Temperature Dependence of Thermal Expansion Coefficient for Palladium-based Binary Alloy

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Temperature dependencies of thermal expansion coefficients for the alloys of Pd-Ag, Pd-Cu and Pd-Co binary systems were measured at temperatures up to 900°C, with heating and cooling rates of 5°C/min. The coefficient of thermal expansion of alloys with no transformation in the temperature range of interest in porcelain firing was well approximated by a linear equation of temperature. The constants in the equation were shown as a function of the weight for the added element. Thermal expansion of the palladium-based alloy with no transformation was well estimated at any temperature range and at any composition by using the constants represented here.

The coefficients of thermal expansion before and after order-disorder transformation and magnetic transformation were measured in Pd-Cu and Pd-Co alloys, respectively. The results suggest that transient and residual stresses in porcelain-fused-to-metal restorations can be effectively controlled by making use of transformation of the alloy.

Key words: Palladium-based alloys, Thermal expansion coefficient, Order-disorder and magnetic transformations

INTRODUCTION

Recently, the use of palladium alloys has increased for ceramic firing. These alloys are based primarily on Pd-Ag, Pd-Cu or Pd-Co systems. These binary systems are illustrated substitutional complete solid solutions.

A difference in the thermal expansion coefficients of porcelain and metal has been recognized as a major parameter in predicting incompatibility of porcelain-fused-to-metal (PFM) restorations. The instantaneous coefficient of thermal expansion for both materials in the glass transition range of porcelain is especially important in determining the residual stress in PFM strips as reported by Asaoka and Tesk

Ordinarily, selected coefficients of thermal expansion for engineering materials are listed at 20°C or are the average value between 20 and 100°C. The alloys used for PFM use the average data from room temperature to 500~700°C. Temperature dependence of thermal expansion has been measured for commercial alloys, Pd-Ag, Pd-Ni and Pd-Co-Ni alloy systems. However, these results only show the average coefficients between the two temperatures which were chosen with no significance.

In general, thermal expansion of pure metals is temperature dependent property, as shown in Table 1. The relationship between composition of the solid solution alloy and its coefficient of thermal expansion has not been discussed. In this study, temperature dependence of the thermal expansion coefficient for a palladium-based binary solid solution alloy was measured. This measurement for thermal expansion of the solid solution alloy may be
useful not only to determine suitable composition of the alloy for PFM restorations but also to consider general empirical rules of temperature dependence of the thermal expansion coefficient for the binary alloy related to the pure metal.

MATERIALS AND METHODS

Experimental methods

Silver, copper and cobalt of over 99.9% purity were alloyed with 99.9% pure palladium in an electric-arc-furnace with high purity argon gas. The palladium-based alloys, with 5 to 50% by weight substitute element, were cast into phosphate-bonded investment by an induction centrifugal casting machine with no flux. The ingots were cut into coupons, 10 mm × 3.0 mm thick, using a slow-speed diamond saw. The alloys were annealed, to eliminate segregation in the casting structures, at 1000°C for 1 h in high purity argon gas and cooled in the furnace (slow cooling). Thermal expansion of each specimen of the as-cast and the annealed alloys was measured by push-rod-dilatometer*. The rates of heating and cooling were 5°C/min over a range from 40 to 900°C. Expansion data of the alloys were corrected by data from platinum measured under the same conditions as each specimen and the temperature dependent recommended data for platinum as shown in Table 1. Instantaneous coefficients of thermal expansion were calculated with temperature intervals 20°C apart. The transformation temperatures for Pd-Cu alloys and Pd-Co alloys were measured by differential thermal analysis (DTA)*. The powder of α-alumina was used as the DTA standard material.

Theoretical analogy of thermal expansion

The instantaneous coefficient of linear thermal expansion, \(a_1\), is defined as

\[ a_1 = \frac{l_2 - l_1}{l_20(T_2 - T_1)} \quad \text{at} \quad T_m = \frac{(T_1 + T_2)}{2} \tag{1} \]

where \(l_20\) is the length at 20°C; and \(l_1\) and \(l_2\) are the length at temperatures \(T_1\) and \(T_2\)°C, respectively. The expansion over a limited temperature range can be approximated by a polynomial.

\[ \frac{l - l_0}{l_0} = a_0 + a_1T + a_2T^2 + a_3T^3 + \cdots \tag{2} \]

where \(l\) is the length at \(T\) °C. From equation (1) and (2),

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* Thermal analysis instrument DT-30, Shimadzu, Kyoto, Japan

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Table 1

Temperature dependence of thermal expansion for pure metals

<table>
<thead>
<tr>
<th>Metals</th>
<th>(a_1) \times 10^{-6}</th>
<th>(a_2) \times 10^{-9}</th>
<th>(a_3) \times 10^{-12}</th>
<th>Temperature range, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>16.733</td>
<td>2.626</td>
<td>0.91</td>
<td>0 – 1000</td>
</tr>
<tr>
<td>Gold</td>
<td>14.103</td>
<td>1.628</td>
<td>1.145</td>
<td>0 – 950</td>
</tr>
<tr>
<td>Platinum</td>
<td>9.122</td>
<td>0.7467</td>
<td>0.4258</td>
<td>20 – 1600</td>
</tr>
<tr>
<td>Palladium</td>
<td>12.10</td>
<td>2.000</td>
<td>0.4859</td>
<td>20 – 900</td>
</tr>
<tr>
<td>Silver</td>
<td>19.494</td>
<td>1.0379</td>
<td>2.375</td>
<td>0 – 900</td>
</tr>
</tbody>
</table>
Thermal Expansion of Pd-Based Binary Alloy

\[ a_1 = a_1 + 2a_2 T_m + a_3 (4T_m^2 - T_1 T_2) + \cdots \]  

(3)

and the coefficient of thermal expansion, \( \alpha \), at \( T_m \) can be represented by

\[ \alpha = \frac{l_{20}}{l} \left( a_1 + 2a_2 T_m + 3a_3 T_m^2 + \cdots \right) \]  

(4)

From these equations it can be shown that

\[ \alpha = \frac{l_{20}}{l} \left( a_1 - a_3 \frac{\Delta T^2}{4} - \cdots \right) \]  

(5)

where \( \Delta T = T_2 - T_1 \). If \( l_{20} \approx l \) and \( \Delta T \to 0 \) then \( \alpha \approx a_1 \). If the expansion can be represented by a quadratic, \( a_3 = 0 \) in equation (5), \( \alpha \) in equation (4) can be used over large temperature intervals.

In the vicinity of the melting point of the metal, thermal expansion is mainly dependent on increased number of vacancies rather than expansion of the crystal lattice. In addition, some metals change volume because of reaction with the atmosphere such as oxidation and gas absorption. The thermal expansion coefficient of the alloy used is less accurate to the term of the third power on temperature when the alloy is under the transition range of the porcelain (upper temperature is \( 600 \sim 700 \)°C). The temperature dependence of thermal expansion can be represented as equation (6) from \( l_{20} = l \) and \( a_3 = 0 \) in equation (4).

\[ \alpha = C_1 + C_2 T \]  

(6)

where \( C_1 \) and \( C_2 \) are \( a_1 \) and \( 2a_2 \), respectively.

The average coefficient of alloy is insufficient to estimate the instantaneous coefficient of its thermal expansion at the transition temperature of porcelain. The coefficient of thermal expansion at any temperature range under \( 600 \)°C can be calculated from equation (6). When we can find the relationship between the constants in equation (6) and amounts of elements added to palladium, the coefficient of thermal expansion for the alloy with any amounts of added element can be calculated at any temperature.

RESULTS

Figure 1 shows the relation between the composition of the annealed Pd-Ag alloys and the constants in equation (6) for the heating process. The constants \( C_1 \) and \( C_2 \) increased with an increase in the silver content. The regression formulae for \( C_1 \) and \( C_2 \) by weight and atomic percents were calculated for the heating and cooling process of the alloys as shown in Table 2. When confidence level of regression coefficients calculated with \( \varepsilon = 0.05 \) in \( t_{n-1} \) \((\varepsilon/2)\), \( C_1 \) and \( C_2 \) for the annealed alloys were within the limits of \( \pm 0.2 \times 10^{-6}/\text{°C} \) and \( \pm 2.5 \times 10^{-10} \), respectively. From these confidence levels, instantaneous coefficient of thermal expansion for the annealed alloys was in error within \( \pm 0.4 \times 10^{-6}/\text{°C} \) at the temperature in 40 to 600°C range. Figure 2 shows the average coefficients of thermal expansion calculated using the regression formulae for the heating process of the annealed alloys. Dotted points show the exact experimental data for the average coefficients. The average coefficient of thermal expansion of the Pd-Ag (Ag<50%) alloy in an arbitrary temperature range under 600°C was accurately estimated by the method proposed here. The constants \( C_1 \) and \( C_2 \) for the as-cast specimens...
Fig. 1 The constants $C_1$ and $C_2$ in equation (6) for the heating process of annealed Pd-Ag alloys.

Table 2 The constants in the formula of temperature dependence of thermal expansion for Pd-Ag alloy as a function of Ag percents

<table>
<thead>
<tr>
<th></th>
<th>Annealed alloy</th>
<th>As-cast alloy</th>
<th>Annealed alloy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heating</td>
<td>Cooling</td>
<td>Heating</td>
</tr>
<tr>
<td>$C_1$</td>
<td>$\times 10^{-6}$</td>
<td>$\times 10^{-10}$</td>
<td>$\times 10^{-6}$</td>
</tr>
<tr>
<td>$C_2$</td>
<td>$\times 10^{-10}$</td>
<td>$\times 10^{-10}$</td>
<td>$\times 10^{-10}$</td>
</tr>
</tbody>
</table>

showed more widely scattered results than these of the annealed alloys because of the homogenizing of the cast structures during heating to high temperature. The $C_2$ was especially remarkable. For the as-cast alloys, confidence levels of regression coefficients of $C_1$ and $C_2$ were $\pm 0.5 \times 10^{-6}/^\circ\text{C}$ and $\pm 16 \times 10^{-10}/^\circ\text{C}$, respectively. The difference in the average
Fig. 2  Average coefficient of thermal expansion in the 40 to 600°C range for the heating process of annealed Pd-Ag alloys. Solid line shows calculated results from equation (6) and $C_1$ and $C_2$ in Table 2. Points are the exact experimental data for the alloys.

thermal expansion coefficients of the annealed and the as-cast alloy was within $0.5 \times 10^{-6}/^\circ\text{C}$ (within 2.5 μm for the initial length of 10 mm).

The Pd-Cu alloy system has composition ranges of order-disorder transformations (PdCu and PdCu$_3$ superlattice). The constants $C_1$ and $C_2$ in equation (6) can, then, be measured only in an alloy which has no transformation. Figure 3 shows the relation of the constants and the weight percents of copper in this alloy system. The calculated results of $C_1$ and $C_2$ as a function of the amounts of added element are shown in Table 3. Confidence levels of regression coefficients of $C_1$ and $C_2$ were within the limits of $\pm 0.3 \times 10^{-6}/^\circ\text{C}$ and $\pm 14 \times 10^{-10}$, respectively.

The Pd-Co alloy system has a magnetic transformation. The equation (6) is, at this point, unsuitable. Figure 4 shows the average coefficient of thermal expansion (40~600°C) for the heating process of Pd-Co binary alloys. The thermal expansion coefficient increased with the increase of cobalt content up to 25%. The temperature of magnetic transformation of alloys with over 30% Co was higher than 600°C. Alloys which had magnetic transformation over 600°C had lower coefficients of thermal expansion than alloys with 25% Co.

**DISCUSSION**

*Coefficient of thermal expansion during transformation*

High strength alloys such as solid solution hardening alloys and age hardening alloys must be developed for PFM restorations because long span PFM restorations are being increasingly used in the dental laboratory. A deeper understanding of thermal expansion
related to transformation is needed for development of new alloy systems for metal-ceramics.

First-order transformation is characterized by a discontinuous change in volume at constant temperature and pressure. In multiphase systems such as alloys, the transition may extend over an appreciable temperature range and, under nonequilibrium conditions, generally begins at higher temperatures on heating than on cooling, with hysteresis as the result.
Second-order transformation is generally characterized by a discontinuous change in the coefficient of thermal expansion at constant temperature and pressure. The instantaneous coefficient of thermal expansion of the alloy for ceramic firing during the transformation causes an interesting problem of residual stress in PFM restorations.

The Pd-Ag alloy system has no transformation. The data as shown in Table 2 are applicable for the relation between composition and the coefficient of thermal expansion.

The Pd-Cu alloy system has superlattices at 37.32 and 64.11% Cu. Figure 5 shows the thermal expansion curves for Pd-45% Cu alloy. Upper curves are the thermal expansion of the as-quenched alloy and lower curves are the annealed alloy with the same composition. Figure 6 shows the results of DTA for the alloy with the same composition. Upper curves are data for the alloy which was measured after solid solution treatment (kept 900°C for 5 min and quenched in water bath). Lower curves are for the alloy annealed at a high temperature (1000°C) and cooled in the furnace (slow cooling). The transformations in this alloy showed typical first-order features. Divergence of the thermal expansion coefficient was observed near 600°C as shown in Fig. 5. It is well known that order-disorder transformation of this alloy is polymorphic (a change in crystal structure without a change in composition). The lattice parameter of the alloy with Pd-41.6% Cu was reported as a = 3.752 Å in the disordered and a = 2.973 Å in the ordered state. From theoretical calculation, this palladium-based alloy expands 0.167% when the order phase (b.c.c.) transforms completely to the disorder phase (f.c.c.). On the contrary, the alloy contracts 0.167% when f.c.c. changes to b.c.c. crystal. DTA data showed an exothermic reaction at 603°C during heating and an endothermic reaction at about 552°C during cooling. The solid-solution-treated alloy also had an endothermic reaction at 372°C. The exothermic reactions are related to the transformation to disorder-phase from order-phase. The endothermic reactions are from disorder-phase to
Fig. 5  Thermal expansion/contraction curves for Pd-45% Cu alloys. Upper curves are for as-quenched alloy. Lower curves are furnace-cooled alloy after annealing at 1000°C.

Fig. 6  The DTA data for as-quenched and annealed Pd-45% Cu alloys.
order-phase transformations. Thermal hysteresis is, then, an important factor in determining the expansion/contraction behaviour of this alloy. The thermal expansion curve for the as-quenched alloy decreased at about 400°C during heating. This phenomenon was caused by the change in crystal structure. The results support the presumption that first-order-transformation as discussed here is a most serious factor in high transient stress in porcelain when an alloy is used for PFM restorations.

The Pd-Co alloy system has a magnetic transformation which seriously affected the coefficient of thermal expansion. The transformation temperature for the 30% Co alloy was in the same temperature range as glass transition of porcelain. When a similar alloy is used for PFM restorations, transient and residual stresses in the porcelain are markedly affected by the transformation of the alloy. The coefficient of thermal expansion for the 35% Co alloy during heating is shown in Fig. 7. The coefficient of thermal expansion was observed as a typical characteristic of second-order-transformation, that is, the coefficient does not diverge but changes discontinuously at the temperature of magnetic transformation. Table 4 shows the coefficient of thermal expansion before and after magnetic transformation. The result suggests that the alloy was transformed during heating when the coefficient of thermal expansion reached almost the same value.

![Graph](image)

**Fig. 7** Instantaneous coefficient of thermal expansion for Pd-35% Co alloy.

**Table 4** Coefficient of thermal expansion of Pd-Co alloy before and after magnetic transformation $\times 10^{-6}/^\circ\text{C}$

<table>
<thead>
<tr>
<th>Co %</th>
<th>Heating Before</th>
<th>Heating After</th>
<th>Cooling After</th>
<th>Cooling Before</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>18.1</td>
<td>13.7</td>
<td>18.4</td>
<td>14.1</td>
</tr>
<tr>
<td>20</td>
<td>20.6</td>
<td>15.6</td>
<td>20.6</td>
<td>15.3</td>
</tr>
<tr>
<td>25</td>
<td>21.6</td>
<td>17.2</td>
<td>19.7</td>
<td>14.5</td>
</tr>
<tr>
<td>30</td>
<td>23.2</td>
<td>18.4</td>
<td>21.1</td>
<td>18.2</td>
</tr>
<tr>
<td>35</td>
<td>22.2</td>
<td>19.6</td>
<td>21.8</td>
<td>18.8</td>
</tr>
<tr>
<td>40</td>
<td>23.5</td>
<td>19.0</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>45</td>
<td>22.4</td>
<td>17.5</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>
The transient stress in the porcelain at the transformation temperature of the alloy is an important factor in residual stress in PFM restorations: it is beyond the scope of this paper and will be considered in other papers to follow.

**Melting temperature and coefficient of thermal expansion**

A general rule for engineering materials with melting temperatures above 600°C is that these materials will expand about 2% on heating from room temperature to melting. A slightly more useful empirical equation for f.c.c., b.c.c. and c.p.h. crystals\(^7\) is

\[
T_M \cdot \alpha(T_M/2) = 0.0244
\]  

where, \(T_M\) is the melting temperature; and \(\alpha(T_M/2)\) is the instantaneous coefficient of thermal expansion at half the melting temperature. Calculated results for pure metals, as shown in Table 1, are 0.026, 0.021, 0.022, 0.027 and 0.025 for copper, gold, platinum, palladium and silver, respectively. These results are in good agreement with the empirical equation. Since the Pd-Ag alloy can be considered as ideal solutions, \(T_s \cdot \alpha(T_s/2)\) and \(T_l \cdot \alpha(T_l/2)\) are 0.026 and 0.027, respectively, for the alloy with <50% Ag. Here, \(T_s\) and \(T_l\) are the temperatures of solidus and liquidus lines. The Pd-Cu alloy is a regular solution. Calculated \(T_l \cdot \alpha(T_l/2)\) was 0.026 for 5% Cu and 0.023 for 30% Cu when the empirical equation for pure metals as shown in equation (7) was applied to the Pd-Cu alloy. The results of \(T_s \cdot \alpha(T_s/2)\) were almost the same because the \(T_l\) is close to the \(T_s\). These results suggest that ideal solutions satisfy the empirical rule represented by the equation (7), but regular solutions do not obey the formula.

Figure 8 shows the relationship between the instantaneous coefficient of thermal expansion at half the solidus temperature of the alloys used in this study and its solidus tempera-

![Graph](image-url)

**Fig. 8** Relationship between the instantaneous coefficient of thermal expansion at half the solidus temperature and the corresponding solidus temperature. Solid and dashed lines are the calculated results from 0.0244 and 0.026 used in the right side in equation (7), respectively.
THERMAL EXPANSION OF Pd-BASED BINARY ALLOY

The results satisfied the general tendency of thermal expansion, that is, the coefficient of thermal expansion for the alloy with no transformation was inversely proportional to its melting point.

CONCLUSIONS

Temperature dependence of the thermal expansion coefficient for palladium alloys was measured. The coefficient of thermal expansion of the alloy with no transformation was approximated by this equation.

\[ a = C_1 + C_2 T \]

The constants \( C_1 \) and \( C_2 \) were considered as a function of the composition of the alloys. These constants were computed for Pd-Ag (Ag<50%) and Pd-Cu (Cu<30%) alloy systems. The relationships between first-order and second-order transformations and the coefficients of thermal expansion were clarified. Thermal expansion behaviour before and after the transformation was discussed for Pd-Cu and Pd-Co alloys.

The relationship between the coefficient of thermal expansion and its melting point suggests that the coefficient of thermal expansion of alloys with no transformation can be controlled by their melting temperatures. A deeper understanding of residual stress in PFM restorations has been acquired by studying transformation temperatures and instantaneous coefficients of thermal expansion before and after the transformation of the alloy, when an alloy with transformation is to be used for PFM restorations.

ACKNOWLEDGEMENT

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REFERENCES

パラジウム基 2 元合金の熱膨張係数の温度依存性について

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パラジウム基の焼付用合金の基本成分である Pd-Ag, Pd-Cu, Pd-Co 2 元合金の熱膨張係数の温度依存性について調べた。その結果, Pd-Ag (Ag<50%), Pd-Cu (Cu<30%)合金の室温から 600℃ までの温度での熱膨張係数が温度の一次式 \( a = C_1 + C_2 T \) で表されることが明らかにされた。また、温度の一次式的定数 \( C_1 \) と \( C_2 \) が添加元素含有量の一次式で表示できた。すなわち、上記の任意の組成の合金について、任意の温度、温度区間での熱膨張係数が、ここで示された結果を利用して推定できることが明らかにされた。

Pd-Cu 合金の規則－不規則変態 (一次相変態)、Pd-Co合金の磁気変態（二次相変態）と熱膨張係数の関係について調べ、相変態前後の熱膨張係数の特徴が明らかにされた。そして、合金の相変態を利用することにより、陶材／合金補織物中の残留応力が制御でき、相変態による合金の強化と残留応力を利用した陶材の強化を同時に図る陶材／合金システムを作成することの可能性が示唆された。

ハイドロキシアバタイト粉末の物性に及ぼす水溶液中での合成条件の影響

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ハイドロキシアバタイト (HAP) 粉末の水溶液中における層式合成において、HAP 粉末の物性に及ぼす合成温度および二酸化炭素の影響を検討した。二酸化炭素が合成系に存在しない場合、合成温度が高くなると HAP 粉末の結晶性がよくなる。一方、合成温度が低いか、カルシウムとリンの比 (Ca/P) が小さい HAP 粉末が得られる。FT-IR で測定したリンと水酸基の比 (P/OH) は Ca/P が異なる HAP 粉末でも一定であり、このことから低い温度での合成では Ca 欠損 HAP が生成していることがわかった。100℃ で合成した Ca 欠損のない HAP 粉末は 1200℃ で 3 時間安定であったが、40℃ で合成した Ca 欠損 HAP 粉末は 800℃ で一部リン酸三カルシウムに分解した。

一方、合成中に二酸化炭素が存在すると A タイプおよび B タイプの炭酸含有 HAP が生成した。低い温度で合成した場合、炭酸カルシウムも副生成した。

粘膜の被圧縮性が義歯床下組織の応力分布に及ぼす影響

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義歯床下粘膜が粘弾性体であることを考慮して、有限要素法を拡張した粘弾性解析法を用いて、3 種類の異なる荷重条件下での義歯床下組織に生じる応力分布の経時的な変化を計算した。

その結果から、時間経過にともなう粘膜の粘性流動および荷重点は義歯床下組織の応力の分布状態を決定する重要な因子であることが示された。そして、義歯床下組織の応力の不均衡を改善する方法について議論した。義歯床下組織の応力は、咬合力を口盖方向に変位させることによって最も均等に分散した。このことは、Pound の