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The Anti-tarnishing, Microstructure analysis and Mechanical properties of Sterling silver with silicon addition

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ABSTRACT

An investigation on the anti-tarnish properties of 0-0.5%wt silicon-added sterling silver was preformed. Mechanical properties such as hardness and tensile strength were also studied. It was found that the surface of as-cast specimens using an investment (lost wax) process became brighter with increasing silicon content. The Anti-tarnish properties of silicon-added silver alloys obtained by inserting specimens under the atmosphere of sulfur was also improved when compared to the silver alloy without silicon. The Anti-tarnish properties also depend on the silver content. For example, an alloy with 95%wt Ag was better tarnish resistant than the 92.5%Ag alloy. However microstructural analysis indicated that with increasing silicon content the microstructure of the silicon-added specimens had a tendency to be a network structure which was formed by the copper silicon rich phase occurring at the grain boundary of the alpha grain (Ag rich phase). As a result, the hardness increased gradually and the ductility decreased significantly with only a 0.04% by weight increase in the amount of silicon.

Keywords: Silver-copper-silicon alloy, Anti-tarnish, Casting surface

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INTRODUCTION

One of the materials most commonly associated with jewelry has been sterling silver. Generally sterling silver was alloyed with copper (7.5 wt%) so that this alloy became harder than fine silver (Olver, 2001). However copper made the alloy less tarnish resistant under ordinary atmospheric conditions than pure silver. Therefore sterling silver with copper addition formed a dark coating on the metal Butts (1967), due to the occurrence of oxide and sulfide film. It was also found by Christopher (1989) that silver itself reacted with compounds containing sulfur such as hydrogen sulfide or sulfur dioxide to produce silver sulfide (Ag_2S) film when the silver content in silver alloy was more than 83% by weight. This sulfide rapidly occurred in the sulfur dioxide-rich environment with high humidity. The color of the film varied, passing through the range of light interference colors with increasing thickness, soon becoming a dark greenish-brown to black, the latter being the true color of silver sulfide. This led to tarnishing on the surface of the silver alloys. Several methods including electroplating with gold or other precious metals (Rhodium or Platinum) and coating with organic agents, were developed and employed in order to prevent tarnishing. Nevertheless coating has had the disadvantage of alteration of the surface and therefore usually affected the appearance of the coated silver jewelry. In addition if the object was to be handled or subjected to wear or possible scratching, the silver will tarnish where exposed. Therefore many researchers White (1985), and Davitz (1991) attempted to improve the anti-tarnishing via selective oxidation methods. This was done by adding some elements, such as aluminium and silicon, in order to produce the oxide films for preventing the tarnishing. Indium tin palladium and zinc Zamojski (1996), and Harigaya, *et al*. (1974) were also employed for this purpose.

The objective of this research was to study the effect of silicon content on microstructure development, anti-tarnish properties and the mechanical properties of sterling silver.

MATERIAL AND EXPERIMENTAL PROCEDURE

In this experiment two grades of silver alloy which were 92.5 wt% and 95.0 wt% Ag were prepared from the mixing of fine silver (99.99%), pure copper (99.99%) shots and copper silicide. Silicon was added in silver in the form of copper silicide which was made with a copper to silicon ratio of 90 to 10. Then the mixtures were melted and casted by using the induction casting machine with a vacuum system in order to prevent the silicon loss. The melting temperature and flask temperature were 980^{o}C and 550^{o}C respectively. After pouring the metal, the flask was left for 20 minutes prior to opening the mould by water injection.

The chemical composition of the specimens after casting, investigated by using several techniques such as atomic absorption, fire assays and wet analysis, are shown in table 1 below.

Table 1 The chemical compositions of silver alloys with silicon addition.

Specimen No.	Silver (wt%)		Copper (wt%)		Silicon (wt%)	
	Expected	Analyzed	Expected	Analyzed	Expected	Analyzed
925Ag-0Si	92.50	Balance	7.50	7.48	0.00	0.00
925Ag-0.1Si	92.50	Balance	7.40	7.80	0.10	0.04
925Ag-0.2Si	92.50	Balance	7.30	7.91	0.20	0.15
925Ag-0.3Si	92.50	Balance	7.20	7.30	0.30	0.23
925Ag-0.4Si	92.50	Balance	7.10	7.07	0.40	0.29
925Ag-0.5Si	92.50	Balance	7.00	7.39	0.50	0.38
950Ag-0Si	95.00	Balance	5.00	4.98	0.00	0.00
950Ag-0.1Si	95.00	Balance	4.90	4.88	0.10	0.10
950Ag-0.2Si	95.00	Balance	4.80	5.71	0.20	0.17
950Ag-0.3Si	95.00	Balance	4.70	5.06	0.30	0.22
950Ag-0.4Si	95.00	Balance	4.60	4.28	0.40	0.32
950Ag-0.5Si	95.00	Balance	4.50	4.59	0.50	0.44

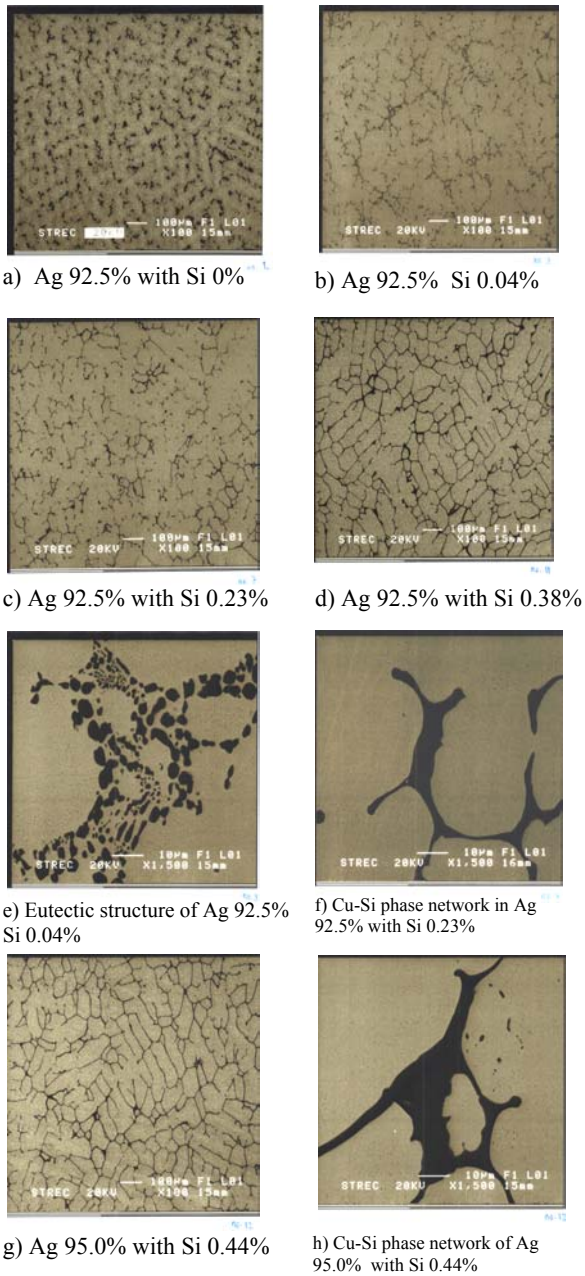
After casting, the microstructure was analyzed by using both optical and scanning microscopes with EDX for local chemical analysis. In order to examine the anti-tarnish property the specimens were cut and ground with silicon carbide paper and polished with 1 micron of diamond polishing powder. Subsequently the specimens were inserted into the bottle where the atmosphere in this testing was full of sulfur gas, occurring from the decomposition of saturated sodium sulfide solution. After testing at 1.5, 2.5, 3.5 and 5.1 hrs, the specimens were brought to measure the color value and the color change values were calculated using a spectrophotometer. The as cast samples were machined to specimens for tensile testing using a strain rate of 0.05 mm/min and the results were collected and analyzed.

RESULTS AND DISCUSSION

As cast specimen investigation

Figure 1 showed twelve pieces of the as cast silver-copper alloy specimens with addition of silicon from 0-0.5% by weight. It was found that the silicon content affected the casting surface of the specimens. An increase in the silicon content altered the colour of the casting surface from a gray colour to a white colour. This was because the copper element in the alloy reacted with oxygen in the air and produced copper oxides with gray or black colours. In addition, at the same amount of added silicon the specimens with a higher silver content as shown on top of Figure 1 had a less dark colour than those with a lower silver content. Consequently it can be concluded that firstly an increase in silver content led to the reduction in the reaction between copper and oxygen. Finally an increase in silicon content produced a protective film and therefore retarded the copper oxide formation.

Figure 1 As cast specimens using the induction caster machine with vacuum system. Silicon content added in the specimens from left hand to right hand as follows.0, 0.1, 0.2, 0.3, 0.4 and 0.5 % by weight (Top row : Silver grade 925 and bottom row : Silver grade 950)



a) Ag 92.5% with Si 0%

b) Ag 92.5% Si 0.04%

c) Ag 92.5% with Si 0.23%

d) Ag 92.5% with Si 0.38%

e) Eutectic structure of Ag 92.5% Si 0.04%

f) Cu-Si phase network in Ag 92.5% with Si 0.23%

g) Ag 95.0% with Si 0.44%

h) Cu-Si phase network of Ag 95.0% with Si 0.44%

Figure 2 Microstructure of silver copper silicon alloy grade 925 and 950 with varying silicon

Microstructural analysis

Figure 2 a-h shows the microstructure of Ag 925 and Ag 950 specimens with various silicon contents, obtained by using a scanning electron microscope. Theoretically, the microstructure of sterling silver with less than 7.5% copper in an equilibrium state is composed of an alpha phase (Ag rich phase) and a beta phase (Cu rich phase). However, for non-equilibrium conditions, eutectic structure was also found due to a high cooling rate after casting. Therefore the as cast microstructure in general was consisted to be an alpha phase, a beta phase and a eutectic structure. With increasing silicon content the microstructure altered the eutectic (alpha+beta) structure to form a network of copper-silicon phase which occurring at the grain boundary, as shown in Figure 2 (a-d). More added silicon produced a more dense and large copper – silicon phase and thereby became a continuous phase network. These phenomena were also found in the microstructure of Ag 950 specimens (Figure 2 g-h). This occurrence of a copper-silicon phase can be explained that the silicon content existed in the copper rich phase more than in the silver rich phase due to a very low solubility limit of silicon in silver. This can be confirmed by examining the phase at a network area using EDX and checking the quantity of silicon. In Figure 3, it can be seen in both alloy groups that silicon contents in the copper-silicon phase depended on silicon increasing.

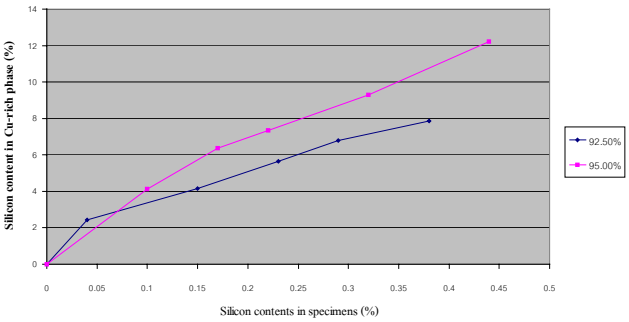


Figure 3 Silicon content in the copper rich phase existing in the network area as a function of the added silicon content

Mechanical properties

The silicon content, silver content and microstructure change significantly affected the mechanical properties. Increasing silver decreased the hardness due to a reduction in copper content whereas increasing silicon improved the hardness of both alloys as shown in Figure 4. For example, increasing the content by 0.38 wt% Si in Ag 925 alloy has increased the hardness from 77.9 Hv to 91.75 Hv. In the Ag 950 specimen with 0.44 wt% silicon the hardness value was of 81.97 Hv while the Ag 950 specimen without silicon has a hardness value of 65.17 Hv. This might be due to the influence of the copper-silicon phase.

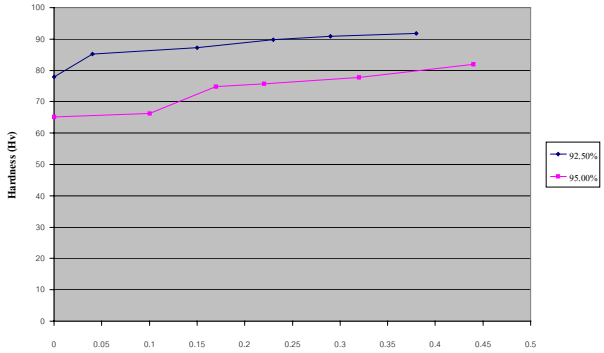


Figure 4 Hardness value of Ag-Cu-Si alloy as a function of silicon content and silver content

Figure 5 shows the ultimate tensile strength after tensile tests depended on silicon and silver contents. Decreasing tensile strength occurred with increasing silicon. This was due to the formation of a network and the volume fraction

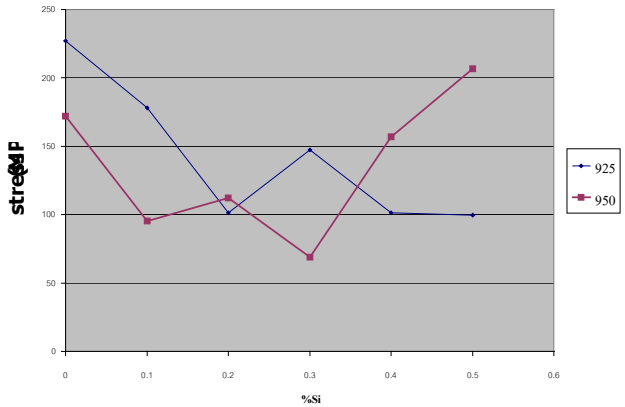


Figure 5 Ultimate tensile strength of Ag-Cu-Si alloy as a function of silicon content and silver content

of the copper silicon phase. If the volume fraction of the copper silicon phase was enough to combine themselves together and eventually form a large and easily broken network, a reduction in strength was obtained. In addition a sharp

decrease in ductility was also obtained in Figure 6. This can be seen in Figure 4 that only 0.04% silicon decreased the ductility by a value of 5%.

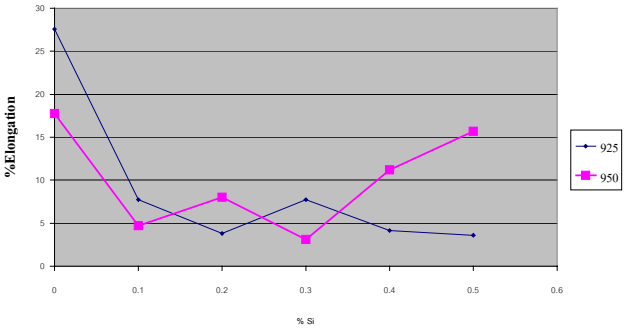


Figure 6 Elongation of Ag-Cu-Si alloy as a function of silicon content

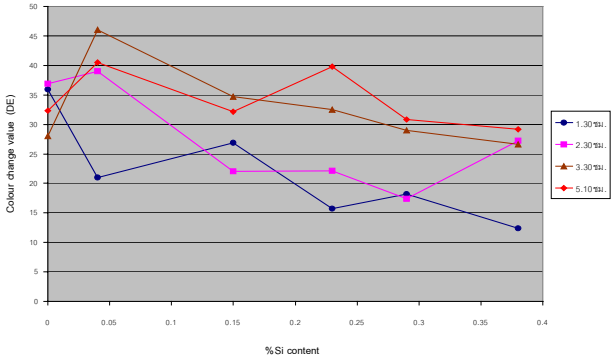


Figure 7 Variation in colour change of Ag 925 alloy with silicon content after tarnish resistance testing at 1.5 (1.30)2.5 (2.30), 3.5 (3.30) and 5.1 (5.10) hrs

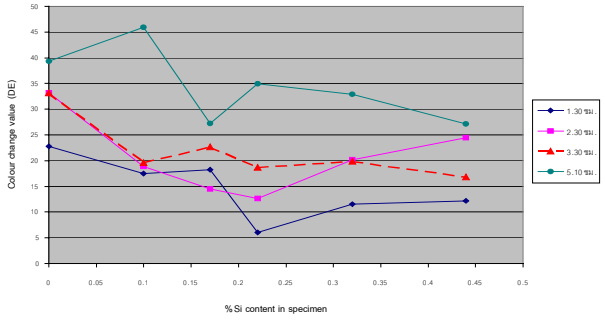


Figure 8 Variation in colour change of Ag 950 alloy with silicon content after tarnish resistance testing at 1.5 (1.30) 2.5 (2.30), 3.5 (3.30) and 5.1 (5.10) hrs

Anti-tarnish properties

After tarnish resistance testing of both silver alloys, it was found that anti-tarnish properties were improved with increasing silicon content. The tarnish resistance was reflected by examining the difference of the colour value which could be obtained by using a spectrophotometer. In Figure 7 and Figure 8 the difference of colour value (DE) of silver alloy specimens after testing were plotted against silicon content. The DE value decreased with increasing silicon content in both Ag 925 and Ag 950 alloys. In addition the specimens with a higher silver content provided tarnish resistance better than those with a lower silver content.

CONCLUSIONS

1. Increasing silicon produced a white bright shiny surface as of cast silver alloys due to the retardation of the copper oxide.

2. Silicon promoted the copper rich (beta) phase with the eutectic structure to copper-silicon phase transformation. In addition the copper-silicon phase combined together to become a network structure. As a result, decreasing mechaninal properties such as strength and ductility were obtained. However hardness was improved gradually.

3. The Anti-tarnish properties of silicon-added silver alloys were improved better than that of silver alloy with no silicon. The Anti-tarnish properties depend on the silver content. A higher silver content provided higher anti-tarnish properties.

4. The silicon content for suitable anti-tarnish resistance combined with good mechanical properties was in the range of 0.02-0.2% by weight.

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REFERENCES

Butts, Allison. 1967. *Silver Economics Metallurgy and use*. Huntington, R.E. Krieger Pub. : 123-136

Christopher, Raub. 1989. Use of Silver in Jewelry. *The Proceeding of The Santa Fe Symposium of Jewelry Manufacturing Technology* : 241-256.

Daniel, Davitz. 1991. Silver Palladium Alloy. *US. Patent No. 5,037,708, Date Aug. 6*.

Harigaya, Hiroshi, Kasai, Kazutoma, Michio Asahina. 1974. Silver Alloys having High Sulphuration Resistance. *U.S. Patent No. 3,811, 876 Date May 21*.

Olver, Elizabeth. 2001. *Jewelry Making Techniques book*. Cincinnati, North Light Book : 16-18.

White, Charles E. T. 1985. *Engineering Applications of Indium*. : 1-18, 83-91, 191-192

Zamojski, Marek R. 1996. Silver Alloy. *US. Patent No 5,558,833 Date Sep. 24*.

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