

# An Oxidative Chloride Stripping Solution for 14K Gold Alloys

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**Abstract** We propose a novel stripping solution containing acids (HCl and HNO<sub>3</sub>), an oxidant [(NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>], and complexing agents (NaCl and citric acid) to remove surface passivation layers from 14K gold alloys fabricated using an investment casting process. The optimized solution employing only HCl acid is determined by varying molar fractions of HCl and HNO<sub>3</sub> on 14K yellow gold samples. Stripping properties are also identified for red and white gold alloy samples under the optimized stripping conditions. The removal of passivation layers, weight loss, and microstructure evolution are characterized using Raman spectroscopy, a precision scale, and optical microscopy. The proposed stripping solution effectively removes passivation layers more rapidly than conventional cyanide stripping. Weight loss increases linearly for up to 5 min for all 14K gold alloys. Red gold exhibits the greatest weight loss, followed by yellow gold and white gold. The results of microstructural analysis reveal that the conformal stripping occurs according to time. These results imply that the proposed oxidative chloride stripping might replace conventional cyanide stripping.

**Key words** gold stripping, oxidative chloride, 14K gold alloy, passivation layer.

## 1. Introduction

Gold jewelry are typically fabricated by an investment casting process using a gypsum mold.<sup>1)</sup> However, this method forms passivation layers on the surfaces of gold alloy products, which must be removed because the layer increase surface roughness and inhibit mechanical polishing.<sup>2)</sup>

The cyanide stripping has been employed to remove the passivation layers generated by the casting process and improve overall surface quality.<sup>3)</sup> In this method, an as-casted gold alloy is immersed in a solution mixed with cyanide salt like potassium cyanide (KCN) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) at 90 °C, which are used as a complexing agent and oxidant, respectively. It has been reported that passivation layers can be removed effectively by dissolving gold alloy surfaces.<sup>4)</sup> The cyanide stripping process is an economical method based on cheap materials and is very efficient, requiring an overall processing time of less than 15 min. Moreover, this method can easily recover the pure gold from the waste water.<sup>5)</sup> However, cyanide solutions can generate toxic cyanide gases, be fatal to humans, and make wastewater treatment a

difficult task.<sup>6)</sup> Therefore, European countries have restricted the use of cyanide solutions.

To overcome this problem, many researches have proposed alternative processes to cyanide stripping. Burnishing, electro-polishing, and other wet stripping have attracted significant attention as alternative processes. Burnishing is a simple mechanical polishing method that removes passivation layers from as-casted gold product surfaces and improves luster simultaneously.<sup>7)</sup> However, this method is likely to create scratches on product surfaces. Furthermore, if a product has an uneven surface or microscopic holes, abrasives are less effective and some parts of the passivation layer may be left intact.

Electro-polishing is one of methods to remove passivation layers and improve surface roughness. In this method, an as-casted gold product is immersed in an electrolyte and its surface is ionized by applying electrical power.<sup>8)</sup> However, because electrical energy is concentrated along sharp edges, fast dissolution occurs in such parts and the shape of a product is distorted.

Therefore, it is necessary to develop a novel wet stripping method that is more eco-friendly than

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conventional cyanide stripping and can uniformly remove passivation layers while maintaining similar economic and time efficiency compared to the conventional cyanide stripping process. To develop such a wet stripping process, many researchers have proposed various stripping that use solution with acids, oxidants, and complexing agents as main components. One of expected method for substitution of cyanide stripping is chloride stripping, which use solution with chloride ion ( $\text{Cl}^-$ ) given from strong acid, oxidant or complex agent.<sup>9,10</sup> This chloride stripping solution rapidly dissolve solid Au into  $[\text{AuCl}_4]^-$  complex without re-precipitation. Jeffrey et al.<sup>11</sup> compared reaction kinetics between chloride and cyanide stripping processes. They reported that when the concentration of an oxidant is sufficient, chloride stripping can progress faster than cyanide stripping. Baghalha et al.<sup>12</sup> stripped ores containing gold by using stripping solutions with different concentrations of hydrochloric acid (HCl) and hypochlorite ( $\text{OCl}^-$ ). They found that as the concentrations of HCl and  $\text{OCl}^-$  increased, stripping speed also increased. Beglin et al.<sup>13</sup> proposed a gold ore stripping process with HCl and nitric acid ( $\text{HNO}_3$ ) as strong acids and solutions containing ammonium persulfate  $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ ,  $\text{H}_2\text{O}_2$ , and NaOCl (sodium hypochlorite) as oxidants. Although, chlorine gas ( $\text{Cl}_2$ ) was generated at  $\text{pH} < 3.3$ , the gold was stripped successfully. It is also known that  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  with sodium chloride (NaCl) and citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ) complex agents can strip Ag and Ni containing gold alloys by improving the solubility of gold and other metals.<sup>14,15</sup>

Previous researches on oxidative chloride stripping have focused only for gold extraction, but not for removing passivation layer or surface microstructure evolution for 14K gold jewelry. In this study, we conducted oxidative chloride stripping to remove passivation layers of as-casted 14K yellow gold (YG), red gold (RG), and white gold (WG) using HCl and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  as a strong acid and oxidant, respectively. We checked optimal  $[\text{HNO}_3]/[\text{HCl}]$  ratio at a given oxidants and complex agents, and then verified stripping effects quantitatively on YG, RG, and WG with optimized stripping solution. The optimized stripping solution was then used in stripping

processes for 14K YG, RG, and WG. The removal of passivation layers, weight loss, and microstructures were analyzed to verify stripping effects quantitatively.

## 2. Experimental Procedure

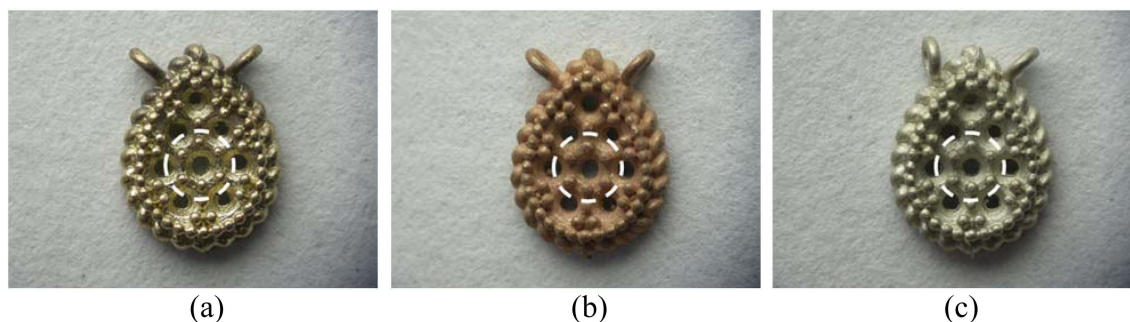
Fig. 1 shows a fabricated gold alloy samples having eight oval holes and 21 prongs with diameters of 0.25 mm and 0.1 mm, as shown in dotted circles. All samples had common dimensions of  $7.2 \times 6.0 \times 1.5$  mm and were fabricated using the conventional investment casting process. The samples all had the same design, but were casted with different alloy compositions, namely (a) YG, (b) RG, and (c) WG. These samples include uneven surface and complex shaped oval holes and prongs, which requiring wet stripping to remove passivation layers.

Table 1 lists the detailed elemental compositions of the 14K YG, RG, and WG samples presented in Fig. 1. Depending on the compositions of samples, various colors of yellow, red, and white can be obtained.<sup>16</sup> It was expected that unstable alloying elements like Cu and Zn would form passivation layers through the surface reactions with gypsum.

As shown in Table 2, four types of stripping solutions were prepared with different molar fractions of acids. Solution types 1, 2, 3, and 4 have  $[\text{HNO}_3]/[\text{HCl}]$  values of zero, one, two, and three, respectively. The acid and oxidant contents are 2.56 M and 0.32 M, respectively. Contents of NaCl and  $\text{C}_6\text{H}_8\text{O}_7$ , which were used as a complex agent, are fixed at 0.684 M and 0.104 M respectively. The prepared stripping solutions were heated to 90 °C and 14K YG samples were immersed in the solutions. The stripping process lasted for 3 min. Additionally, the solution yielding the greatest weight

**Table 1.** Composition of prepared 14K alloys. (wt %)

14K Alloy type	Au	Ag	Cu	Zn	Ni
Yellow gold (YG)	58.5	2.3	29.7	9.5	-
Rose gold (RG)	58.5	2.5	38.2	0.8	-
White gold (WG)	58.5	-	29.1	7	5.4



**Fig. 1.** As-casted 14K (a) YG, (b) RG, (c) WG.

**Table 2.** Composition of stripping solution in this study.

[M]

Solution Type	[HNO <sub>3</sub> ]/[HCl]	Chemical composition				
		Acid composition		Oxidant	Complex agent	
		HCl	HNO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	NaCl	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>
Type 1	0	2.56	-	0.32	0.684	0.104
Type 2	1	1.28	1.28	0.32	0.684	0.104
Type 3	2	0.85	1.71	0.32	0.684	0.104
Type 4	3	0.64	1.91	0.32	0.684	0.104

loss was used for stripping 14K RG and WG samples for 5 min under the same conditions. For comparison, the cyanide stripping process reported by Grimwade<sup>4)</sup> was applied to the same gold alloys. This cyanide stripping process utilized a mixed 90 °C solution of KCN and H<sub>2</sub>O<sub>2</sub>. The same process was repeated twice.

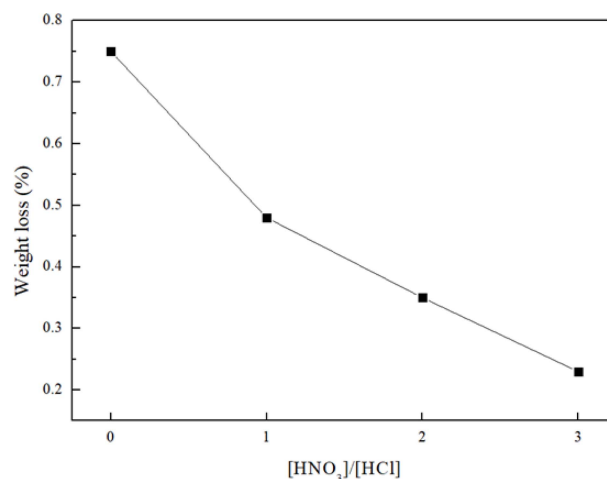
Micro Raman spectroscopy (UniRaman, Unithink) was used to analyze the compositions of the passivation layers before and after stripping with a 531 nm light source. Measurements were repeated 15 times and exposure lasted for 5 min. To analyze variations in weight loss according to stripping time, the samples were measured to an accuracy of five decimal places using a sensitive scale (AS 60/220/C/2, Radwag). Changes in microstructure according to stripping were observed using optical microscopy (AX-10, ZEISS).

### 3. Results and Discussion

Fig. 2 shows the weight loss of 14K YG during 3 min stripping processes with different concentrations of strong acids in the stripping solutions. Following the 3 min stripping processes, the weight losses are 0.75 %, 0.47 %, 0.35 %, and 0.23 % for the [HNO<sub>3</sub>]/[HCl] values of zero, one, two, and three, respectively. As the ratio of [HNO<sub>3</sub>]/[HCl] decrease, that means [HCl] increases, weight loss also increases. This is because an increase in HCl concentration is accompanied by an increase in Cl<sup>-</sup> concentration, resulting in a greater stripping rate.

It is known that because the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> used as an oxidant generates Cl<sub>2</sub> from Cl<sup>-</sup>, a stripping solution contains Cl<sub>2</sub>/Cl<sup>-</sup>.<sup>13)</sup> According to Diaz et al.,<sup>17)</sup> because Cl<sub>2</sub>/Cl<sup>-</sup> contributes to dissolving gold by generating [AuCl<sub>4</sub>]<sup>-</sup> complexes, an increase in Cl<sup>-</sup> concentration is accompanied by an increase in stripping rate.

We also found that as the HCl concentration increases, the Cl<sup>-</sup> concentration increases, increasing the stripping rate of gold.<sup>18)</sup> Meanwhile, because the NO<sub>3</sub><sup>-</sup> generated from HNO<sub>3</sub> does not form a complex with gold, it significantly does not affect the stripping rate. Consequently, the case of [HNO<sub>3</sub>]/[HCl] = 0 (type 1 solution) yields the greatest weight loss.

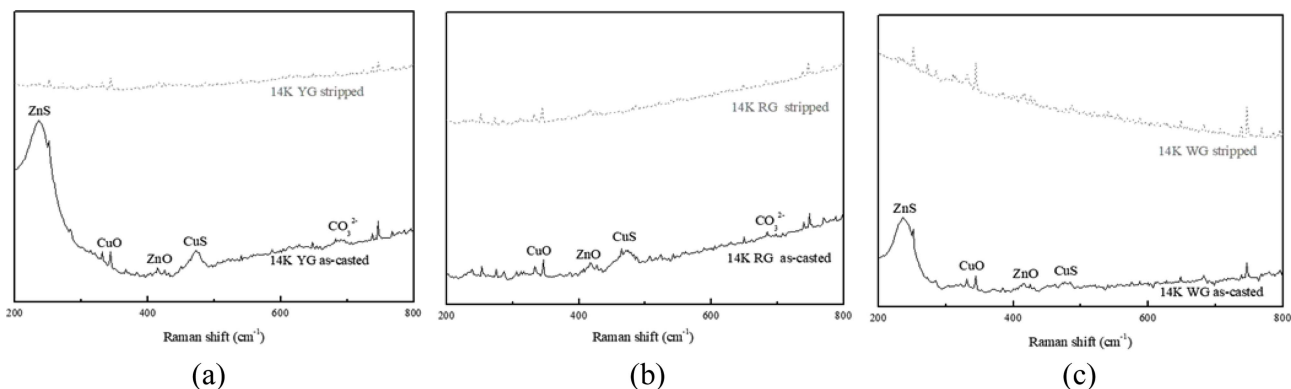


**Fig. 2.** Weight loss according to [HNO<sub>3</sub>]/[HCl].

Fig. 3 shows the Raman spectroscopy analysis results for 14K YG, RG, and WG samples before and after stripping processes using the type 1 solution with [HNO<sub>3</sub>]/[HCl] = 0. In the graph, the x axis represents the Raman shift and the y axis represents relative intensity. The Raman results for an as-casted sample are presented in the lower part of the graph and those for samples stripped for 5 min are presented in the upper part.

Fig. 3(a) indicates the Raman results for 14K YG before and after stripping. Before stripping, peaks of ZnS, CuO, ZnO, CuS, and CO<sub>3</sub><sup>2-</sup> are identified. This result is the same as that found by Ingo et al.,<sup>19)</sup> who noted the presence of Cu(II) and Zn(II) passivation layers on the surfaces of as-casted gold products. Additionally, the peak for CO<sub>3</sub><sup>2-</sup> can be attributed to the presence of CaCO<sub>3</sub>, which is a gypsum flask component. This result is the same as that found by Phetrattanrangsi et al.,<sup>2)</sup> who noted the formation of a CaCO<sub>3</sub> layer on the surfaces of gold alloys immediately after casting. After stripping, the ZnO, CuS and CO<sub>3</sub><sup>2-</sup> peaks are no longer visible. These results are caused by the removal of passivation layers during stripping. However, the CuO peak remains.

Fig. 3(b) shows the Raman results for 14K RG before and after stripping. Similar to the results above for YG, CuO, ZnO, CuS, and CO<sub>3</sub><sup>2-</sup> are identified. However, ZnS



**Fig. 3.** Results of Raman spectroscopy analysis stripping with type 1 solution; 14K (a) YG, (b) RG, (c) WG.

is not visible. This is because the elemental composition of RG contains only a small amount of Zn. After stripping, similar to the YG, the ZnO, CuS and  $\text{CO}_3^{2-}$  peaks are eliminated, but the CuO peak remains. These results indicate that the passivation layer was removed.

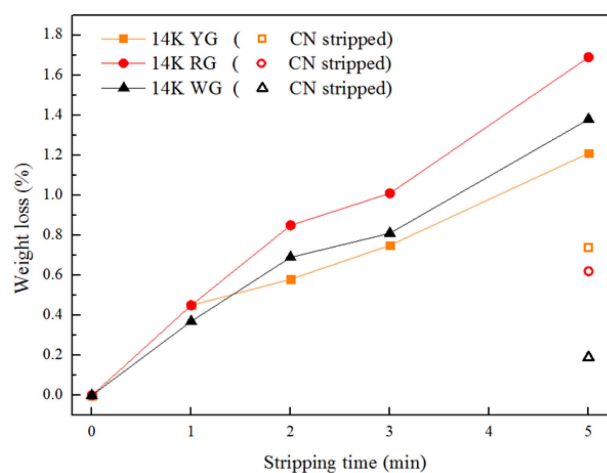
Fig. 3(c) shows the results for 14K WG. Again, CuO, ZnO, and CuS are visible and the ZnO and CuS peaks are eliminated after stripping, demonstrating that the passivation layers were removed.

The stripping process successfully removed the passivation layers from all three alloys. However, CuO, which was one of the components of the passivation layers, remained. According to Bello et al.,<sup>20)</sup> a dissolved Cu forms a  $\text{Cu}(\text{OH})_4^{2-}$  complex, then transforms into a CuO at high temperatures. Based on this report, we concluded that stripped Cu is regenerated into CuO on the sample surfaces.

Fig. 4 shows the weight loss of 14K YG, RG, and WG samples over time in stripping processes using a solution with  $[\text{HNO}_3]/[\text{HCl}] = 0$ . One can see that stripping time is linearly proportional to weight loss.

In the case with 1 min of stripping, the 14K YG, RG, and WG samples exhibit weight losses of 0.25 %, 0.35 %, and 0.28 %, respectively. These values are within the margin of error from each other. However, when stripping proceeds for 2 min, there are clear differences in weight loss between the alloys. With extended stripping time, 14K RG exhibits the greatest weight loss, followed by WG and YG. The differences in weight loss between the alloys are attributable to differences in the reduction potentials, compositions, and atomic densities of major alloying elements.

The standard reduction potentials for Cu, Ni, and Zn are 0.34 V, -0.23 V, and -0.76 V, respectively.<sup>21)</sup> Therefore, as far as reduction potential is concerned, Zn is stripped relatively quickly, while Cu is stripped more slowly. As shown in Table 1, the 14K YG, RG, and WG samples contain similar contents of Au and Ag. However, the contents of alloying elements (Cu, Zn, and Ni) are



**Fig. 4.** Weight loss of 14K alloys stripped with type 1 solution according to stripping time.

significantly different between the alloys. In YG, the mass fractions of Cu and Zn are 29.7 wt% and 9.5 wt%, respectively. In RG, the fractions of Cu and Zn are 38.2 wt% and 0.8 wt%, respectively. In WG, the fractions of Cu, Zn, and Ni are 29.1 wt%, 7.0 wt%, and 5.4 wt%, respectively. The atomic densities of Cu, Ni, and Zn are 8.96, 8.90, and 7.14  $\text{g}/\text{cm}^3$ , respectively. Cu exhibits the largest atomic density, followed by Ni and Zn.

Comparing RG and YG, Cu and Zn exhibit significant concentration differences. RG has a higher Cu content than YG, but contains little Zn. Accordingly, in the case of RG, Zn content is negligible and Cu, which is a heavier element, is removed more quickly. In the case of YG, because Zn has a lower reduction potential, Zn is removed more quickly. Consequently, RG has a faster stripping rate than YG.

When comparing WG and YG, Ni and Zn exhibit significant concentration differences. WG has a lower content of Zn and higher content of Ni. YG has a high content of Zn but does not contain Ni. Accordingly, in



the case of WG, Zn, which has a lower concentration, is removed quickly, followed by Ni, which is heavier. In the case of YG, it is expected that Zn will be preferentially removed for a significant duration. Consequently, WG has a faster stripping rate than YG. Similarly, comparing RG and WG, Zn exhibits a significant concentration difference. RG contains little Zn, while WG has high Zn content. Accordingly, in the case of RG, Cu, which is a heavier element, is removed more quickly. In the case of WG, Zn, which is a lighter element, is removed more quickly. Consequently, RG has a faster stripping rate than WG.

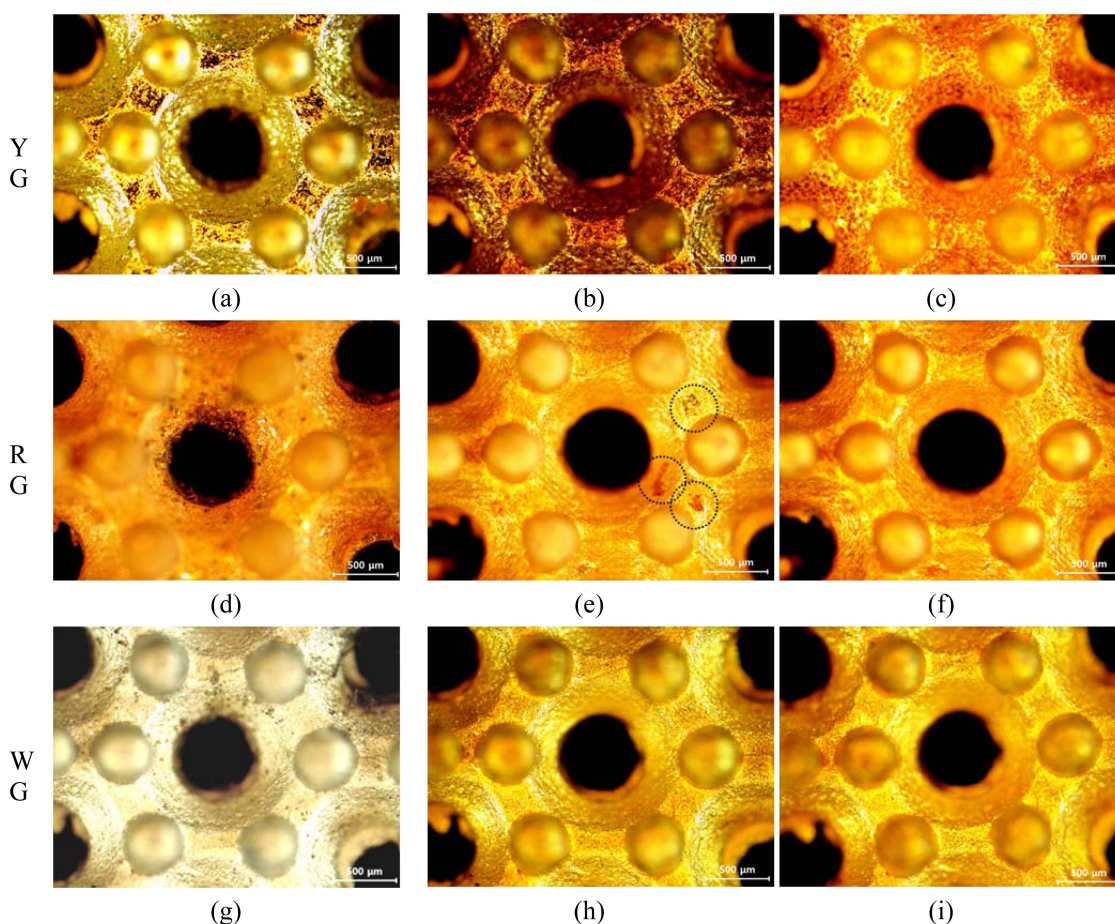
When the conventional cyanide stripping process is applied, 14K YG, RG, and WG exhibit weight losses of 0.74 %, 0.62 %, and 0.19 %, respectively, as shown in blanks in the graph. In this study, similar results were obtained by applying the chloride stripping solution to YG for 4 min, RG for 2 min, and WG for 1 min. In other words, the chloride stripping method proposed in this paper can produce similar results to those of the conventional cyanide stripping method in a shorter time. Furthermore, because cyanide stripping requires the

immersion of gold products until eruptive bubbles are generated, controlling reaction time is difficult. In contrast, the proposed chloride stripping method enables reaction time to be controlled precisely. Therefore, the proposed chloride stripping method can remove passivation layers in a shorter time with less weight loss.

Fig. 5 shows microstructure images of different alloys according to stripping time. Those are the magnified by 50 times image of the areas in the dotted lines in Fig. 1.

Fig. 5(a), (b), and (c) represent the microstructures image of 14K YG samples after casting and after stripping for 1 min and 5 min, respectively. Fig. 5(a) reveals that there is a passivation layer with different colors between an oval hole and prong on the as-casted sample. In Fig. 5(b), brightness decreases over 1 min of stripping. This is because the rapid initial stripping of YG results in a difference in surface brightness Fig. 5(c) presents sample images after 5 min of stripping, revealing an increase in brightness. This is because the passivation layer is removed by the stripping process, resulting a more uniform surface.

In the case of 14K YG, 5 min of stripping completely removes the passivation layer and stripping must be



**Fig. 5.** Micro structure of alloys stripped with type 1 solution; 14K YG stripped for (a) 0 min, (b) 1 min, (c) 5 min, 14K RG stripped for (d) 0 min, (e) 1 min, (f) 5 min, 14K WG stripped for (g) 0 min, (h) 1 min and (i) 5 min.

conducted for at least 1 min.

Fig. 5(d), (e), and (f) show magnified images of 14K RG samples that were obtained after 0 min, 1 min, and 5 min of stripping, respectively. For the sample with 1 min of stripping, the area surrounded by dotted lines represents the residue of the passivation layer. After 5 min of stripping, the passivation layer was completely removed. Although the surface luster decreases during stripping due to excessive etching, subsequent mechanical polishing processes can easily increase surface luster.

Fig. 5(g), (h), and (i) show the microstructures of 14K WG samples that were photographed immediately after stripping for 0 min, 1 min, and 5 min, respectively. After 1 min of stripping, the passivation layer of the sample is almost removed. In case of 5 min stripping, the layer was completely removed. Therefore, in the case of 14K WG, 1 min of stripping is sufficient to remove most of the passivation layer. When the stripping process is performed, the surface color of WG turns yellowish. It is because Zn and Ni, which are bleaching agents, are removed first, and thus the yellow color of Au becomes dominant. When subsequent mechanical polishing processes generate a uniform surface finish, the color should change back to white.

In summary, when 14K YG, RG, and WG samples are stripped, 5 min of stripping is appropriate for YG and RG, while 1 min of stripping is sufficient for WG.

#### 4. Conclusion

We proposed a novel 14K gold alloy stripping solution consisting of acids, oxidants, and complexing agents.

When chloride stripping solutions with different molar fractions of HCl and HNO<sub>3</sub> were applied to 14K YG, the maximum stripping rate was achieved by adding HCl alone. When stripping process using the proposed solution [HCl, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, NaCl, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>] was applied to 14K gold alloys with different colors of YG, RG, and WG passivation layers were removed in approximately 3 min. The stripping rate increased linearly over time. RG exhibited the greatest stripping rate, followed by WG and YG. Stripping rates vary because the alloying elements in each alloy have different reduction potentials, compositions, and atomic densities. The microstructure changes in all alloys revealed that the majority of a passivation layer could be successfully removed within 1 min of stripping, followed by conformal etching. The proposed oxidative chloride stripping can replace the cyanide process by providing less weight loss and stripping time.

#### References

1. S. Pattnaik, D. B. Karunakar and P. K. Jha, *J. Mater.*

*Process Tech.*, **212**, 2332 (2012).

2. T. Phetrattanrangi, C. Puncreobutr, A. Khamkongkao, C. Thongchai, B. Sakkomolsri, S. Kuimalee, P. Kidkhunthod, N. Chanlek and B. Lohwongwatana, *Thermochim. Acta*, **657**, 144 (2017).
3. J. V. Lorea, T. F. O'Rourke, US patent 2,612,898 (1952).
4. M. Grimwade, *Gold Technol.*, **26**, 16 (1999).
5. M. E. Wadsworth, X. Zhu, J. S. Thompson and C. J. Pereira, *Hydrometallurgy*, **57**, 1 (2012).
6. S. S. Konyratbekov, A. Baikunurova and A. Akcil, *Miner. Proc. Ext. Met. Rev.*, **36**, 198 (2015).
7. S. Alviti, In processing 23rd Santa Fe Symposium Jewelry Manufacturing Technology, (New Mexico, USA, 2003) p.25.
8. S. I. Galanin and I. V. Kalinnikov, *Surf. Eng. Appl. Electrochem.*, **44**, 359 (2008).
9. G. Senanayake, *Miner. Eng.*, **17**, 785 (2004).
10. X. H. Wang, In processing 3rd international symposium Electrochemistry in Mineral and Metal Processing, (1992) p.425.
11. M. I. Jeffrey, P. L. Breuer and W. L. Choo, *Metall. Mater. Trans. B*, **32B**, 979 (2001).
12. M. Baghalha, *Int. J. Miner. Process.*, **82**, 178 (2007).
13. E. G. Baglin, J. M. Gomes, T. G. Carnahan and J. M. Snider, United States Department of the Interior, Bureau of Mines Report of Investigation 8970 (1985).
14. A. Alzate, M. E. Lopez and C. Serna, *Waste Manag.*, **57**, 113 (2016).
15. F. D. R. Thesauro, V. Brusica, C. C. Thompson and B. P. Bayer, US Patent 7,161,247 (2007).
16. C. Cretu and E. V. D. Lingen, *Gold Bull.*, **32**, 15 (1999).
17. M. A. Diaz, G. H. Kelsall and N. J. Welham, *J. Electroanal. Chem.*, **361**, 25 (1993).
18. J. Vinals, C. Nunez, and O. Herreros, *Hydrometallurgy*, **38**, 125 (1995).
19. G. M. Ingo, G. Chiozzini, V. Faccenda, E. Bemporad and C. Riccucci, *Thermochim. Acta*, **321**, 173 (1998).
20. A. Bello, D. D. Arhin, K. Makgopa, M. Fabiane and N. Manyala, *Am. J. Mater. Sci.*, **4**, 64 (2014).
21. J. O. Marsde and C.L. House, *The chemistry of gold extraction*, 2nd ed., p.118 (2006).

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