[논　문] 한국재료학회지
Korean J. Mater. Res.
Vol. 28, No. 4 (2018)

https://doi.org/10.3740/MRSK.2018.28.4.221

Properties of the Green Gold Alloys with Indium Content

Jeongho Song and Ohsung Song†

Department of Materials Science and Engineering, University of Seoul

(Received February 2, 2018 : Revised March 19, 2018 : Accepted March 19, 2018)

Abstract The property changes of 18, 14, and 8K green gold alloys for jewelry are observed by adding 0.0, 3.0, and 5.0 wt% of indium (In), respectively. To check the composition of the alloys, an energy dispersive spectroscopy (EDS) analysis is conducted. Color and microstructure analysis is executed through bare-eye, macro camera, UV-VIS-NIR-colormeter, and optical microscope. The melting point, wetting angle, and hardness are measured using TGA-DTA, a wetting angle tester, and a Vickers hardness tester. The EDS analysis result demonstrates that each of the green gold alloys was manufactured with purposed contents. The color analysis result shows that the color of the alloys is similar to the color of the conventional 4 wt%-Cd 18K green gold, and the green color improves as the In content increases. The micro structure analysis result demonstrates that grain refinement improves as the amount of In increases. Enhancements in the melting point, wettability, and Vickers hardness changes appear as the In content increases and Au content decreases. The hardness is up to 260, which implies good durability. Therefore, the results suggest that the proposed 18, 14, and 8K In-added green gold alloys enhance the properties of jewelry products with regard to the green color, castability, and durability.

Key words gold alloys, green gold, wetting angle, color difference.

1. Introduction

Usually, 14 and 18K Au-Ag-Cu alloys containing 58.5 and 75.0 wt% of Au are used to enhance the hardness and strength by solid solution strengthening to achieve durability for jewelry usage.[1,2] In the past, an 18K alloy containing 75.0 wt% of Au was in the market; however, jewelry with 14K (Au 58.5 wt%) alloy has formed the largest market lately due its decreased manufacturing cost.[3] Also, the development of 5K (Au 20.8 wt%) and 8K (Au 33.3 wt%) alloys are in progress according to the increasing cost of gold, and the alloys with a low content of Au should maintain similar quality in color from the alloys with a high content of Au.

Meanwhile, the colored gold alloy with a new color is gaining interest along with economic feasibility. Not only yellow, white, and red golds are of interest, but also purple, blue, and green golds as well. It is difficult to use purple and blue golds for jewelry due to the color formation that occurs by the intermetallic compounds, such as $AuAl_2$ and $AuIn_2$; while, the desired color reveals by alloying Al and In with gold respectively.[4] Since the green gold alloys can be fabricated with Au-Ag-Cu ternary alloy elements, it is expected that they will show similar properties even with the conventional jewelry casting facilities.

In general, the origin of the colored alloy has been reported due to the difference in the absorbance of the photon according to the surface fermi energy level difference when the interaction between the metal surface electron and light occurs.[5] In other words, the surface incidence energy affects the visible light range within a range of 1.5~3.1 eV in revealing metal color. Yellow-colored pure Au shows up to 2.3 eV of high reflectance relevant to the red and yellow color, and all other visible light range is absorbed. It was reported that alloy elements, such as Ag, Zn, Pd, Cd, and Mn, affect the surface fermi energy level.

The green gold can be manufactured even with a low gold content. A pale greenish-yellow color can be revealed in alloys that range of 42.0~48.0 wt% Ag with an 8K composition according to the Au-Ag-Cu ternary phase diagram.[2] However, there is still no report indicating the quantification of the color and properties of the green

†Corresponding author
E-Mail : songos@uos.ac.kr (Ohsung Song, Univ. of Seoul)

gold that contains this low of a gold content.

Cretu et al.,[4] reported that the light green colored alloy through the 75Au-23Cu-2Cd alloy and dark green colored alloy through the 75Au-15Ag-6Cu-4Cd alloy can be revealed. Green golds with various green colors were suggested by controlling the amount of Cd in 18K gold alloy. However, this method should be excluded; because the elution of a harmful element could happen easily by sweat from the human body. Leach et al.,[6] reported the manufacturing of green colored alloy of a 75Au/6~7Ag/9~11.7Cu/Zn composition for an 18K green gold without Cd addition since the enhancement of a index (–1.5~–3.0) which is related to the green color in the CIE Lab scale. Meanwhile, Victor et al.,[7] manufactured green gold alloy successfully with 50Au/12Cu/1Ti/Mn/Ag as reduced Au content without Cd by considering economic feasibility. However, the possibility of creating green gold through only Au-Ag-Cu elements without the Cd element was not verified.

As mentioned above, for popularization of new green gold alloy with low Au content and no Cd content: 1) a green color should be revealed; 2) the melting point should be under 1,000 ^oC to use the conventional melting equipment with comparing typical gold alloys; 3) excellent wettability of the gypsum flask is required for the casting process; and, 4) excellent hardness is required for durability in use.

Meanwhile, In can replace Cd and reveal other colors on Au besides yellow as it partially shifts the surface reflection energy. In has a low melting temperature of 156.6 ^oC; thus, it can reduce the consumption of energy by lowering the melting point during alloying. Also, the enhancement of castability is expected during the casting process, which is an investment for product manufacturing due to the good wettability of molten alloy. Enhancement of the durability of the final product is expected by the solid solution strengthening, due to 15.9 % of the atom radius difference between In and gold.[8] In this research, property changes and the possibility of revealing a green color in 18, 14, and 8K gold alloys with In addition were confirmed.

2. Experimental Procedure

Table 1 provides the composition of 10 green gold samples. Sample #1 is a conventional 18K green gold alloy with 4 wt%-Cd.[4] Then, an 18K (samples #2-#4), 14K (samples #5-#7), and 8K (samples #8-#10) samples were prepared with 0.0, 3.0, and 5.0 wt% of In, respectively. Each sample was manufactured with prepared alloys as weighed and melted with borax by using a LPG-oxygen torch in a magnesia crucible in the atmosphere.

To check the quantitative composition of the green gold alloys, a mapping mode analysis was conducted by magnifying by 1K with 20KV of voltage and maintaining 10 mm of working distance through the energy dispersive X-ray spectroscopy(EDS; JEOL, JSM-6010PLUS/LA model).

Optical microscopy(GIA Instruments, 815000 model) was used to check the macro images and color of the green alloys under an overhead light. A digital camera (Nikon, Coolpix4500 model) attached to an ocular was used to obtain optical microscopy images.

Reflectance was measured by using UV-VIS-NIR (Shimadzu, UV-3105PC model) in the reflectance mode at slit size 5, medium scan speed, and 380~780 nm of visible light range to check the color change in each sample according to the amount of added In. Afterwards, the Lab index was obtained by using the Color Analysis program, and the color was compared with the conventional 4.0 wt%-Cd 18K green gold.

High magnification optical microscopy(Carl Zeiss, AXIO-

Table 1. Sample description for green gold. [wt%]

Sample No. \ Elements	Au	Ag	Cu	In	Cd	Total	Note
1	75.0	15.0	6.0	0.0	4.0	100.0	18K-Cd4.0wt%
2	75.0	20.0	5.0	0.0	-	100.0	18K-In0.0wt%
3	75.0	12.0	5.0	3.0	-	100.0	18K-In3.0wt%
4	75.0	15.0	5.0	5.0	-	100.0	18K-In5.0wt%
5	58.5	32.0	9.5	0.0	-	100.0	14K-In0.0wt%
6	58.5	32.0	6.5	3.0	-	100.0	14K-In3.0wt%
7	58.5	30.0	6.5	5.0	-	100.0	14K-In5.0wt%
8	30.0	45.0	25.0	0.0	-	100.0	8K-In0.0wt%
9	30.0	42.0	25.0	3.0	-	100.0	8K-In3.0wt%
10	30.0	40.0	25.0	5.0	-	100.0	8K-In5.0wt%

A1 model) was used to check the micro structure of each sample at 500x magnification. The surface of each sample was observed after polishing and 10 seconds of etching by an aqua-regia solution.

A TGA-DTA(Shimadzu, DTG-60 model) analysis was proceeded to check the melting point of each sample. For this analysis, 30 mg of the sample was used at a temperature range of 20~1100 °C while increasing it by 20 °C/minute in each condition. The analysis was conducted in a N_2 atmosphere to minimize the error range due to oxidation. The melting point was selected by choosing the valley point in the centraflexure curve from the endothermic reaction by melting.

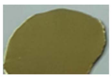
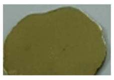
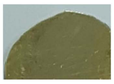
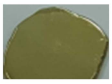
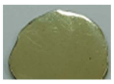
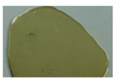
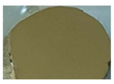
The wettability was checked to confirm the castability. 0.30 g of alloy was positioned on the gypsum mold for the cast and melt in 1100 °C for 10 minutes, by increasing the temperature incrementally by 10 °C/minute using an electric furnace(Thermotec Co., SK1700-B30 model) in air atmosphere. The cap type solid sample contacting the cast was obtained from the melt, and the wetting angle was determined after the optical image was such that the light went through from the back side of the solid sample.

Vickers hardness of the green gold alloy sample was measured by using a micro Vickers hardness tester (Mitutoyo, MVK-H1 model). The value was measured while the sample was loaded with 0.5 kgf of force for 15 seconds. The hardness was determined by the average value of the three measurements for each sample in order to decrease the error rate.

Table 2. EDS results of Au and In contents in green gold samples. [wt%]

Element \ Sample No.	2	3	4	5	6	7	8	9	10
Au(t)	75.00	75.00	75.00	58.50	58.50	58.50	30.00	30.00	30.00
Au	75.37	75.22	75.31	59.78	58.91	59.91	30.03	30.12	30.09
In(t)	0.00	3.00	5.00	0.00	3.00	5.00	0.00	3.00	5.00
In	ND	2.74	4.46	ND	2.79	4.85	ND	2.88	4.92

Table 3. Lab color index results and macro images of green gold alloys.

Sample No.	Sample Description	Macro Images	L	a	b	Color Difference
1	18K-Cd 4.0 wt%		92.31	−2.68	24.19	0.00 (reference)
2	18K-In 0.0 wt%		91.96	−0.91	23.23	2.04
3	18K-In 3.0 wt%		93.12	−1.91	25.62	1.81
4	18K-In 5.0 wt%		93.30	−2.79	22.09	2.32
5	14K-In 0.0 wt%		91.14	−2.68	23.51	1.35
6	14K-In 3.0 wt%		92.70	−2.84	23.26	1.02
7	14K-In 5.0 wt%		92.31	−2.96	24.19	0.28
8	8K-In 0.0 wt%		91.45	−1.30	18.36	6.05
9	8K-In 3.0 wt%		92.01	−1.77	18.46	5.81
10	8K-In 5.0 wt%		91.15	−1.80	19.51	5.38

3. Results and Discussion

The proposed amount of added Au and In ('t') in each of the manufactured green gold alloys and actual EDS measurement results are provided in Table 2. In the case of the Au element, a small '+' error occurred according to the partial oxidation of the alloying elements, except for Au, in the melting process with a LPG-oxygen torch. However, this error could be ignored considering the measurement error range of the EDS equipment. Therefore, the green gold samples in this study were prepared successfully with the proposed composition even with a typical torch melting process.

Table 3 provides each macro image and Lab color index. From the results of the macro image, a green color was revealed and all the In-samples displayed a green color as well in the case of 4.0 wt%-Cd 18K green gold as the reference sample. There was no green color difference through bare-eye observation.

From the Lab index result, 92.31/-2.68/24.19 were shown in the case of 4.0 wt%-Cd 18K green gold, and the other alloys had over 90 of the 'L' values and negative 'a' values. Usually, metal alloys have over 90 of the 'L' values due to the high reflection and negative 'a' values, which indicates a green color while the positive value implies a red color.[9)]

Therefore, the revealing of the green color was observed to be the same as the macro image results in the Lab index from each alloy. Distinguishing the color difference with bare-eye was difficult since the color difference between the reference 4.0 wt%-Cd 18K green gold had a small value of 6.05.

Meanwhile, the enhancement of green color occurred as the 'a' index increased to a negative value according to the increase in additional In in the gold content in each composition. When Ag was added into pure Au, the green color revealed due to the reflecting energy shifts to a high value.[4)] And, by adding the In partially instead of Ag, this value increased. For this reason, it was considered that the green color was enhanced due to the increase in In content, which replaced part of the Ag, and improved the reflectance at a higher energy level than the Au-Ag binary alloy.

Fig. 1 displays the optical images for the observation of the grain size of the green gold alloys. They are shown according to the amount of added In in each of the different contents of gold.–In the case of 18K green gold, the grain size decreased as the In content increased. The average grain sizes were 34, 26, and 24 μm as the In content increased to 0.0, 3.0, and 5.0 wt% respectively. In the case of 14K green gold, the grain size decreased to 82, 46, and 17 μm as the In content increased to 0.0, 3.0, and 5.0 wt% respectively. In the case of 8K green gold, the grain size also decreased to 33, 29, and 21 μm as the In content increased.

This phenomenon corresponds with the report from Becerra et al.,[10)] that the grain size decreases as the amount of added In increases in Mg-In alloy. Also Song

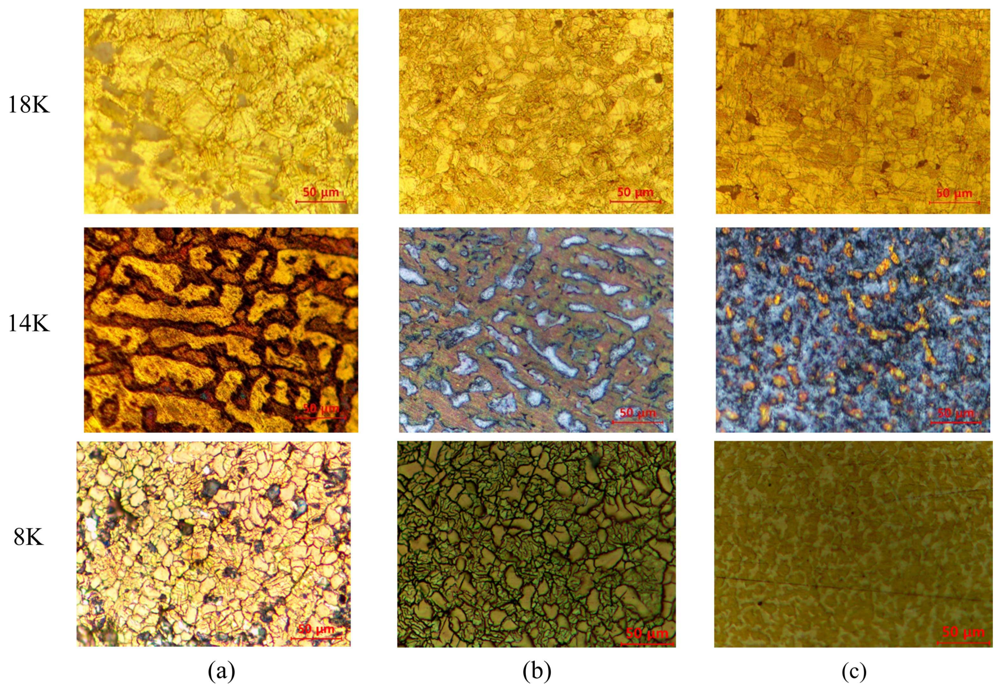


Fig. 1. Optical microscopy images of 18, 14, and 8K green gold with In (a) 0.0 wt%, (b) 3.0 wt%, and (c) 5.0 wt%.

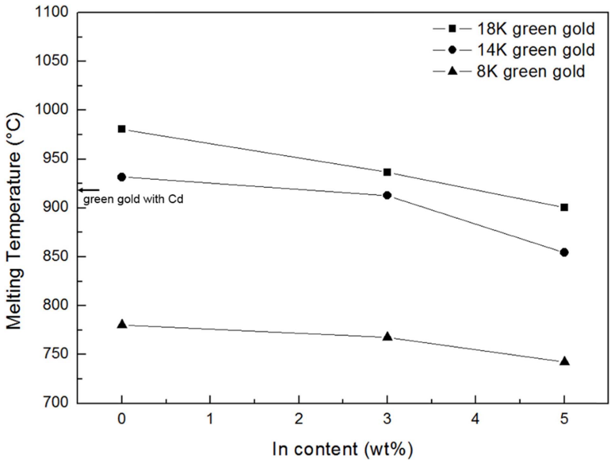


Fig. 2. Melting temperature results of green gold alloys.

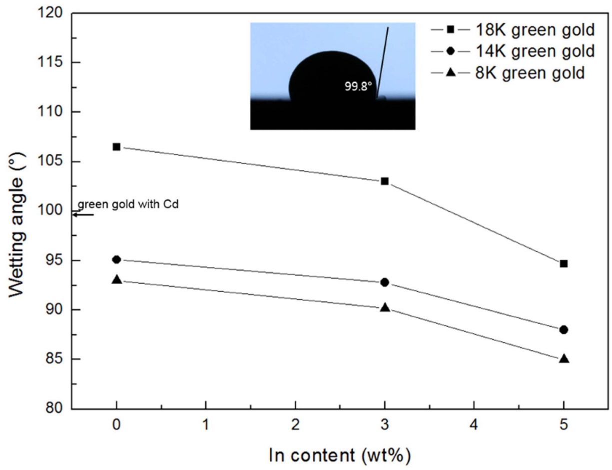


Fig. 3. Wetting angle results of green gold alloys.

et al.,[8] reported that In addition affects the grain refinement. The grain size decreased to 12 μm from 43.4 μm as the In increased up to 5.0 wt% in the red gold alloys. Therefore, the grain size of the green gold alloy decreased as the amount of the In increased.

Fig. 2 displays the change in the melting point in the TGA-DTA analysis of the green gold alloy for each composition. An arrow shown in the Y-axis indicates the melting point of the 4.0 wt%-Cd 18K green gold. In the case of 18K green gold, the sample without In had a melting point of 980.67 °C, and the melting point decreased to 936.65 and 900.44 °C when 3.0 and 5.0 wt% of In were added, respectively. In the case of 14K green gold, the melting point decreased to 931.70, 912.85, and 854.27 °C when 0.0, 3.0, and 5.0 wt% of In were added, respectively. In the case of 8K green gold, the melting point decreased to 780.21, 767.48, and 742.55 °C as the In increased. Eventually, the green gold alloys had a property that lowers melting point as the In content increased and Au decreased. Therefore, the conventional casting facility process could be employed due to each alloy having a melting point under 1,000 °C, which is a typical casting temperature for equipment.

The result of the wetting angle of the green gold alloy for each composition is provided in Fig. 3. In the case of 18K green gold, 106.5, 103.0, and 94.7° resulted as In increased to 0.0, 3.0, and 5.0 wt%, respectively. In the case of 14K, the wettability was enhanced as well according to the increase in the In content. In the case of 8K, the wetting angle was relatively low compared to 14K and 18K, and better wettability was exhibited as the In content increased. Meanwhile, the wetting angle of 4.0 wt%-Cd 18K green gold was 99.8° which was greater than all 14K, 8K, and 18K-5.0 wt% In samples.

There is applicability of the casting process for all green gold alloys in this experiment according to the report from Baumeister et al.,[11] that the casting process is possible by the capillary effect in real product manufacturing even though general gold alloys have over 140° of a wetting angle. Particularly, better castability was expected for green gold alloys with higher In content. Therefore, better wettability was expected in In-green gold alloys compared to 4.0 wt%-Cd 18K green gold due to the low Au content and increased In content.

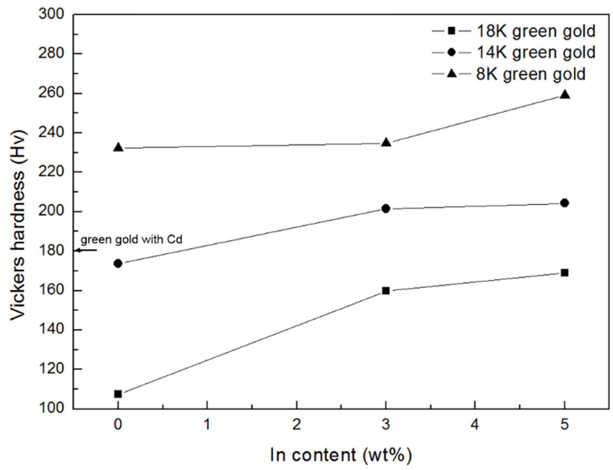


Fig. 4. Vickers hardness results of green gold alloys.

Fig. 4 provides the Vickers hardness results of each alloy. In the case of 18K green gold, the hardness increased to 107.3, 159.8, and 169.0 when the In contents increased to 0.0, 3.0, and 5.0 wt%, respectively. In the case of 14K green gold, the hardness was enhanced as the amount of inserted In increased as well, and the maximum hardness value was 204.3 at 5.0 wt% of In. In the case of 14K green gold, a better hardness value was observed than 14K and 18K, and the maximum hardness value was 259.3 according to the increases In content.

Increasing hardness according to the increase in the In content would be caused by solid solution strengthening and grain refinement as displayed in the aforementioned microstructure analysis results. Meanwhile, 14K green gold alloys with over 3.0 wt% of In and all 8K green gold alloys had better hardness compared to the arrow on Y-axis, which indicates 180.7 for the 4.0 wt%-Cd 18K green gold. The Vickers hardness of usual 18K yellow gold is between 150 and 200.[12] All green gold alloys containing In in each composition was expected to have better or equal durability than the conventional yellow and red gold alloys.

4. Conclusion

A change in the properties of 8, 14, and 18K green gold alloys for jewelry usage was confirmed by replacing 4.0 wt%-Cd and adding 0.0, 3.0, and 5.0 wt% of In, respectively. There was no difference in color according to the bare-eye between all of the In added to the green gold samples and 4 wt%-Cd 18K green gold. The enhancement of hardness and wettability and decrease in the melting point were observed as the In increased with a low Au content. Therefore, all of the suggested 18, 14, and 8K In added to green golds exhibited better properties in revealing green color, applicability of the casting process, and durability compared to the conventional Cd-added green gold alloy.

Acknowledgement

This work(Grants No. C0512925) was supported by the Business for Cooperative R&D between Industry, Academy and Research Institute funded the Korea Small and Medium Business Administration in 2017.

References

1. K. E. Saeger and J. Rodies, Gold Bull., **10**, 10 (1977).
2. W. S. Rapson, Gold Bull., **23**, 125 (1990).
3. J. Smith, Honor Thesis (in English) p.19, Ball State University, Muncie (2008).
4. C. Cretu and E. Lingen, Gold Bull., **32**, 115 (1999).
5. K. Yonemitsu, Precious Metals Science and Technology., p13, ed. L.S. Benner, T. Suzuki, K. Meguro and S. Tanaka, International Precious Metals Institute, Allentown (1991).
6. Leach & Garner Company, “18-Karat green gold alloy compositions”, US Patent, US 6406568 B1.
7. Gen Plate Co., “Gold alloy” US patent, US 1731213 A.
8. J. H. Song and O. S. Song, Korean J. Mater. Res., **27**, 379 (2017).
9. R. D. Douglas and M. Przybylska, J. Prosthet. Dent., **82**, 143 (1999).
10. A. Becerra and M. Pekguleryuz, J. Mater. Res., **24**, 1722 (2009).
11. G. Baumeister, S. Rath and J. Hausselt, Microsyst. Technol., **12**, 773 (2006).
12. J. Schroers, B. Lohwongwatana, W. L. Johnson and A. Peker, Appl. Phys. Lett., **87**, 061912 (2005).