Development of Casting Investment Preventing Blackening of Noble Metal Alloys

Part 2. Application of Developed Investment for Type 4 Gold Alloy

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The objective of this study was to evaluate the efficacy of the developed investment for the prevention of blackening of a cast Type 4 gold and to analyze the oxides on its surface in relation to the blackening of the alloy. The experimental investments were prepared using a gypsum-bonded investment in which boron (B) or aluminum (Al) was added as a reducing agent. A Type 4 gold alloy was cast into the mold made of the prepared investment. The effect of the additives was evaluated from the color difference (ΔE^*) between the as-cast surface and the polished surface of the cast specimen. B and Al were effective to prevent the blackening of a Type 4 gold alloy and the color of the as-cast surface approached that of the polished surface with increasing B and Al content. The prevention of the blackening of the gold alloy can be achieved by restraining the formation of CuO.

Key words : Casting investment, Color of cast surface, Gold alloy

INTRODUCTION

In a previous study¹⁾, a casting investment which could prevent blackening of a cast Ag-Pd-Cu-Au alloy was developed using boron (B) and aluminum (Al) as an additive to a gypsum-bonded investment. These additives helped produce a reducing atmosphere in a casting mold and thus were effective to prevent the formation of oxide film on the surfaces of the Ag-Pd-Cu-Au alloy.

In addition to Ag-Pd-Cu-Au alloys, Type 4 gold alloys produce relatively black surfaces after the casting process. Type 4 gold alloys have relatively low gold content and high copper content in comparison with the other gold alloys. Based on this composition, it is very likely that the blackening mechanism of Type 4 gold alloys is similar to that of Ag-Pd-Cu-Au alloys and the color of the as-cast surfaces of the gold alloys can be improved using a developed investment containing B or Al as a reducing agent.

The objective of the present study was to evaluate the efficacy of the developed investment for the prevention of the blackening of a cast Type 4 gold alloy and to analyze the oxides on its surface in relation to the blackening of the alloy. It is expected that the polishing processes such as a pickling to remove the oxidation on the cast surface can save a cast Type 4 gold alloy by preventing blackening.

MATERIALS AND METHODS

The experimental investment was prepared using the materials listed in Table 1. B and Al were selected as reducing agents based on previous findings¹⁾. These agents were individually added to a commercially available gypsum-bonded investment powder (Newcrivest, Mutsumi Plaster Industries Co. Ltd., Mie, Japan). The investment and the reducing agent were blended by hand before mixing. The content of the additives was 0, 0.063, 0.125, 0.250 and 0.500 mass% for B, and 0, 5, 10, 15 and 20 mass% for Al.

Preparation of cast specimen

A mold was prepared using the prepared investment and an acrylic resin plate (20 × 25 × 1 mm) as a casting pattern. The experimental investment was mixed at a water/powder ratio of 0.33 recommended by the manufacturer. The original investment without the reducing additives was also used as a control. Three molds were prepared for each investment. The mold was heated at 650°C at a heating rate of 5°C/min and was kept for more than 30 min at this temperature. A commercially available Type 4 gold alloy (Casting Gold M. C. Type IV, GC Corp., Tokyo, Japan) was melted using a town gas-air torch, and cast into the mold using a centrifugal casting machine (Caster VC500, The Daiei Dental MFG. Co. Ltd., Osaka, Japan). The alloy composition disclosed by the manufacturer is shown in Table 2. The mold was bench-cooled to room temperature for about 5 min. The cast specimen was removed from the mold and the surface of the casting was cleaned in water for 2-3 min using a toothbrush until the investment was sufficiently removed from the surface.

Table 1 Materials for preparation of experimental investment

<u>Investment material</u>		
Newcrivest, Mutsumi Plaster Industries, Japan, Lot. No.10930303		
<u>Additives to investment material as a deoxidizer</u>		
Additives	Purity	Particle size
Boron*	96.45%	Ave. 0.91 μm
Aluminum**	>99.70%	75-150 μm

*H. C. Starck GmbH & Co., KG. Goslar, Germany

**Minalco Co. Ltd., Osaka, Japan

Table 2 Composition of Type 4 gold alloy

Product					
Casting gold M. C. Type IV			GC, Japan	Lot. No.0106281	
Composition					
Au	Pt	Pd	Ag	Cu	Others
70%	2%	3%	8%	16%	1%

The same procedure was also employed for the original investment without additives. For the control specimens, both as-cast specimens and polished specimens were prepared. The as-cast specimen was regarded as 0 mass% of additive content. The polishing was carried out using #1,000 SiC paper.

Evaluation of blackening of cast surface

Evaluation of blackening of the cast surface was performed to measure the color difference (ΔE^*) between the as-cast surface and the polished surface. The color difference (ΔE^*) was calculated using the brightness index (L^*) and the chromaticness index (a^* , b^*) of each specimen, which was computed from the intensity of total reflection measured using a spectrophotometer (Color analyzer type 307, Hitachi, Tokyo, Japan). Measuring area, scanning range of wavelength, and sampling interval of the spectrophotometer were 18×22 mm, 380-780 nm, and 5 nm respectively. Three specimens were prepared for measurement of each condition of the reducing agents. The effect of the reducing agent on the prevention of blackening was analyzed using one-way analysis of variance and Tukey's multiple comparison.

Surface analysis using X-ray photoelectron microscopy

The surfaces of four different specimens were analyzed to determine the existence of copper and its oxides using an X-ray photoelectron spectroscopy (JPS-9000MC, JEOL Co. Ltd., Tokyo, Japan). Three of the four specimens were as-cast ones prepared from 0%additive investment, 0.5%B investment and 20%Al investment, and the fourth was a polished specimen. The analysis was carried out with Al K α radiation at 10 kV and 30 mA under a pressure of 6×10^{-7} Pa. Before the analysis, all surfaces were cleaned using argon etching at 500 V for 30 sec. The binding energy of the measured photoelectron peak was calibrated using the Au 4f_{7/2} peak at a binding energy of 84.0 eV. Copper and its oxides on the surfaces were determined using the reported values^{2,3)}.

RESULTS

Color difference of the casting surface

The color difference (ΔE^*) between the as-cast surface and the polished surface of specimens, which were cast using the experimental investments, are shown in Figs.1 and 2. For the control specimen (0% additive) the mean value of the ΔE^* was 42.8. The values of ΔE^* ranged from 14.3 to 19.9 for B-added investment and 12.6 to 28.1 for Al-added investment. The results of ANOVA and Tukey's multiple comparison suggest that the ΔE^* significantly decreased with the addition of B and Al at all contents ($p < 0.05$). For the B-added investment, the ΔE^* significantly decreased as the B content increased from 0.063% to 0.125% ($p < 0.05$), but no significant decrease was found at greater than 0.125%. For the Al-added investment, the ΔE^* significantly decreased as the Al content increased from 5% to 15% ($p < 0.05$), but no significant difference was found between 15% and 20%.

Fig. 1 Color difference between the as-cast surface and the polished surface (B added investment).

Fig. 2 Color difference between the as-cast surface and the polished surface (Al added investment).

Fig. 3 As-cast surfaces (sprue: left side of specimen).

Typical surfaces of the as-cast specimens are shown in Fig. 3. A decrease in the blackening was clear under visual inspection for both B- and Al-added investment. Although the color difference showed improvement in the color for both additives, these photographs show the difference in the uniformity of the color improvement between these two additives. As shown in Fig. 3, the surface obtained from B-added investment was uniformly brightened. On the other hand, that from Al-added investment consisted of bright and dark areas.

Surface analysis using X-ray photoelectron microscopy

Figs. 4 and 5 show the Cu 2p_{3/2} spectra and O 1s spectra, respectively, for four different surfaces. As shown in Fig. 4, the peak at 933.2 eV corresponding to CuO was

Fig. 4 Cu 2p_{3/2} spectra by X-ray photoelectron spectroscopy.

Fig. 5 O 1s spectra by X-ray photoelectron spectroscopy.

observed on the surface of the specimen prepared from 0%additive investment. The other three specimens had a peak in the range of 932.4-932.6 eV corresponding to either Cu or Cu₂O. This was differentiated from the O 1s spectra. In Fig. 5 for O 1s spectra, the peak at 529.8 eV corresponding to CuO was found on the surface of the specimen prepared from 0%additive investment. On the two specimens prepared from B- and Al-added investments, a peak in the range of 531-532 eV corresponding to Cu₂O was observed, which differentiated that the peak in Cu 2p_{3/2} spectra was Cu₂O. On the other hand, no clear peak was found on the surface of the polished specimen, which differentiated that the peak in the Cu 2p_{3/2} spectra was Cu. Thus, the existing element or oxide was Cu on the polished surface, CuO on the surface from the 0%additive investment and Cu₂O on the surfaces from B- and Al-added investments.

DISCUSSION

The previous study¹⁾ showed that B and Al were effective to decrease the blackening of an Ag-Pd-Cu-Au alloy. Based on this result, these two materials were chosen as a reducing additive. Both B- and Al-added investments significantly decreased the blackening of the as-cast Type 4 gold alloy, indicating that B and Al are also effective to reduce the blackening of the gold alloy. In the previous study¹⁾, it was reported that B and Al produced the reducing atmosphere in a casting mold, and thus the oxidation of the as-cast surface was restrained. This theory is also applicable for the Type 4 gold alloys.

For the gold alloy casting, however, the liquidus temperature should be considered. The melting temperatures of B and Al are 2080°C and 660.4°C, respectively⁴⁾, while the liquidus temperature that of the Type 4 gold alloy is 945°C according to the manufacturer's information. The melting temperature of B was significantly higher than that of the gold alloys, which suggests that B is not melted during the casting

process. On the other hand, Al in the mold may be melted due to the higher temperature of the molten gold alloy and diffused into some area of the molten gold alloy surfaces and can then form some solid solutions with major alloy elements such as Au, Ag and Cu⁵⁾. In addition, the result of X-ray photoelectron microscopy for oxygen suggested the possibility of aluminum oxide. The oxygen peak at 532.3 eV in Fig. 5 corresponds to the binding energy of the aluminum oxide suggesting the existence of Al on the surface. It is very probable that the Al particles are alloyed with the metal in the gold alloy during the casting process. Therefore, the result for the Al-added investment could be influenced by the melting or alloying of Al. A further study is necessary to determine whether the Al is involved in the alloy surface.

Ohno⁶⁾ heated 10 different noble metal alloys in the atmosphere and reported that CuO and Cu₂O were formed on the surface of the alloys. In the present study the X-ray photoelectron analysis was carried out to determine the formation of these oxides on the surfaces of the as-cast Type 4 gold alloy. CuO was observed on the surface of the alloy which was cast into the original investment without additives. On the other hand, Cu₂O was found on the cast surfaces obtained from both B- and Al-added investments. These results suggest that less oxygen is supplied to the alloys in B- and Al-added investments than in the original investment and thus the oxidation of the alloy surface was restrained resulting in the formation of Cu₂O which is the precursor of CuO. According to previous findings⁷⁾, CuO is black whereas Cu₂O is red. The results of the X-ray photoelectron microscopy and the color of copper oxides suggest that the prevention of the blackening of the gold alloy is achieved by restraining the formation of CuO.

CONCLUSIONS

The objective of this study was to evaluate the efficacy of the developed investment for the prevention of blackening cast Type 4 gold alloy and to analyze the oxides on its surface in relation to the blackening of the alloy.

The effect of the additives was evaluated from the color difference (ΔE^*) between the as-cast surface and the polished surface of the cast specimen. The results of the color difference measurement suggested that B and Al were effective to prevent the blackening of a Type 4 gold alloy, and the color of the as-cast surface approached that of the polished surface with increasing B and Al content.

CuO was observed on the surface of the control specimen which was prepared from the original investment without additives. On the other hand, Cu₂O was found on the cast surfaces obtained from both B- and Al-added investments. Based on these results and the color of CuO and Cu₂O, the prevention of the blackening of the gold alloy can be achieved by restraining the formation of CuO.

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