contain a large amount of indium show high values of the deflection. To further clarify the effect of the additional elements, it is necessary to examine the interaction between the components of the mother alloys and the additional elements, for example, solubility of the added elements, and precipitation of the phases. The effect of the elements on the mechanical properties is also important to understand the present results. The relation between the deflection and another properties would be discussed in the future paper.

CONCLUSION

Two alloys, 90Au-10Pd and 80Au-20Pt, were used as the mother alloys, and iron, indium and/or tin were added to these alloys. The total amount of the additional elements was 0.75 wt%. The deflection and the deflection-beginning temperature were measured.

The following results were obtained.

1. The deflection decreased by addition of Fe, In and/or Sn in both alloy systems. The amount of decrease was from 27 to 108 μm in the 90Au-10Pd alloy system, and from 37 to 209 μm in the 80Au-20Pt alloy system.
2. The deflection-beginning temperature increased by addition of Fe, In and/or Sn in both alloy systems. The amount of increase was from 0 to 72°C in the 90Au-10Pd alloy system, and from 67 to 200°C in the 80Au-20Pt alloy system.
3. Both results showed that the mechanical properties at high temperatures were improved by addition of Fe, In and/or Sn.
4. The deflection at high temperatures and the deflection-beginning temperature were negatively correlated. The alloy that showed larger deflection began to deflect at lower temperature.
5. Indium appears to increase the deflection in both alloy systems.

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による上向き切削・研削および下向き切削・研削の仕上面に及ぼす影響を調べた。本研究から次の結論が得られた。

1) 切削工具（カーバイドバー7664）によるマイクロフィル型コンポジットレジンの切削仕上面は従来ファイラー型コンポジットレジンに比べて著しく改善された。これは分散相ファイラーの粒径とそれに基くコンポジットレジンの不均質性によって切削抵抗とその変動が影響されることを示唆する。

2) 研削工具（ダイヤモンド工具 F 201 R）による研

削仕上面はカーバイドバーによるそれよりも改善されると共に、コンポジットレジンの差異が減少した。これは負のすくい角の増加によって切込みが減少したことに起因すると考えられる。

3) 両工具において、上向き切削・研削の仕上面の方が下向き切削・研削のそれよりも良くなった。これは接線切削・研削抵抗が上向き切削・研削では切削・研削予定面の上方に働き、下向き切削・研削では逆に下方に働くことから説明できる。

光線重合レジンの細胞毒性 (in vitro)

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光線重合レジン5製品, すなわち, 可視光線重合タイプ4製品, 紫外線重合タイプ1製品の硬化試料が HeLa S3 細胞に対しておよぼす影響を調べるために, in vitro 環境下で細胞コロニー形成法を駆使して実験を行った。2週間の単位浸漬期間を合計6週間にわたって, 従来から行っている口腔内の動的環境のシミュレーションを目ざした旋回投入浸漬を続け, 各時期の浸漬液を実験に用いた。テストした各材料で初期に浸漬液の濃度があがると中等度から強い細胞毒性を示した。しかし, その後は

細胞毒性は急速に消失し去った。この結果は同時にテストした従来型のクリアフィル F と似ていたし, 以前にテストした MFR タイプなどを含む従来型製品とも軌を一にするものであった。以上の実験結果はテストした2種類の光線重合レジンが細胞に対して従来型製品ときわめてよく似た影響を及ぼすことを示している。

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貴金属修復物の高温における変形機構

(第2報) 高温たわみに対する鉄, インジウム, スズ添加の影響

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鉄, インジウムおよび/あるいは, スズを2種の母合金, 90 Au-10 Pd, 80 Au-20 Pt, に添加し, 各母合金につき10種の合金を試作した。添加元素の合計は, 0.75%であった。高温たわみ(試験片を1050℃まで加熱した後の最終たわみ量)および, 変形開始温度(20 μm のたわみを生じる温度)を測定し, これらの性質に対する添加元素の影響を調べた。

鉄, インジウム, スズの添加により, いずれの合金系においても, 高温たわみは減少し, 変形開始温度は増大した。これらの結果は, 鉄, インジウム, スズの添加により, 高温における機械的性質が改善された事を証明している。高温たわみと変形開始温度の間には, 負の相関関係がみられた。インジウムはいずれの合金系においても, 高温たわみを増大させる様である。