Development of Casting Investment Preventing Blackening of Noble Metal Alloys. Part 4: Effect of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ as Additives

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The objective of this study was to develop a casting investment that prevents the blackening of the cast surface of noble metal alloys. Experimental investments were prepared using a gypsum-bonded investment in which a hydroxide, namely $\text{Mg}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$, was added. An Ag-Pd-Cu-Au alloy was cast into the mold made of the prepared investment. The addition of both hydroxides showed a significant effect on the color of as-cast surfaces, which was improved with increase in additive content. When $\text{Mg}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$ was added at more than 4.0 mass% to the investment, it was useful in preventing the blackening of the as-cast surfaces of an Ag-Pd-Cu-Au alloy. As for differences in the effects between $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$, they were not found.

Keywords: Casting investment, Color of cast surface, Noble metal alloy

INTRODUCTION

Some noble metal alloys, especially Ag-Pd-Cu-Au alloys consisting of 20% Pd and 12% Ag, frequently exhibit blackened surfaces after the casting process. In a previous study¹⁾, it was reported that the addition of either boron (B) or aluminum (Al) particles to a commercially available gypsum-bonded investment was effective in preventing the blackening of as-cast surfaces of Ag-Pd-Cu-Au alloys. Furthermore, in another study, the same effect was also found on Type 4 gold alloy²⁾. The efficaciousness of boron and aluminum could be attributed to two reasons. Standard free energy changes ($-\text{dG}^\circ_{650^\circ\text{C}}$) of oxide formation for boron and aluminum are higher than those of CuO (black color³⁾) and Cu_2O (reddish color³⁾), and that the oxidation of these additive elements during mold heating could reduce the oxygen concentration in the mold. As a result, the blackening of the as-cast surfaces of Ag-Pd-Cu-Au alloys could be restrained by adding these elements to gypsum-bonded investments.

Calcium (CaO) is chemically very active⁴⁾, and this compound is frequently used as a flux for the refining of metals⁵⁾. Magnesia (MgO), like CaO, has a similar effect⁴⁾. On this ground, these two compounds are expected to improve the color of cast surfaces. From our preliminary experiments, however, we found that investments containing these two compounds as additives failed to make good slurries with a suitable consistency for the investment mixing procedure when they were mixed with water. Instead of Ca and Mg oxides, their hydroxides produced suitable investment slurries in our preliminary experiment. In other words, Ca and Mg hydroxides could be good candidates to improve the surface blackening of Ag-Pd-Cu-Au alloys based on the high reactivity of these elements.

The objective of the present study was to develop an effective gypsum-bonded investment that prevents the formation of a black film on the as-cast surface. To this end, two hydroxides, magnesium hydroxide ($\text{Mg}(\text{OH})_2$) and calcium hydroxide ($\text{Ca}(\text{OH})_2$), were used as additives to the gypsum-bonded investment.

MATERIALS AND METHODS

Color evaluation of cast specimens

Table 1 lists the materials used in this study. Calcium hydroxide ($\text{Ca}(\text{OH})_2$; Wako Pure Chemical Industries Ltd., Osaka, Japan) and magnesium hydroxide ($\text{Mg}(\text{OH})_2$; Wako Pure Chemical Industries Ltd., Osaka, Japan) were selected as additives to gypsum-bonded investments. These additives were individually added to a commercially available gypsum-bonded investment (Cristobalite Micro II, GC Corp., Tokyo, Japan). The content of $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ in the experimental investment powder ranged from 2 to 10 mass% at an interval of 2 mass% respectively.

A casting mold was made from the prepared investment, and an acrylic resin plate ($20 \times 25 \times 1$ mm) was used as the casting pattern. The experimental investment was mixed at a water/powder ratio of 0.33 as recommended by the manufacturer. The original investment without any additive was also used as a control. Three molds were prepared for each investment. The mold was heated to 650°C at a heating rate of $5^\circ\text{C}/\text{min}$ and was kept for more than 30 minutes at this temperature. A commercially available Ag-Pd-Cu-Au alloy (Castwell M.C. 12% gold, GC Corp., Tokyo, Japan) was cast into the mold using a centrifugal casting machine, and then the mold was bench-cooled. Cast specimen was removed from the mold, and the cast surface was cleaned in water for about five minutes using an ultrasonic cleaner until

Table 1 Materials used in this study

Material		Company
Investment	Cristobalite Micro II	GC Corp.
Additives	Mg(OH) ₂	Wako Pure Chemical
	Ca(OH) ₂	Wako Pure Chemical
Casting alloy	Castwell M.C. 12%gold (Ag 46%, Pd 20%, Cu 20%, Au 12%, Others 2%)	GC Corp.

the investment was sufficiently removed from the surface. Six specimens were prepared for the control specimens using the original investment (0 mass%), whereas three as-cast specimens and three polished specimens (using #1,000 SiC paper) were prepared from the six specimens. Three as-cast specimens were prepared using each of the experimental investments containing different contents of Ca and Mg hydroxides.

The brightness index (L^*) and chromaticness index (a^* , b^*) of each as-cast specimen and polished specimen were measured using a spectrophotometer (Color Analyzer Type 307, Hitachi, Tokyo, Japan). Color difference (dE^*) between the as-cast surface and polished surface was calculated to evaluate the effect of the additives on the color of cast surfaces. The effects of the additives and their contents on dE^* were statistically analyzed using two-way analysis of variance and Tukey's interval to evaluate the efficacy of the additives in the prevention of surface blackening.

Thermogravimetric-differential thermal analysis (TG-DTA) and X-ray diffraction analysis of experimental investments

After setting, each experimental investment was powdered for thermogravimetric-differential thermal analysis (TG-DTA) and X-ray diffraction analysis. Subsequently, powdered investment was heated at a heating rate of 5°C/min to 650°C and was kept for 30 minutes at this temperature using a thermogravimetric analyzer (Thermo Plus II, Rigaku Corp., Tokyo, Japan) to investigate the reaction of the original investment and each additive during heating. By means of an X-ray diffractometer (Rint-1200, Rigaku Corp., Tokyo, Japan), set and heated investments were also powdered to analyze the resultant substances after setting and heating. The heating condition for X-ray diffraction analysis was the same as that for TG-DTA.

RESULTS

Figure 1 shows the cast surface of each condition. Brightness of as-cast surfaces obtained from experimental investments significantly increased with the

Fig. 1 The cast surfaces (sprue gate on left side). Lower number is the content rate (mass%) of each additive in the investment.

Fig. 2 Color differences between as-cast and polished surfaces (vertical line indicates 95% confidence interval).

Fig. 3 TG-DTA curve of the investment containing 10 mass% Ca(OH)₂.

increase of additive content. However, a small part of the specimen beneath the sprue gate was blackened when the investment contained 10 mass% of both additives. The highest mean of color difference (dE^*) was obtained from the original investment mold (without additives), and the value was 47.5. The lowest mean

Fig. 4 TG-DTA curve of $\text{Ca}(\text{OH})_2$. Fig. 5 TG-DTA curve of investment containing 10 mass% $\text{Mg}(\text{OH})_2$.

Table 2 Detected substances by X-ray diffraction analysis

	Before heating	After heating
Original investment	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaSO_4
	Cristobalite	Cristobalite
	Quartz	Quartz
10 mass% $\text{Ca}(\text{OH})_2$ -containing investment	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaSO_4
	Cristobalite	Cristobalite
	Quartz	Quartz
	$\text{Ca}(\text{OH})_2$	CaO
10 mass% $\text{Mg}(\text{OH})_2$ -containing investment	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaSO_4
	Cristobalite	Cristobalite
	Quartz	Quartz
	$\text{Mg}(\text{OH})_2$	MgO

value (22.9) was obtained from the investment containing 10 mass% $\text{Mg}(\text{OH})_2$. Result of two-way analysis of variance showed that differences in dE^* between $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ addition at each varying content level were not significant. However, significant differences were found among the additive contents for each additive ($p < 0.01$).

Figure 2 shows the average dE^* values at different additive contents. As shown in this figure, dE^* significantly decreased by 23% at 2.0 mass% additive content and by 46% at 0.0 mass% additive content in comparison with that at 0 mass% content. Tukey's interval was 10.4 ($p = 0.05$) for the statistical comparison between mean values, and dE^* was significantly decreased with increase in additive content from 2.0 mass% to 10.0 mass% for both additives. However, no significant changes in dE^* were observed at additive contents more than 4.0 mass% for both additives.

Figure 3 shows the thermogravimetric-differential thermal analysis (TG-DTA) curve of the investment containing 10 mass% $\text{Ca}(\text{OH})_2$, while that of $\text{Ca}(\text{OH})_2$

Fig. 6 TG-DTA curve of $\text{Mg}(\text{OH})_2$.

powder is shown in Fig. 4. For $\text{Ca}(\text{OH})_2$ -added investment, an endothermic peak and large weight loss were observed at about 130°C, while another endothermic peak was observed at about 430°C with small weight loss (Fig. 3). This peak was also found on the TG-DTA curve of $\text{Ca}(\text{OH})_2$ powder (Fig. 4). In X-ray diffraction analysis, some anhydrites were identified in $\text{Ca}(\text{OH})_2$ -added investment (Table 2). This result together with TG-DTA result indicated that dehydration of gypsum induced anhydrite formation. Besides anhydrites, CaO was also identified in the heated investment by X-ray diffraction analysis (Table 2). In $\text{Ca}(\text{OH})_2$ powder, CaO was identified only after heating. These results together with TG-DTA results indicated that $\text{Ca}(\text{OH})_2$ decomposed to CaO at about 430°C.

Figure 5 shows the TG-DTA curve of the investment containing 10 mass% $\text{Mg}(\text{OH})_2$, while that of $\text{Mg}(\text{OH})_2$ powder is shown in Fig. 6. For $\text{Mg}(\text{OH})_2$ -added investment, two endothermic peaks were also observed at about 130°C and 400°C (Fig. 5). The peak

at about 130°C was accompanied with large weight loss due to the dehydration of gypsum, just as that which occurred in Ca(OH)_2 -added investment. In X-ray diffraction analysis, MgO was identified in the X-ray diffraction patterns for both heated investment and Mg(OH)_2 powder. These results indicated that Mg(OH)_2 decomposed to MgO at about 400°C. By means of X-ray diffraction analysis, some $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, cristobalite, quartz, and Ca(OH)_2 were identified in set Ca(OH)_2 -added investment powder, while some $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, cristobalite, quartz, and Mg(OH)_2 were identified in set Mg(OH)_2 -added investment powder (Table 2). No other new substances were detected. Based on this result, it was probable that Mg(OH)_2 or Ca(OH)_2 did not react with every component of the investment during setting. Some CaSO_4 , cristobalite, quartz, and CaO were identified in heated Ca(OH)_2 -added investment powder, while some CaSO_4 , cristobalite, quartz, and MgO were identified in heated Mg(OH)_2 -added investment powder (Table 2). No new substances were detected in X-ray diffraction analysis. Based on this result, it was probable that Mg(OH)_2 or Ca(OH)_2 did not react with every component of the investment during heating.

DISCUSSION

Three approaches have been proposed to prevent the blackening of cast surfaces by previous studies^{1,2)}. One is to reduce or eliminate oxygen in a casting mold by the oxidation of additives such as boron and aluminum. To this end, a reducing additive is blended into the casting investment. Oxygen in the mold cavity is then lowered by the oxidation of the reducing additive during mold heating. Previous reports^{1,2)} were designed based on this hypothesis. The second approach is to reduce oxide formation on the cast surface by employing reducing additives with high standard free energies ($-dG^\circ_{650^\circ\text{C}}$). The third approach is to remove some oxides from the molten metal or alloy by using additives as a flux.

In the present study, two hydroxides — namely Ca(OH)_2 and Mg(OH)_2 — were used to prevent the surface blackening of an Ag-Pd-Au-Cu alloy. For Ca(OH)_2 , its selection was based on its efficacy as a flux for steel refining⁵⁾. As for Mg(OH)_2 , it also has an effect similar to that of Ca(OH)_2 ⁵⁾. It is very probable that these hydroxides — when contained in the investment — play an important role in functioning as a flux to remove metal oxides such as CuO and Cu_2O from the cast surface. Indeed, color difference (dE^*) between the as-cast and polished surfaces significantly decreased at more than 4 mass% of additive content for both additives. This result thus indicated that for both additives, an additive content of more than 4 mass% was required to effectively work as a flux, and thereby prevent the blackening of cast

surfaces.

TG-DTA analysis was employed to investigate the reactivity of the additives with the original investment components and their reaction temperatures. The investments before and after heating were analyzed using an X-ray diffractometer. Results indicated that Mg(OH)_2 and Ca(OH)_2 were dehydrated during heating and formed MgO and CaO respectively. In other words, CuO (black color³⁾) and Cu_2O (red color³⁾) — which were the main oxides that contributed to the blackening — could have reacted with MgO or CaO and were thus removed from the cast surfaces. As mentioned previously, both Mg(OH)_2 and Ca(OH)_2 are effective as a flux for steel refining. However, it is unknown if this effect is likewise applicable for Cu oxides.

To investigate if these hydroxides could likewise work as a flux for Cu oxides, an additional experiment was carried out. A powder specimen consisting of 50 mass% Mg(OH)_2 or 50 mass% Ca(OH)_2 and 50 mass% CuO was heated to 1,000°C. Their crystal structures were analyzed using an X-ray diffractometer. In the diffraction patterns of the specimens after heating, no peaks were found for both Mg(OH)_2 and Ca(OH)_2 , indicating that both specimens formed non-crystalline structures after heating. This thus soundly suggested that both hydroxides worked efficiently as a flux for Cu oxides.

In a previous study¹⁾, it was reported that boron (B) and aluminum (Al) were useful additives in preventing the blackening of an Ag-Pd-Cu-Au alloy. Color difference (dE^*) of B-added investments significantly decreased as the content of B increased. The value of dE^* decreased by about 30% at 0.125 mass% of B content and by about 54% at 0.25 mass% in comparison with that of 0 mass% content. For Al-added investments, dE^* significantly decreased at all three Al contents in comparison to that of 0 mass% content. The decrease in dE^* was 38% at 15 mass% of Al content in comparison with that at 0 mass%.

In the present study, the dE^* values for both Mg(OH)_2 - and Ca(OH)_2 -added investments significantly decreased as the contents of both additives increased. The values of dE^* decreased by 33% at 4.0 mass% and by 46% at 10.0 mass% for both additives in comparison with that at 0 mass% content. Based on the results obtained, it could be seen that the effect of Mg(OH)_2 or Ca(OH)_2 addition to the investment ranked between those of B and Al additions. At this juncture, it must be mentioned that with the addition of the hydroxides, the surfaces of both as-cast specimens were partially blackened, especially beneath the sprue gate. A further study should be carried out to prevent the blackening of as-cast surfaces.

In a previous study⁶⁾, the influence of reducing additives on expansion was investigated. Despite a decrease in the content of cristobalite in the invest-

ments, the thermal expansion of B- and Al-added investments significantly increased. B and Al were oxidized during heating to 650°C. As a result, the volumes of both metals increased, thereby leading to increase in thermal expansion. However, with hydroxide-added investments, lower thermal expansion was expected by virtue of dehydration during heating to 650°C. Therefore, these investments may need some substances to increase their thermal expansion.

The fluidity of hydroxide-added investments in this study decreased with increase in additive content. As a result, manipulative difficulty was encountered upon mixing with water. In particular, this difficulty was heightened at more than 8 mass% content of either $\text{Mg}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$. Results of dE^* measurement showed that when $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$ was added at more than 4 mass%, it was sufficiently effective in improving the surface blackening of Ag-Pd-Au-Cu alloy. In view of the results obtained, additive content in the investment should exceed 4% but must be less than 8%.

CONCLUSIONS

Experimental investments were prepared by adding an additive such as $\text{Mg}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$ to a gypsum-bonded investment. Using these investments, an Ag-Pd-Cu-Au alloy was cast. The effects of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ additions and their contents on the color of the Ag-Pd-Cu-Au alloy was evaluated.

Color difference (dE^*) for both $\text{Mg}(\text{OH})_2$ - and $\text{Ca}(\text{OH})_2$ - added investments significantly decreased as the contents of these additives increased. The value of dE^* decreased by 33% at 4.0 mass% of each additive content and by 46% at 10.0 mass% in comparison to that of 0 mass% content. However, among the varying contents, there were no significant differences in dE^* . At more than 4 mass% content of $\text{Mg}(\text{OH})_2$ or $\text{Ca}(\text{OH})_2$, the addition was effective in preventing the blackening of the as-cast surfaces of

Ag-Pd-Cu-Au alloy.

By means of X-ray diffraction analysis, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, cristobalite, and quartz were identified in both set investments containing $\text{Ca}(\text{OH})_2$ or $\text{Mg}(\text{OH})_2$. Besides, $\text{Ca}(\text{OH})_2$ was identified in the set $\text{Ca}(\text{OH})_2$ -added investment powder, while $\text{Mg}(\text{OH})_2$ was identified in the set $\text{Mg}(\text{OH})_2$ -added investment powder. After heating, CaSO_4 , cristobalite, and quartz were identified in both investments by X-ray diffraction analysis. CaO was identified in $\text{Ca}(\text{OH})_2$ -added investment after heating, while MgO was identified in $\text{Mg}(\text{OH})_2$ -added investment after heating. No new substances were detected by X-ray diffraction analysis of both set and heated investment powders. Based on the results obtained, it could be said that $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ did not react with every component of the investment.

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