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Influence of Casting Techniques on Hardness, Tarnish Behavior and Microstructure of Ag-Cu-Zn-Si Sterling Silver Jewelry Alloys

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Abstract

The effects of Zn and Si on the hardness, tarnish resistance and microstructures of experimental Ag-Cu-Zn-Si alloy were investigated by means of vickers hardness, tarnish testing, optical and scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The various compositions of 935 sterling silver alloys produced by different casting techniques, investment (lost wax) process and metal mould casting, were compared. An induction casting machine with a vacuum system was used for investment casting at 1,025°C with the mould temperature at 600°C whereas a LPG/oxygen single flame tip torch was used for the metal mould process. Vickers hardness of the samples produced via metal mould casting has higher hardness than that of the samples obtained by investment casting. The hardness of standard 935Ag sterling samples produced by metal mould casting was around 66 HV while it was around 56 HV for the investment cast samples. The increase in hardness is related to differences in the cooling rate of solidification rather than to the addition of third elements. The tarnish test was performed by immersing the samples in 0.1% Na_2S solutions for 15-180 min. To specify the color change by tarnishing, the surface color differences (DE*) were measured according to the Commission International d' Eclairage (CIELAB) standard. It was found that the tarnish resistance was improved with high additions of elements especially Si. Furthermore, Si addition plays an important role in a complete microstructural modification, which coincides with the increase in tarnish resistance of sterling silver alloys, in terms of transforming a lamellar eutectic structure to a predominantly Cu-Si continuous structure.

Key words: Sterling silver alloy, Microstructure, Tarnish resistance, Vickers Hardness

Introduction

Sterling silver alloy is a well known and most commonly used silver-copper alloy in the jewelry industry. The word 'sterling' represents a silver content of at least 92.5% by weight. However, finer grades of silver are too soft and weak. Alloying elements such as Cu are therefore needed to improve the mechanical properties, especially in strength and hardness, usually providing hardness levels of 60-70 HV for standard as-cast sterling silver alloys. In mechanical jewelry fabrication considerable attention is paid to the effects of pre-cold work, grain size, annealing and working temperature on hardening behavior. The major drawback of the Ag-Cu alloy is corrosion which appears as yellow-brown discoloration which gradually becomes a continuous film and darkens the surface. In general, a eutectic structure of silver-rich and copper-rich phases is normally formed in the as-cast condition and the addition of alloying elements to the alloy may modify its microstructure. The addition of the third element such as Zn, Si, Ge, Mn, Ir and B were therefore suggested for jewelry manufacturing for improving the chemical, mechanical and casting properties.(1-4) Silicon has ability on deoxidizing as well as improving the castability and mould filling during melting process.(5-6) Small additions of 0.02-0.20wt%Si can improve the tarnish resistance as well as increasing its hardness due to the structural change from a lamellar eutectic to a

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Cu-Si phase network structure on sterling silver has been reported.(3) However, the optimum of Si concentration must be determined for each alloy to avoid the detrimental effect from grain coarsening and embrittlement structure. It was reported in the previous study that mould filling, melt fluidity and castability of Ag925Cu alloys improved by Zn addition and 3.5wt%Zn significantly reduced the porosity of the as-cast microstructure but induced their grains coarsening during intermediate annealing.(7) Despite of the interest in additional alloying elements in lost-wax casting, no specific investigations of the effects of third elements in conventional metal mould casting have been reported.

The purpose of the present study therefore is to elucidate the influence of Zn and Si in sterling silver jewelry alloys produced by two different techniques; investment and conventional torch flame casting into a metal mould. The effects of additional elements on hardness, tarnish resistance, characteristic microstructure, elemental distribution and phase transformation during the solidification mechanism of the sterling silver jewelry alloys will be discussed.

Materials and Experimental Procedures

An experimental 935 sterling silver alloys, Ag-Cu-Zn-Si, was prepared in order to study the effects of two different casting techniques: investment (lost-wax) process and torch flame metal mould casting. Various chemical compositions of seven experimental alloys were made by melting the fine silver (99.98%) and copper (99.86%) together with the additive elements in the induction casting machine (INDUTHERM VC-400) under a protective atmosphere of high purity Argon. Master alloys of Cu-Zn (Cu:Zn = 67:33) and Cu-Si (Cu:Si = 90:10) were used to introduce the Zn and Si additions into the Ag-Cu-Zn-Si alloys. Fifty gram sterling silver samples with a size of 10x10x2 mm were prepared by pouring at a temperature of 1,025°C into a gypsum-bonded investment mould preheated to 600°C. After pouring, the mould was held for 2 minutes under vacuum in the flask chamber, then 15 minutes in air prior to water quenching. For metal mould casting, a LPG/oxygen single flame tip was used for melting 20 g weight of alloy in a graphite crucible. The molten metal was poured into a ferrous mould to produce a rod with a size of approximately 5x5x70 mm. After solidification the rod was quenched in water. The as-cast surface was cleaned by immersion in 10% HF acid solution to remove oxides and other contamination. Chemical compositions, as given in Table 1, of the prepared alloys were determined using an Inductively Couple Plasma (ICP) technique at The Gem and Jewelry Institute of Thailand (Public Organization).

Table 1. Chemical composition of the specimens analyzed by using ICP technique.

* ICP was conducted only in the samples performed by investment casting.

Systems	Sample code		Expected (wt%)			Analyzed (wt%)		
	Metal mould casting	Investment casting	Cu	Zn	Si	Cu	Zn	Si
Ag-Cu	Ag-Cu T	Ag-Cu V	6.50	-	-	6.22	-	-
Ag-Cu-Zn-Si	Zn-Si T1	Zn-Si V1	6.00	0.50	-	6.09	0.38	-
	Zn-Si T2	Zn-Si V2	6.45	-	0.05	6.32	-	0.04
	Zn-Si T3	Zn-Si V3	5.90	0.50	0.05	5.80	0.65	0.04
	Zn-Si T4	Zn-Si V4	5.40	1.00	0.10	4.87	0.79	0.09
	Zn-Si T5	Zn-Si V5	5.20	1.00	0.30	5.93	1.04	0.31
	Zn-Si T6	Zn-Si V6	4.45	2.00	0.05	4.88	2.02	0.04

Prior to metallographic grinding and polishing, cross-section samples of the rods prepared by the torch/metal mould technique were taken and embedded in a Bakelite MultiFast resin by a hot-press technique at 180ºC for 6 min while there was no need for hot mounting of the samples produced by investment casting. The samples were mechanically ground using silicon carbide papers from 360-1200 grits and polished down using 1 μm alumina paste following conventional metallographic practice. The hardness measurements were carried out using a Vickers hardness tester (GALILEO MICROSCAN OD V.98) with a load of 1 kgf and a dwell time of 10 s following ASTM E92-00. Vickers hardness (HV) results were recorded as the average values of five measurements.

Tarnish tests were performed in a sulphur vapor atmosphere produced by 0.1% sodium sulphide nanohydrate ($Na_2S \cdot 9H_2O$) aqueous solution for 0, 15, 30, 45, 60, 120 and 180 mins. The chamber was closed to avoid rapid and extensive evaporation of sulfides. To specify the surface discoloration obtained by tarnishing, the surface color differences (DE*) were measured following the Commission International d' Eclairage (CIELAB) standard. For every composition, a well-polished as-cast sample (0 min test) was used as a reference specimen. In each case three measurements were obtained on the 10x10 mm surface area by using an X-Rite spectrophotometer (Model 972). The color difference was measured before and after the test and calculated using_Eq. 1.

$$DE^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \qquad (1)$$

Where $\boldsymbol{L^*}$ is the huge tone ($L^* = 0$ yields black and $L^* = 100$ indicates diffuse white), $\boldsymbol{a^*}$ is the red-green color coordinate ($+a^*$indicate red while $-a^*$indicate green) and $\boldsymbol{b^*}$is the yellow-blue color coordinate ($+b^*$indicate yellow while $-b^*$indicate blue), respectively

X-ray diffraction profiles on the as-cast specimens were recorded by an X-ray diffractometer (X'Pert Power Diffractometer, PANalytica). The X-ray diffractometer was operated at 40 KV and 30 mA at the 2θ range 20-60°, using a Cu Kα radiation with a resolution of 0.012° steps.

For microstructure analysis, the plate-like samples were polished by a standard metallographic technique as described above. A freshly prepared aqueous solution of 50%H_2O_2+25% NH_4OH+25% H_2O was utilized for the final etching for 5-10 s. The etched surface was then observed at 50, 100 and 200 magnifications by using an optical microscope (OLYMPUS BX60M) under a bright-field illumination. Backscattering electron imaging (BEI) of as-polished (un-etched) surfaces was used to examine the microstructures of the silver alloys using a scanning electron microscope (JEOL JSM 5910LV) operated at 15 kV with a working distance (WD) of 11 to 13 mm. Microanalysis was performed by using energy dispersive X-ray spectroscopy (EDS) with equipment and controls by Inca Software, Oxford Instruments. The specimens were analyzed using a detection time of 100 s.

Results and Discussion

Vickers Hardness Measurement

Figure 1. shows the effects of Zn and Si on Vickers hardness of the sterling silver alloys produced by investment and metal mould casting. It is clearly seen that the samples prepared by the torch melting/metal mould route have higher hardness levels than the samples prepared by investment casting. The standard 935Ag sterling alloy cast in a metal mould has a hardness around 66 HV compared to around 56 HV for the alloy cast into an investment mould. The hardness level in investment cast samples is about 5-10 HV lower than for the equivalent samples cast in a metal mould. Independent from alloy composition the Vickers hardness depends on the cooling rate during solidification and is always consistently higher for samples obtained by metal mould casting due to the higher cooling rate.

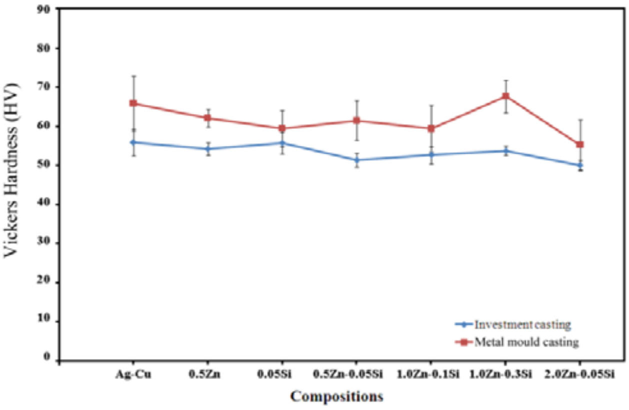


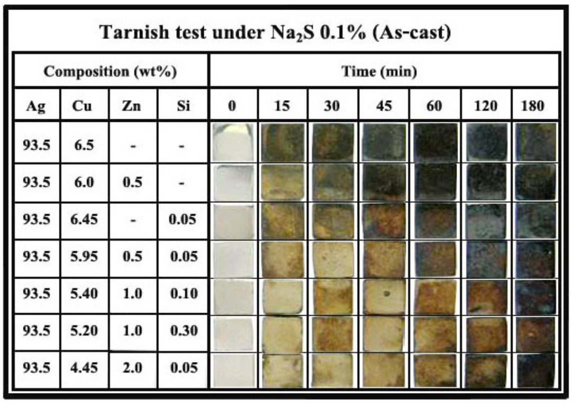
Figure 1. Comparison of Vickers hardness of the samples produced by investment and metal mould casting.

Tarnish Behavior

It is well known that silver tarnishes especially when it is exposed to an atmosphere enriched in sulphur. According to the reaction represented in Eq. 2, the surface initially becomes covered with a yellow-brown discoloration that gradually becomes a continuous dark film and causes a detrimental effect to the surface luster.

$$2Ag + H_2S + \frac{1}{2} O_2 \rightarrow Ag_2S + H_2O \qquad (2)$$

The results of tarnish testing of the sterling silver under an atmosphere of 0.1% Na_2S are shown in Figure 2. It was seen that increasing the amount of additional element increased the tarnish resistance for testing times from 15-120 min. For prolonged testing time at 180 min, nearly all the samples show a tarnished, dark-brown surface color. The sterling silver alloy containing with the highest percentage of Si at 0.3wt% showed the best tarnish resistance of all the compositions. The effects of additional elements on the measured color difference (DE*) Ag-Cu-Zn-alloy is shown in Figure 3. A lower DE value indicates better tarnish resistance. However, the DE values in Figure 3 suggest that the samples with 0.1%Si provide optimum tarnish resistance than that of 0.3%Si in all testing time. The tarnishing is non-uniform and, regarding severity, can be distinguished as three types : 1) general tarnish which is light brown in color, 2) local attack which is dark brown in color, and 3) severe local attack which is very dark in color. It appears that, although overall tarnish resistance is improved, the alloy additions can result in localized attack that is related with the phase distribution in the microstructure. In general it would concluded that an increase in alloying elements (i.e. decrease in copper content or decrease in eutectic structure) increases tarnish resistance as also mentioned in a previous study. However, it is also mentioned(4) that tarnishing is possibly form by more than one chemical reaction, several other tests and tarnish mechanisms exist can lead to different results. It was reported that silicon-oxide layer formation on the surface can be formed on the silicon added silver sterling. Microstructure-related mechanism from this layer can be contributed to tarnish resistance.



Tarnish test under Na_2S 0.1% (As-cast)

Composition (wt%)				Time (min)						
Ag	Cu	Zn	Si	0	15	30	45	60	120	180
93.5	6.5	-	-							
93.5	6.0	0.5	-							
93.5	6.45	-	0.05							
93.5	5.95	0.5	0.05							
93.5	5.40	1.0	0.10							
93.5	5.20	1.0	0.30							
93.5	4.45	2.0	0.05							

Figure 2. Effect of Zn and Si on tarnish resistance tested under 0.1% Na_2S solution for 0-180 min.

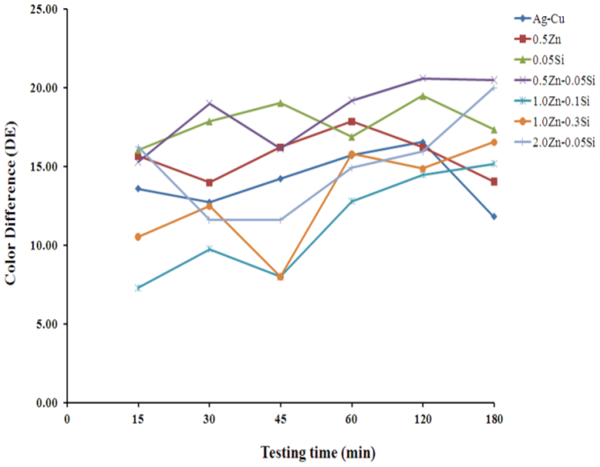


Figure 3. The color difference (DE*) on tarnish resistance of the Ag-Cu-Zn-Si alloys.

Microstructure and Phase Transformation

X-ray diffraction analysis of the as-cast sterling silver surfaces revealed the presence of FCC structure characterized by two main peaks of α-Ag(111) and α-Ag(200) at 2θ of 38.202 and 44.402 degrees (JC-PDS file number 87-0720). Lower intensity peaks that appear at 2θ of 43.317 and 50.449 degrees are related to FCC β-Cu(111) and β-Cu(200) reflections (JC-PDS file number 87-0720), respectively. The α-Ag(111) appears as a main peak in all samples except for the samples containing 1.0Zn-0.1Si which have a higher proportional ratio of the α-Ag(200) peak.

The as-cast microstructures of the standard 935 sterling silver alloy (93.5Ag-6.5Cu) prepared by investment and metal mould casting are given in Figure 4. Both microstructures consist of cored Ag-rich (α-phase) dendrites with small amounts of interdendritic eutectic constituent. The faster cooling rate during solidification of the sample cast in the metal mould has given a much finer grain size and dendrite arm spacing than the investment cast sample resulting in the higher observed hardness of the metal mould sample. Almost no macropores appeared in the as-cast microstructure of the standard sterling (no Zn or Si addition) prepared by investment casting, while macropores in size of 10 μm are normally appeared in the metal mould cast sample.

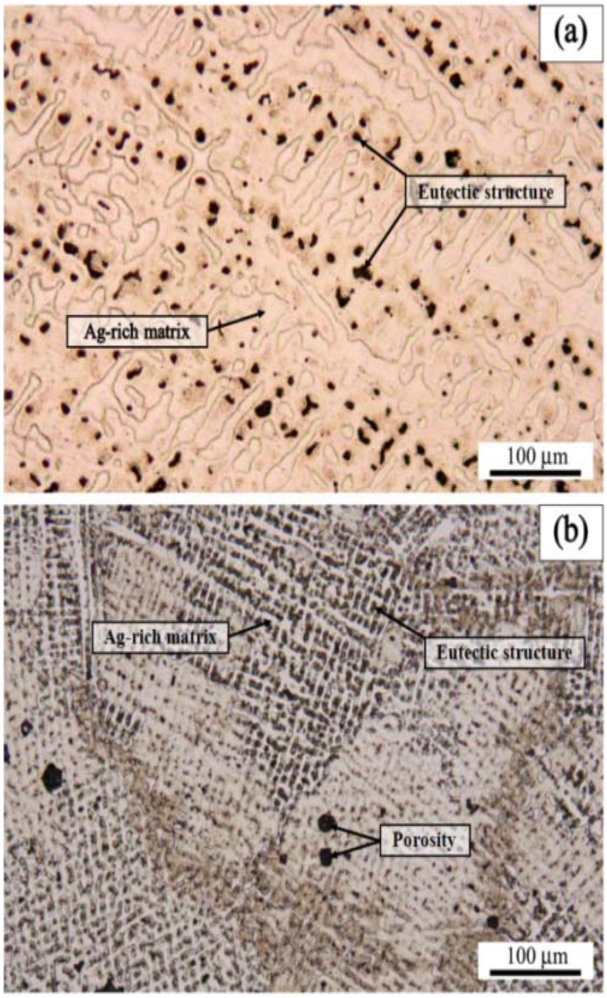


Figure 4. Optical micrographs of the standard 935 sterling silver alloy produced by (a) investment casting and (b) metal mould casting

Figure 5. shows the microstructures of an as-cast sterling silver alloy produced by investment casting. The amounts of interdendritic eutectic structure presented in these alloys tend to decrease at high silicon (0.1-0.3wt%Si) addition, as seen in Figure 5(c-d). Figure 6. shows that the metal mould samples all have much finer dendrite structures, finer grain size and consequently finer eutectic structures. At high Si level Figure 7(d), interdendritic eutectic has predominantly transformed and appeared as a continuous structure. Comparing to the standard sterling microstructure in Figure4(b), micropores are significantly decreased with Zn and Si addition to the sterling silver alloys. show the improving of the microstructure by the castibility as well as phase homogenization.

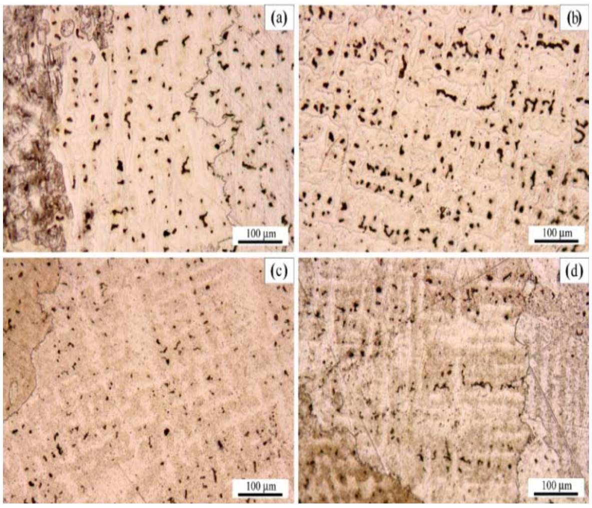


Figure 5. Optical micrographs of the alloy produced by investment casting (a) 0.5%Zn (b) 0.05%Si (c) 1.0%Zn-0.1%Si and (d) 1.0%Zn-0.3%Si.

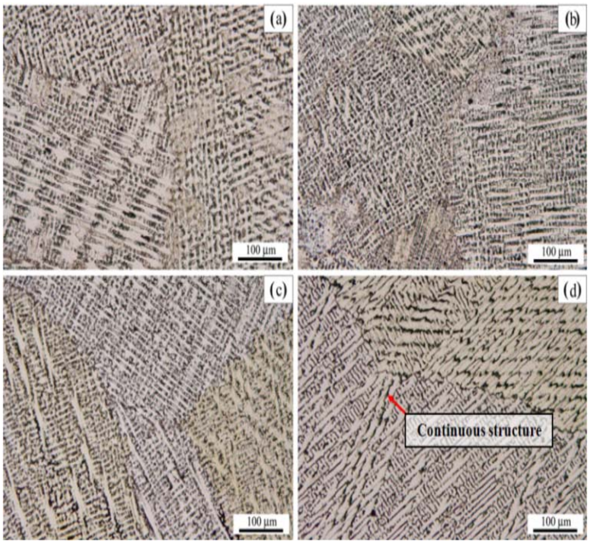


Figure 6. Optical micrographs of the alloy produced by metal mould casting (a) 0.5%Zn (b) 0.05%Si (c) 1.0%Zn-0.1%Si and (d) 1.0%Zn-0.3%Si.

The samples were all examined at higher magnification by SEM backscattered electron imaging (BEI). Figure 7 shows the investment-cast samples containing Zn and Si. Cu-rich areas (β-phase) are revealed by dark contrast (due to their lower atomic number) in the lamellar and degenerate eutectic structure in the interdendritic regions. There is no significant difference in microstructure between the lower Zn- and Si- containing samples as well as the standard sterling silver alloy sample. However, a major microstructure change appears in the samples containing 0.1-0.3wt%Si in which, the lamellar eutectic structure tends to change to a degenerated structure. The excess Cu dissolved in the α-phase during solidification has formed small precipitates within the interdendritic area. Figure 8 represents the changes from a lamellar eutectic structure to the continuous structure. From this result, it is obviously seen that Si additions effect directly the phase transformation of the sterling silver alloy. It was shown in the results that no significantly difference between the lamellar eutectic structure and chemical composition of the sterling silver alloys preparing by investment and metal mould casting. However, it is clearly seen that the lamellar eutectic structure is transformed partially to a continuous Cu-Si structure when the Si content is increased to 0.05-0.1wt% and it has completely changed to a continuous Cu-Si structure at 0.3wt%.

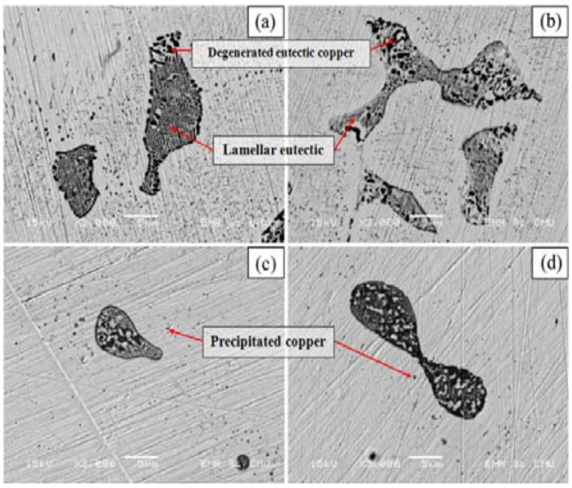


Figure 7. SEM-BEI micrographs of eutectic transformation in Ag-Cu-Zn-Si alloy produced by investment casting (a) 0.5%Zn (b) 0.05%Si (c) 1.0%Zn-0.1%Si and (d) 1.0%Zn-0.3%Si.

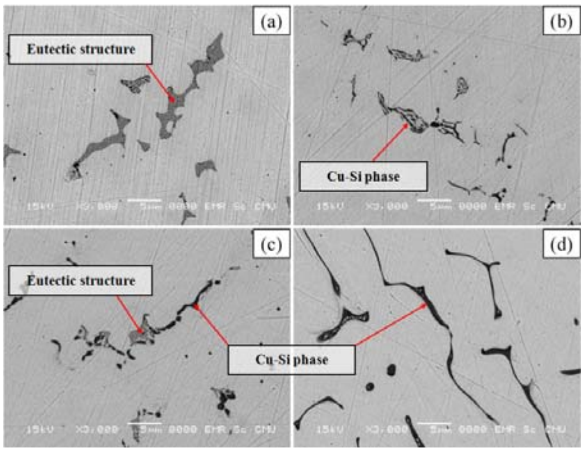


Figure 8. SEM-BEI micrographs of eutectic structure in Ag-Cu-Zn-Si alloy produced by metal mould casting (a) 0.5%Zn (b) 0.05%Si (c) 1.0%Zn-0.1%Si and (d) 1.0%Zn-0.3%Si.

The EDS analyses in the samples prepared by investment casting and conventional metal mould casting were taken at four different regions: α-phase, dendrite edges, lamellar eutectic structure and degenerated eutectic copper. According to EDS analysis listed in Table 2, the compositions of the investment cast sample are almost the same to that of the metal mould casting but the more relate in chemical composition with respect to nominal composition in the investment cast sample than that produced by metal mould casting. Silver enrichment of the dendritic α-phase are approximately above 90wt%Ag. The dendritic α-phase has same structure but difference in silver concentration due to the formation of coring structure during solidification. Copper are dissolved in the α-phase as a solid solution and small amounts of Zn can be found. The interdendrite region or dendrite edge shows an higher in copper content while the amount of silver was decreased. It should be noted that all the α-phase have the same structure with only difference in concentration gradient due to coring structure. The EDS analysis confirmed a strong enrichment of Cu as a main constituent in the degenerated eutectic structure with a significantly amount of Si. This would be due to the higher solubility of Si in copper than in silver.(8) However, Carbon was presented especially in the Cu-rich phase and tends to decreased when increasing Zn and Si.

Conclusions

The present results confirm that there are four regions observed in the microstructure of as-cast 935 sterling silver alloys: Ag-rich matrix (α-phase), dendrite arms as a Ag-Cu solid solution, lamellar eutectic structure and degenerated eutectic copper. It can be concluded that the different in casting method, investment and metal mould casting, influence to the chemistry of the alloy and micropore but no significantly influence on cooling behavior and microstructure.

The hardness of standard 935Ag sterling samples produced by metal mould casting is around 66 HV while it is around 56 HV for the investment cast samples. The increase in Vickers hardness is related more to the differences in cooling rate during solidification rather than to an addition of third elements.

Zn present in the alloys influence the microstructure in terms of decreasing the amount of lamellar eutectic structure and supporting the formation of degenerated eutectic structure, which coincides with higher tarnish resistance in as-cast state. Si additions play an important role, leading to a completely modified lamellar microstructure which coincides with an increase in tarnish resistance of sterling silver alloys; the lamellar eutectic structure is transformed into a predominantly continuous Cu-Si structure.

Acknowledgements

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Table 2. Summary of the chemical composition in the Ag-Cu-Zn-Si alloy produced by investment casting and torch flame casting in four difference areas: matrix (α-phase), dendrite arms, eutectic structure and degenerated eutectic copper analyzed by EDS.

Sample code	**Composition, Ag-Cu-Zn-Si-C (wt%)**			
	α-phase	**Dendrite edges**	**Lamellar eutectic structure**	**Degenerated eutectic copper**
Ag-Cu V	91.01-4.24-0.24-0.00-4.51	89.26-6.41-0.00-0.12-4.21	61.18-32.21-0.00-0.17-6.45	11.76-74.25-1.87-0.21-11.92
Zn-Si V1	87.26-6.35-0.62-0.14-5.63	87.54-6.48-0.62-0.09-5.27	83.89-10.91-0.37-0.25-4.58	32.40-55.50-3.03-0.00-9.06
Zn-Si V2	89.99-6.73-0.00-0.00-6.27	90.02-4.85-0.25-0.09-4.79	59.68-31.93-0.95-0.00-7.44	26.95-63.55-0.86-0.00-8.64
Zn-Si V3	91.57-4.19-0.06-0.02-3.62	89.70-5.51-1.32-0.00-3.47	78.75-15.11-1.12-0.22-4.71	24.49-63.82-2.97-0.22-6.50
Zn-Si V4	91.17-3.93-1.53-0.00-3.37	90.23-5.19-1.28-0.04-3.25	50.17-40.75-3.08-0.64-5.36	18.17-70.34-3.67-1.40-6.42
Zn-Si V5	92.57-2.39-1.29-0.00-3.75	80.58-13.86-1.60-0.10-3.85	78.81-14.21-2.20-0.08-4.69	26.40-58.94-4.44-1.51-8.72
Zn-Si V6	94.60-2.68-0.69-0.00-2.02	89.71-5.32-2.95-0.08-1.95	47.60-45.07-3.17-0.85-3.31	24.53-54.16-5.59-2.25-3.47
Ag-Cu T	92.65-3.89-0.00-0.00-3.46	89.29-7.70-0.00-0.00-3.01	62.47-31.76-0.00-0.00-5.78	47.06-46.89-0.00-0.00-6.05
Zn-Si T1	91.05-3.18-0.00-0.00-5.77	84.87-8.76-0.00-0.05-6.32	56.23-34.43-0.00-0.00-9.34	50.60-39.72-0.59-0.00-9.09
Zn-Si T2	91.21-4.09-0.00-0.00-4.70	86.76-7.02-0.84-0.00-5.38	77.63-20.79-0.00-0.15-1.43	38.50-59.17-0.00-0.20-2.13
Zn-Si T3	88.17-5.62-0.99-0.18-5.04	85.08-9.22-0.54-0.00-5.16	58.77-32.90-0.58-0.06-7.68	36.99-52.06-2.23-0.12-8.60
Zn-Si T4	92.39-2.97-0.00-0.12-4.52	86.91-7.01-1.32-0.00-4.76	50.52-40.53-1.83-0.55-6.57	11.11-70.06-4.76-2.12-11.95
Zn-Si T5	91.78-3.25-0.00-0.06-4.90	90.46-2.96-1.48-0.18-4.92	*	16.49-66.67-0.56-5.11-11.16
Zn-Si T6	90.35-2.96-1.33-0.00-5.42	85.08-6.72-2.06-0.20-5.94	*	36.77-48.87-4.35-1.00-9.02

* no eutectic structure found in microstructure.

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