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Influence of Alloy Addition on Properties of Silver Alloys

รักษา บุญยืน และ ณัฐพล ชมแสง*

Raksa Boonyeun and Natthaphol Chomsaeng*

คณะอัญมณี มหาวิทยาลัยบูรพา วิทยาเขตจันทบุรี

Faculty of Gems, Burapha University, Chanthaburi Campus

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บทคัดย่อ

งานวิจัยนี้ได้ทำการศึกษา สี การต้านทานการหมอง ความแข็ง และ โครงสร้างจุลภาค ในโลหะผสมเงินด้วยเทคนิคยูวีวิสสเปคโตรโฟโต้มิเตอร์ เครื่องทดสอบความแข็งแบบวิคเกอร์ และ กล้องจุลทรรศน์แสง ตามลำดับ ได้ทำการศึกษาทดลองโลหะผสมแบบ 2 องค์ประกอบ ประกอบด้วย เงิน-ทองแดง-ซิลิกอน และ เงิน-ทองแดง-ซิลิกอน-สังกะสี รวมถึงการปรับเปอร์เซ็นต์ทองแดงให้สูงเพื่อศึกษาการเปลี่ยนสีในโลหะผสมนี้ การเติมซิลิกอนและสังกะสีเพื่อเพิ่มการต้านทานการหมอง ตัวอย่างถูกหล่อที่อุณหภูมิ 960 องศาเซลเซียส ด้วยหัวเชื่อมแก๊ซ และ ปล่อยให้เย็นตัวในอากาศ ผลการทดลองแสดงให้เห็นว่าสีของโลหะผสมที่ผสมทองแดงในปริมาณสูงจะมีสีเหลืองจากการศึกษาด้วย ยูวีวิสสเปคโตรโฟโต้มิเตอร์ ค่าความแข็งสูงสุดพบในตัวอย่าง A2 ที่มีองค์ประกอบเงิน 69.5 เปอร์เซ็นต์โดยน้ำหนัก ทองแดง 30 เปอร์เซ็นต์โดยน้ำหนัก และ ซิลิกอน 0.5 เปอร์เซ็นต์โดยน้ำหนัก ที่ 120.60 HV เพราะมีองค์ประกอบใกล้กับจุดยูเทคติก ความแข็งลดลงเล็กน้อยเมื่อเติมสังกะสีในทุกตัวอย่าง โครงสร้างจุลภาคของตัวอย่าง A1 ที่มีองค์ประกอบเงิน 74.5 เปอร์เซ็นต์โดยน้ำหนัก ทองแดง 25 เปอร์เซ็นต์โดยน้ำหนัก และ ซิลิกอน 0.5 เปอร์เซ็นต์โดยน้ำหนัก คล้ายกับเงินสเตอร์ลิงแต่เดนไดรต์มีขนาดสั้นกว่า ตัวอย่าง A2 ที่มีองค์ประกอบใกล้เคียงจุดยูเทคติกแสดงให้เห็นโครงสร้างลักษณะกลมและพบเฟสหลักที่มีทองแดงสูง ตัวอย่าง A3 ที่มีองค์ประกอบเงิน 49.5 เปอร์เซ็นต์โดยน้ำหนัก ทองแดง 50 เปอร์เซ็นต์โดยน้ำหนัก และ ซิลิกอน 0.5 เปอร์เซ็นต์โดยน้ำหนัก โครงสร้างหลักจะเป็นเฟสเบต้าเนื่องจากมีองค์ประกอบของทองแดงสูงถึง 50 เปอร์เซ็นต์ โครงสร้างของตัวอย่างที่เติมสังกะสีพบเฟสที่ 3 ในเฟสยูเทคติกซึ่งจะศึกษาต่อไป

คำสำคัญ : โลหะผสมเงิน, การต้านทานการหมอง, โครงสร้างจุลภาค, ความแข็ง

***Corresponding author. E-mail** : natthaphol@buu.ac.th

Abstract

The color, tarnish resistance, hardness and microstructure of silver alloys were studied by using portable UV-vis spectrophotometer, Vickers hardness tester and light microscope, respectively. Two systems of alloys were investigated including Ag-Cu-Si and Ag-Cu-Si-Zn. High percentage of Cu was varied to study color changes of the alloys. Si and Zn were added for tarnish resistance enhancement. Samples were cast at 960 °C by flame torch and then cooled in air. The result shown that color of high Cu-adding alloys was yellow with an investigation by portable UV-vis spectrophotometer. The highest hardness was found in A2 sample, 69.5 wt%Ag-30 wt%Cu-0.5 wt%Si, at 120.60 HV because the composition is near eutectic point. The hardness was slightly decreased after adding Zn in all samples. The microstructure of A1 sample including 74.5 wt%Ag-25 wt%Cu-0.5 wt%Si was similar to sterling silver but its dendrite was shorter than that of sterling silvers. In A2 sample, composition near eutectic point, showed the spheroidal-like shape of phase. Moreover, high content of Cu was found in the matrix phase of this sample. The matrix phase of A3 sample, 49.5 wt%Ag-50 wt%Cu-0.5 wt%Si, was β phase due to a high Cu content (50wt%). All samples added Zn showed a third phase in eutectic-phase area, which will be investigated in future.

Keywords : silver alloys, tarnishing resistance, microstructure, hardness

Introduction

Silver alloys are major materials for making jewelry due to its lower price compared with other precious metals. However, cost of pure silver has been continuously increased as a result of gold demand. Usually, pure silver is malleable metal which has hardness around 55 HV (Reti, 1997). Silver alloys containing Cu less than 7.5 wt% are called sterling silver (Girmwade, 2009). The Cu element is added to increase the hardness (60-70 HV) of the alloys (Reti, 1997). However, this alloying element induces tarnish and color changing. Moreover, 8.8 wt% copper can be soluble in silver at 775°C (Youssef, 1996). The microstructure of the alloys consists of two phases that are alpha phase (α) and eutectic phase. The alloying element such as silicon was suitably added to increase the hardness and toughness as well as tarnish resistance.

The aim of this work is to study influence of alloying elements on color, tarnish resistance, hardness property and microstructure of silver alloys.

Methods

The silver alloys were cast as bar about 10x10 mm by conventional casting. The chemical compositions of the samples are shown in Table 1. Raw materials were melted at around 960 °C by flame torch. The molten metal was poured in metal mold and then cooled in air.

Table 1 Chemical compositions of the silver alloys

Sample	Chemical composition (wt%)			
	Ag	Cu	Si	Zn
A1	74.5	25	0.5	-
A2	69.5	30	0.5	-
A3	49.5	50	0.5	-
A4	73.5	25	0.5	1
A5	68.5	30	0.5	1
A6	48.5	50	0.5	1

Cast samples were cut with a cutting machine and mounted with epoxy resin. Typical grinding and polishing methods were used to get mirror surface and a solution of 0.5 g chromic, 0.5 g sulfuric acid and 50 ml distilled water was used as an etchant to reveal microstructures in light microscopy (LM). The Vickers hardness testing was utilized to measure hardness of samples. The samples for the hardness test were subsequently used for LM investigation. Samples for the hardness test were likewise but without polishing. An Instron, model 751 universal macro hardness tester was employed for the hardness measurement. The samples were indented using 10 kgf load for 10 sec dwelling time. To obtain an average hardness value, the measurement was performed on five different areas of the samples. The tarnish resistance was tested in sodium sulfide for 60 min. and color of tested samples was measured at every 10 min. The color changing of samples was measured by portable UV-vis spectrophotometer. The measurement distance between probe and sample was approximately 7 mm.

Results and discussion

Microstructure Observation

The microstructure from LM of the samples was shown in Figure 1. Microstructural constituents of A1 sample were mainly the primary phase (α) and the eutectic structure of α and β as shown in Figure 1 (a). A dendrite structure was formed in the as-cast sample. The dendrite arm structure was shot because the sample was rapidly quenched in air. Moreover, the composition of this sample was in a narrow gap of solidification as of the Ag-Cu phase diagram (Reti, 1997). The primary phase of A2 sample was β phase with spheroidal shape while eutectic phase was also found as shown in Figure 1(b). The composition was close to eutectic point from a β-phase side of phase diagram. Therefore, β phase was surrounded by eutectic phase (α+β). Microstructure of A3 sample contained the fine primary phase and eutectic phase as shown in Figure 1(c). The dark phase was possible a β phase because this alloy had 50wt% Cu. After cooling, the β phase was solidified and followed by eutectic phase.

The microstructure of A4, A5 and A6 samples with 1 wt%Zn addition was similar to that of A1, A2 and A3 samples, respectively. All samples with Zn adding showed third phase in eutectic phase. It possible are an intermetallic phases.

Hardness Testing

The overall macrohardness was shown in Figure 2. Samples were separated into two groups that were with Si (A1, A2 and A3 samples) and Si-Zn (A4, A5 and A6 samples) additions. In the first group, the highest hardness was 120.60 HV in 30wt%Cu sample with an effect of eutectic structure. The hardness of A3 sample was decreased compared with that of A2 and A1 samples, respectively. Si addition in range of 0.5-2wt% improves the strength and hardness (Sakultanchareonchai *et al*., 2010). In another group, Si and Zn elements were added in the alloys. The hardness was lower than that of Si-added samples. Zn element is possibly reduce the hardness. Anyhow, the hardness sequence of this group was the same as that of the first one that is 30wt% Cu sample possessed the highest hardness.

Color and Tarnish Resistance

The color of as-cast samples was yellow as shown in Figure 3. The value of color was reported with CIE L*a*b* system following the Commission International de l'Eclairage (CIE). a* and b* values of all samples located in the yellow zone. L* value of samples was 99.9-100 in bright zone. Color of sterling silver was changed to red which high Cu content. Therefore, Si and Zn were filled to improve whiteness, brightness and deoxidization (Girmwade, 2009; Sakultanchareonchai *et al.,* 2010).

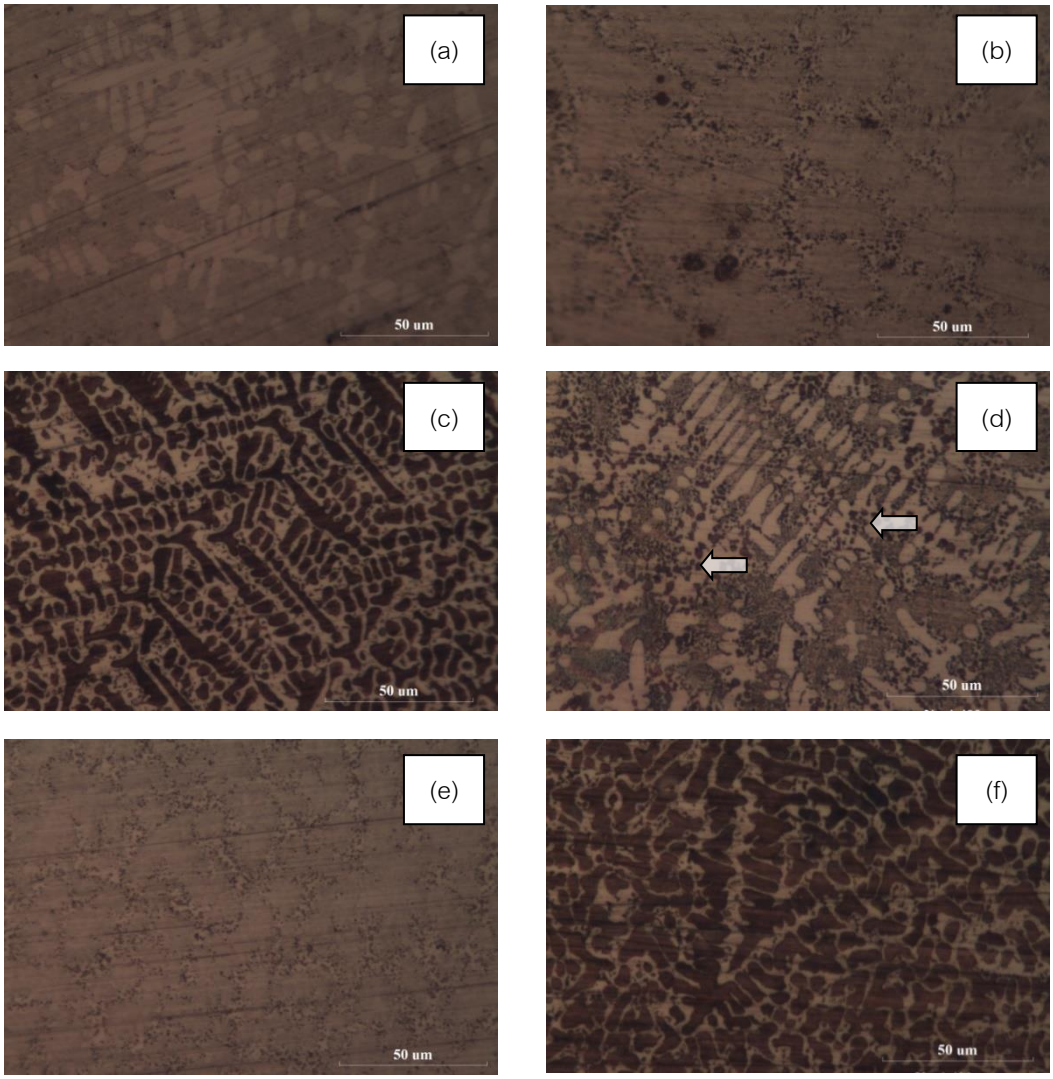

Figure 1 Light micrographs of (a) A1 sample, (b) A2 sample, (c) A3 sample, (d) A4 sample, (e) A5 sample and (f) A6 sample and white arrows are intermetallic phases. (Etchant: chromic acid)

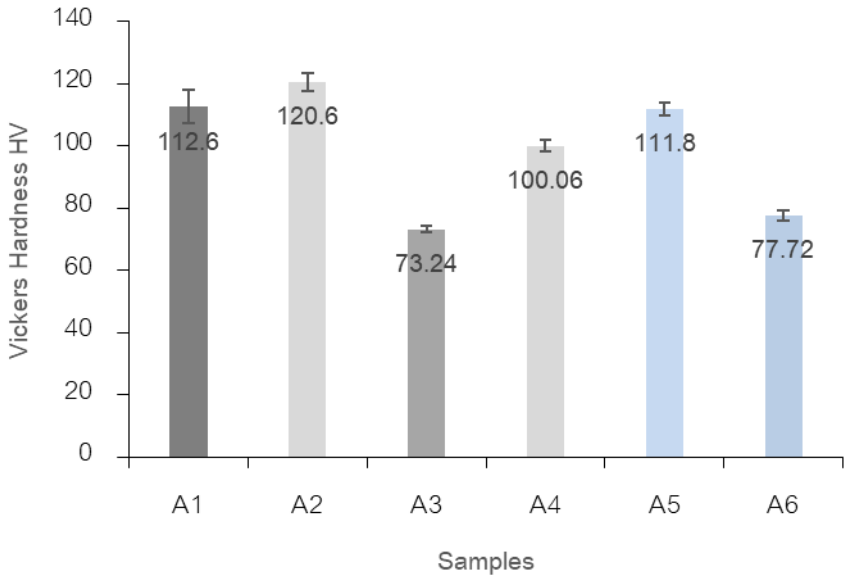

Figure 2 Vickers macrohardness of silver alloy samples

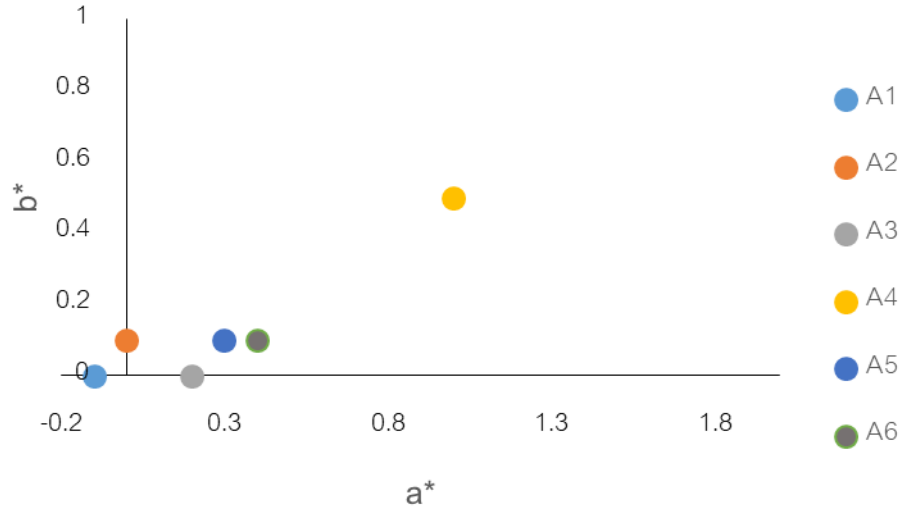

Figure 3 CIELAB color graph of as-cast samples

The tarnish resistance was explained by color difference (ΔE) calculated as follow;

$$\Delta E = ((L_1^*-L_2^*)^2+(a_1^*-a_2^*)^2+(b_1^*-b_2^*)^2)^{1/2} \quad (1)$$

where L_1 is color lightness of sample surface before tarnish testing. $a_1^*$and b_1^* are color saturation of sample surface before testing. L_2 is the lightness of the sample after tarnish test. $a_2^*$and b_2^* are the saturation of surface-tested

sample. Results of color difference are shown in Figure 4. The trend of color changing increases with testing time. However, A4 and A5 sample possessed the lowest color difference after testing for 40 minutes. It can be explained that Zn element increased whiteness and acts as a deoxidant (Nisaratanaporn, 2005). Si is well known for deoxidization and brightening function (Mccloskey *et al.*, 2001).

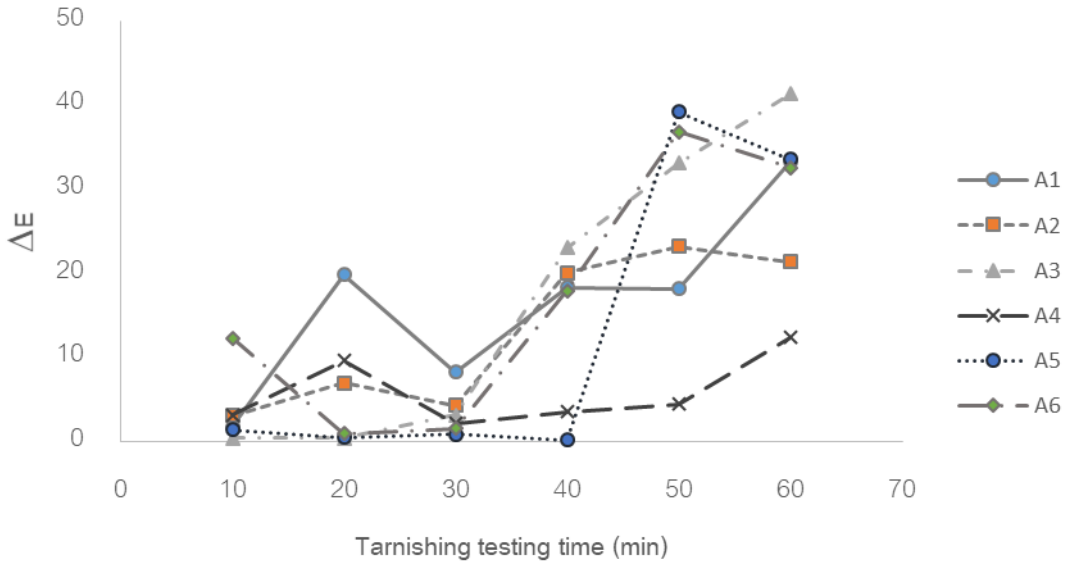

Figure 4 Color difference of samples after tarnish test

Conclusions

The microstructure of A1 sample, 74.5 wt%Ag-25 wt%Cu-0.5 wt%Si, similar to sterling silver but dendrite of this sample was shorter than that of sterling silver. 69.5 wt%Ag-30 wt%Cu-0.5 wt%Si sample (A2), whose composition was near eutectice point, showed the spheroidal shape phase. High content of Cu was found in the matrix phase of this sample. The matrix phase of A3 sample including 49.5 wt%Ag-50 wt%Cu-0.5 wt%Si was β phase due to high Cu content (50wt%). All samples with Zn added showed third phase in the eutectic phase. The highest hardness was A2 sample at 120.60 HV because the composition is near eutectic point. The hardness was decreased after adding Zn element in all samples. The tarnish resistance increased with addition of Si and Zn.

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