Factors affecting the optical properties of Pd-free Au–Pt-based dental alloys

TAKANOBU SHIRAISHI*, YASUKO TAKUMA, ERI MIURA, YASUHIRO TANAKA, KUNIHIRO HISATSUNE
Division of Dental and Biomedical Materials Science, Department of Developmental and Reconstructive Medicine, Nagasaki University Graduate School of Biomedical Sciences, 1-7-1 Sakamoto, Nagasaki 852-8588, Japan
E-mail: siraisi@net.nagasaki-u.ac.jp

The optical properties of experimental Au–Pt-based alloys containing a small amount of In, Sn, and Zn were investigated by spectrophotometric colorimetry to extract factors affecting color of Au–Pt-based high-karat dental alloys. It was found that the optical properties of Au–Pt-based alloys are strongly affected by the number of valence electrons per atom in an alloy, namely, the electron : atom ratio, *e*/*a*. That is, by increasing the *e*/*a*-value, activities of reflection in the long-wavelength range and absorption in the short-wavelength range in the visible spectrum apparently increased. As a result, the maximum slope of the spectral reflectance curve at the absorption edge, which is located near 515 nm (approximately 2.4 eV), apparently increased with *e*/*a*-value. Due to this effect, the *b**-coordinate (yellow–blue) in the CIELAB color space considerably increased and the *a**-coordinate (red–green) slightly increased with *e*/*a*-value. The addition of a third element with a higher number of valence electrons to the binary Au–Pt alloy is, therefore, effective in giving a gold tinge to the parent Au–Pt alloy. This information may be useful in controlling the color of Au–Pt-based dental alloys.

1. Introduction

The color of a dental gold alloy is sensitive to its chemical composition. It would be naive for consumers to discount the strong emotional response to the color of restorative alloys containing gold. For manufacturers, therefore, color control should be taken into account when designing chemical compositions of gold alloys for use in dentistry. Historically, Leuser [1] investigated the relationships between color and chemical composition in the ternary Au–Cu–Ag system, which constitutes a basic system of dental casting gold alloys, by visual examination. Leuser divided the whole range of the Au–Cu–Ag system into several areas according to color. This color chart, however, does not represent numerical data. Later, Roberts and Clarke [2] and German *et al*. [3, 4] performed spectrophotometric colorimetry on the Au–Cu–Ag alloys and provided numerical color data based on the CIE (Commission Internationale de l'Eclairage) 1976 *L***a***b** (CIELAB) color space.

Recently, palladium-free high-karat gold alloys for porcelain-fused-to-metal restorations were developed and introduced into the market. These Pd-free gold alloys can also be used as materials for crown and bridge restorations, and may be attractive to patients who are allergic to palladium. This new type of dental gold alloy is composed of gold and platinum with small additions of alloying elements, such as indium and zinc. The addition of these alloying elements is known to be effective in improving bonding strength between porcelain and metal and in improving the mechanical properties of metallic frameworks. We consider that the color of the alloy may also be affected by these alloying elements depending on the species and contents of the elements added. However, little information has been supplied on the relationship between optical properties and chemical composition in these Pd-free Au–Pt-based dental alloys. Further, factors affecting the color of Au–Pt-based dental alloys are not known. Knowledge of the relationship between optical properties and chemical composition is important in designing and developing a new gold-based dental alloy.

In this research, the effects of small additions of In, Sn, and Zn to a binary Au–Pt alloy on its optical properties were investigated by spectrophotometric colorimetry. By analyzing the collected numerical color data, factors affecting the optical properties of Au–Pt-based multi-component dental alloys were extracted.

2. Materials and methods

2.1. Sample preparation

Analyzed chemical compositions of the alloys examined are given in Table I. The chemical compositions of the

*Author to whom all correspondence should be addressed.

TABLE I Chemical compositions of the alloys examined (analyzed values)

Alloy	Composition (at %)					Pt/Au Ratio
	Au	Pt	In	Zn	Sn	
AP10	90.11	9.89	0	0	0	0.110
AP10–In1.0	89.12	9.93	0.95	0	0	0.111
AP10–In1.7	88.35	9.91	1.74	0	0	0.112
AP10–Sn0.9	89.15	9.93	0	0	0.92	0.111
AP10–Sn2.0	88.22	9.81	0	0	1.97	0.111
AP10–Zn1.7	88.47	9.83	0	1.70	0	0.111
(AP10–In2)–Sn1.0	87.33	9.77	1.95	0	0.95	0.112
(AP10–In2)–Zn2.1	86.34	9.55	1.99	2.12	0	0.111

experimental alloys were designed on the basis of atomic percentage. Since most commercial Pd-free Au–Pt-based dental alloys contain approximately 10% Pt, a binary Au-10 at % Pt alloy was designed as a reference alloy to know the effects of various alloying elements on optical properties including chromaticity indices in the CIELAB color space. Since platinum has a strong decolorizing effect on gold [5], the ratio of platinum to gold content was controlled to be constant, as shown in the right hand column in Table I.

All the experimental alloys were prepared from high-purity constituent metals in a high-frequency induction furnace. The ingot obtained was subjected to alternate cold rolling and homogenizing heat treatment at high temperatures. Finally, a number of homogenized plate samples with size of $10 \times 10 \times 0.5\,mm^3$ were obtained.

2.2. Spectrophotometric colorimetry

Three plate samples per each alloy were individually embedded in cold-curing-type epoxy resin and mechanically ground using waterproof abrasive papers adhered to an automatic polishing apparatus (MA-150, Musashino Denshi Co., Ltd., Tokyo, Japan). After grinding down to a 2000-grit finish, the samples were successively polished using alumina suspension with a grain diameter of 0.3 and 0.06 μm on an automatic polishing apparatus (Doctor-Lap ML-180, Maruto Instrument Co., Ltd., Tokyo, Japan). The polished samples were rinsed with pure water and dried.

They were subsequently mounted on a computer-controlled spectrophotometer (CM-3600d, Minolta Co. Ltd., Osaka, Japan) and the spectral reflectance data for the incident CIE standard illuminant D65 were collected at 10 nm intervals from 360 to 740 nm under the visual field of 10°. Three-dimensional color coordinates, i.e. L^* (lightness), a^* (red–green chromaticity index), b^* (yellow–blue chromaticity index) in the CIELAB color space, were determined for each sample. Three samples in each alloy were subjected to the spectral reflectance measurements. Similarly, spectral reflectance curves for three samples of pure gold were also obtained.

3. Results

3.1. Spectral reflectance curves

Figs. 1–3 show effects of small additions of indium, tin, and zinc to the parent AP10 alloy on its spectral reflectance curve, respectively. In these figures, and in the following Fig. 4, standard deviation for three measurements at each wavelength is also presented as error bars. However, standard deviation was so small that most of the error bars are embedded in data points. It is clear that alloying the AP10 alloy with a small amount of indium apparently increased the reflectance in the long-wavelength range and decreased the reflectance in the short-wavelength range (Fig. 1). As a result, the step in the spectral reflectance curve became prominent with increasing indium content. Similar effects were observed when the parent AP10 alloy was alloyed with a small

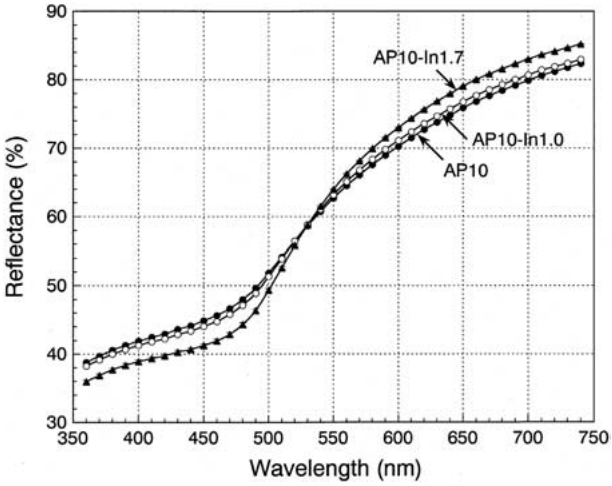

Figure 1 The effects of small indium additions to the binary AP10 alloy on its spectral reflectance curve.

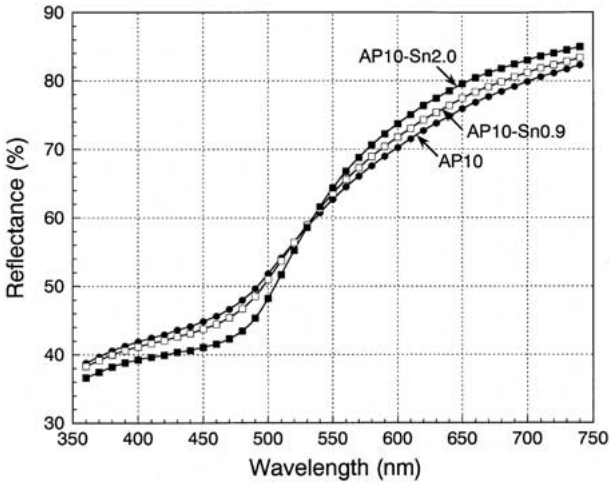

Figure 2 The effects of small tin additions to the binary AP10 alloy on its spectral reflectance curve.

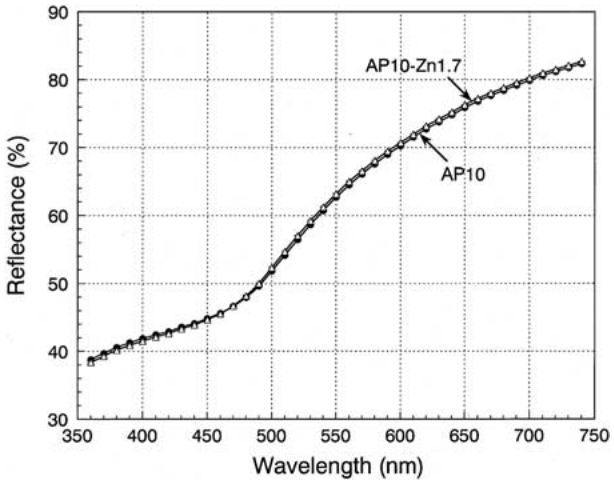

Figure 3 The effects of a small zinc addition to the binary AP10 alloy on its spectral reflectance curve.

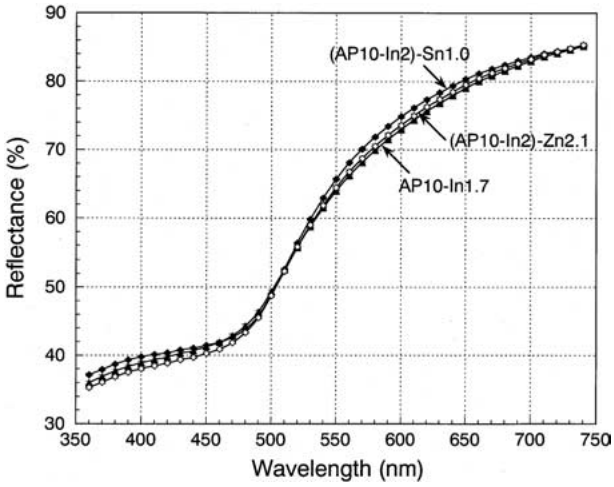

Figure 4 Spectral reflectance curves for the ternary AP10–In1.7 and quaternary (AP10–In2)–Sn1.0 and (AP10–In2)–Zn2.1 alloys.

amount of tin, as shown in Fig. 2. On the other hand, the effects of zinc addition to the AP10 alloy on its spectral reflectance curve were very weak (Fig. 3). That is, the addition of 1.70 at % Zn to the AP10 alloy only slightly increased the reflectance in the long-wavelength range and slightly decreased the reflectance in the short-wavelength range.

Fig. 4 shows the effects of small additions of tin and zinc to the AP10-In2 alloy on its spectral reflectance curve. Although the amount of tin added was as small as 0.95 at %, reflectance in the wavelength range between about 550 and 650 nm appreciably increased. On the other hand, only a slight change in the spectral reflectance curve was observed in the (AP10–In2)–Zn2.1 alloy even though the amount of zinc added was 2.12 at %.

3.2. Chromaticity indices *a** and *b** in the CIELAB color space

Chromaticity indices *a** and *b** obtained for all the experimental alloys are plotted in Fig. 5. The *a** and *b** coordinates for pure gold are also shown for comparison. The addition of indium or tin to the parent AP10 alloy

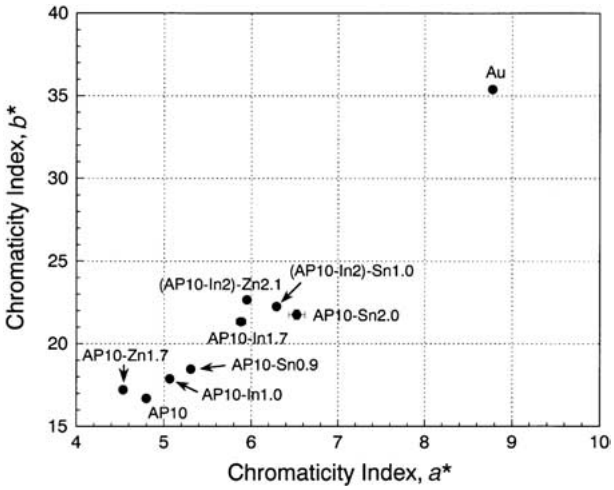

Figure 5 Chromaticity indices, *a**, *b**, evaluated for all the experimental alloys and pure gold.

considerably increased the *b**-value and slightly increased the *a**-value. As a result, points for these In and Sn-added alloys moved towards the point for gold. This finding indicates that the addition of a small amount of indium or tin to the AP10 alloy gives a gold tinge to the parent AP10 alloy. Similar results were obtained for the quaternary (AP10–In2)–Sn1.0 and (AP10–In2)–Zn2.1 alloys. On the other hand, the effects of the sole addition of 1.70 at % Zn to the AP10 alloy on its chromaticity indices were weak.

4. Discussion

4.1. Factors affecting the spectral reflectance curves for the Au–Pt-based alloys

The perceived color of a metal is determined by the wavelength distribution of the radiation that is reflected and not absorbed [6]. Hence, the position of the absorption edge and the slope of the spectral reflectance curve near the absorption edge may greatly affect the perceived color of metals and alloys. By differentiating spectral reflectance data (R) with respect to wavelength (L), we are able to know both the position of the absorption edge and the slope at the absorption edge of the spectral reflectance curve. For example, Fig. 6 shows

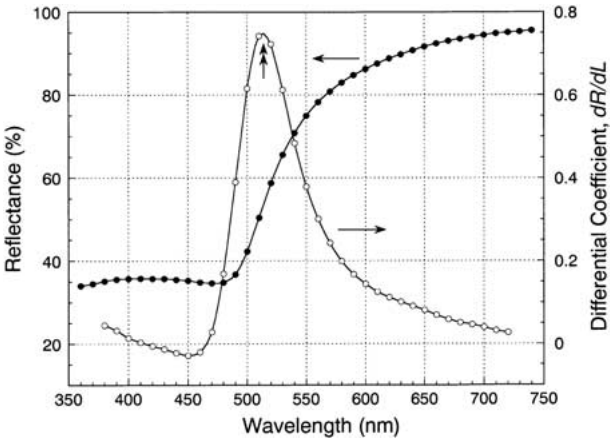

Figure 6 Spectral reflectance curve (solid circles) and its differential coefficient curve (open circles) for pure gold.

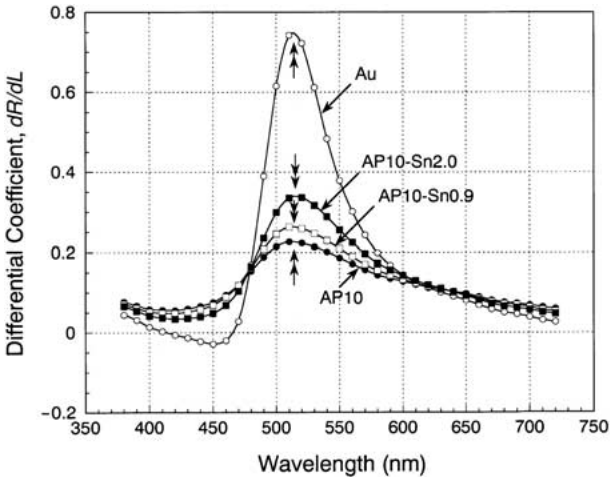

Figure 7 Differential coefficient curves for the spectral reflectance data for the binary AP10, ternary AP10-Sn alloys, and for pure gold.

a typical spectral reflectance curve (marked with solid circles) and its differential curve (dR/dL, marked with open circles) for gold. The peak position of the dR/dL curve, indicated by a double arrow, corresponds to the absorption edge and the peak height indicates the maximum slope of the spectral reflectance curve at the absorption edge. This figure shows that the absorption edge is located near 515 nm, i.e. approximately 2.4 eV. This energy is very close to the previously reported value of 2.45 eV [7] or approximately 2.3 eV [8, 9], which is interpreted to be the energy required for transitions of d electrons to the energetically higher conduction band at the Fermi level [7, 9, 10].

Similar treatment was performed for spectral reflectance data for all the present experimental alloys. Fig. 7 shows typical dR/dL curves for the binary AP10 and the ternary AP10–Sn alloys, obtained from the spectral reflectance data shown in Fig. 2. The dR/dL curve for gold is also presented in this figure for comparison. It is seen that the addition of tin to the parent AP10 alloy did not change significantly the position of the absorption edge within the experimental error. However, the peak height of the dR/dL curve apparently increased with tin content. This indicates that the addition of tin to the AP10 alloy effectively increases the slope of the spectral reflectance curve at the absorption edge. Similarly, increases in the peak height of the dR/dL curve were observed when the parent AP10 alloy was alloyed with small amounts of indium or zinc.

We will discuss factors affecting the slope near the absorption edge of the spectral reflectance curve for the present Au–Pt-based alloys. Since optical properties of metals and alloys are determined by the interaction between the photons of incident light and the electrons in a metallic material, it is suggested that the number of valence electrons per atom, i.e. electron : atom ratio (e/a), in the metallic material may greatly affect both absorption and reflection processes. That is, the degree of both reflection and absorption of light may increase with e/a-value of the alloy. To examine this hypothesis, we investigated relationships between e/a-value and maximum dR/dL-value at the absorption edge for all the present alloys.

We searched for references in which the number of valence electrons per atom in the constituent elements are concerned. According to such surveys, the number of valence electrons per atom is 1 for Au [11, 12], 0 for Pt [11, 13], 3 for In [11, 12, 14], 2 for Zn [11, 14, 15], and 4 for Sn [11, 15]. Based on these reported numbers of valence electrons for each element and chemical compositions in atomic percentage given in Table I, we estimated e/a-values of the present alloys according to the following method. That is, by expanding the method for getting the number of valence electrons per atom in a binary alloy [16], we calculated e/a-values of the present multi-component alloys with the following formula:

$$e/a = \Sigma f_i N_i$$

where f_i is the mole fraction of the component i and the N_i is the number of valence electrons per atom of the component i. The results of these estimations are summarized in Table II. It is seen that the addition of a small amount of indium, tin, and zinc to the parent AP10 alloy increases the e/a-value depending on the species of alloying elements and their amounts. Using these estimated values, we investigated the effects of the electron : atom ratio (e/a) on the maximum slope (dR/dL) at the absorption edge for all the alloys examined. The results are presented in Fig. 8. It is clear that the dR/dL-value at the absorption edge apparently increases with e/a-value. This result strongly supports the validity of the previously described hypothesis that the degree of both reflection and absorption of light may increase with e/a-value of the alloy.

TABLE II Estimated electron : atom ratio (e/a) of the alloys

Alloy	e/a
AP10	0.9011
AP10–In1.0	0.9197
AP10–In1.7	0.9357
AP10–Sn0.9	0.9283
AP10–Sn2.0	0.9610
AP10–Zn1.7	0.9187
(AP10–In2)–Sn1.0	0.9698
(AP10–In2)–Zn2.1	0.9655

With regards to the flattening of the spectral

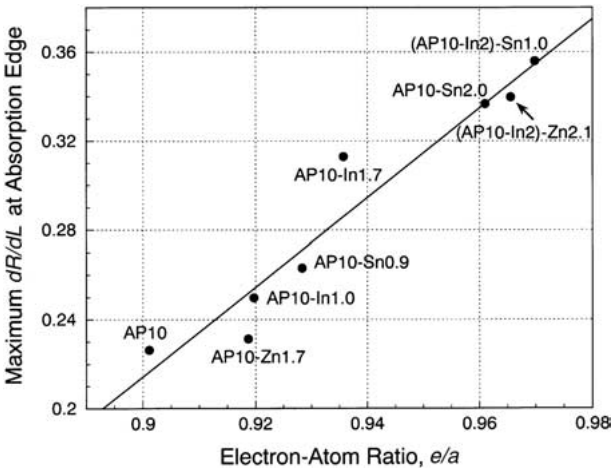

Figure 8 The relationship between the maximum slope at the absorption edge of the spectral reflectance curve and electron : atom ratio for all the experimental alloys.

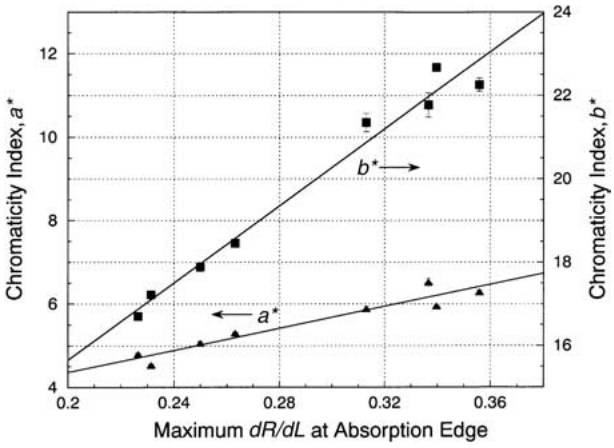

Figure 9 The relationships between chromaticity indices in the CIELAB color space and the maximum slope at the absorption edge for all the experimental alloys.

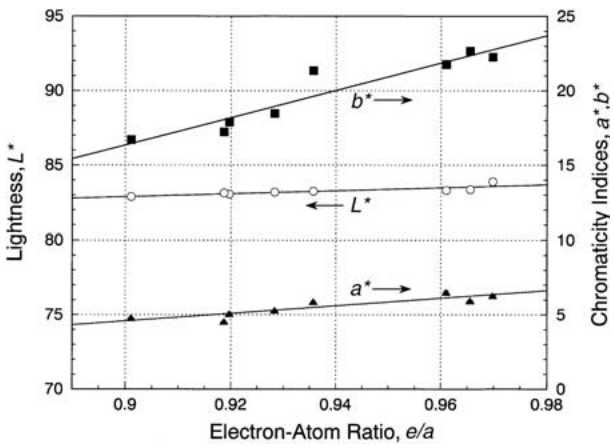

Figure 10 The relationships between three-dimensional coordinates in the CIELAB color space and electron : atom ratio for all the experimental alloys.

reflectance curve due to the addition of platinum to gold, we previously reported that this phenomenon is derived from the occurrence of ''virtual bound states'' [5], as suggested by Friedel [17]. That is, when monovalent noble metals are alloyed with transition metals, so-called ''virtual bound states'' would occur and, as a result, the absorption process of light starts in the infrared range [17]. Based on this ''virtual bound states'' theory for the binary Au–Pt alloys, the present experimental evidences that the reflectance in the long-wavelength range appreciably increased with the addition of In, Sn, and Zn, to the parent AP10 alloy suggest that the degree of ''virtual bound states'' may become weak with increasing *e*/*a*-value. This is considered to be the reason why the slope of the spectral reflectance curve at the absorption edge systematically increased with *e*/*a*-value.

4.2. Effects of alloying elements on the chromaticity indices

Fig. 9 shows the relationships between chromaticity indices, *a**, *b**, and the maximum slope of the spectral reflectance curve at the absorption edge. It is shown that with increasing the maximum *dR*/*dL*-value at the absorption edge the *b**-value markedly increased and the *a**-value slightly increased.

By combining the relationships shown in Figs. 8 and 9, we can know how the *e*/*a*-value affects both chromaticity indices. Fig. 10 summarizes the effects of *e*/*a*-value in an alloy on *L**-, *a**-, and *b**-coordinates in the CIELAB color space. It is clearly shown that by increasing the *e*/*a*-value, yellow–blue index *b**-value markedly increased and red–green index *a**-value slightly increased. On the other hand, the lightness *L**-value did not change significantly.

It is concluded, therefore, that in Au–Pt-based dental alloys the electron : atom ratio in an alloy greatly affects the optical properties and that alloying the parent AP10 alloy with a third element with a higher number of valence electrons per atom is effective in giving a gold tinge to the parent Au–Pt alloy.

5. Conclusions

The optical properties of Pd-free Au–Pt-based dental alloys are strongly affected by the number of valence electrons per atom in an alloy, namely, the electron : atom ratio (e/a). That is, by increasing the *e*/*a*-value, the activities of reflection in the long-wavelength range and absorption in the short-wavelength range in the visible spectrum apparently increases. As a result, the chromaticity index *b**-value (yellow–blue) considerably increases and *a**-value (red–green) slightly increases. This fact suggests that the addition of a third element with a higher number of valence electrons to the binary Au–Pt alloy is more effective in giving a gold tinge to the parent Au–Pt alloy. This information may be useful in controlling the color of Au–Pt-based high-karat dental alloys.

Acknowledgments

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