

## Investigation of Supersaturated Silver Alloys for High Hardness Jewelry Application

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### Abstract

Sterling silver is one of the most widely used precious metal alloys in jewelry industry. 92.5 wt% silver content is the standard for sterling products, while 7.5 wt% is reserved for other alloying elements. Because the mechanical properties of pure silver such as yield strength and hardness are extremely low. In the bounds of 7.5 wt% solute addition, different approaches have been introduced in order to improve the properties of sterling silver. For example, to increase the hardness of the jewelry pieces, metallurgists introduced age hardening, cold working, and surface treatments. We reported on the trend of intrinsic hardness increase of the alloyed silver matrix and possibilities to supersaturate the silver matrix by different alloying elements. Relationship between the hardness increase and ability for each solute species to distort the mean lattice parameters as functions of solute percent increase (at%) had been identified. Similar trends were observed for supersaturation and Lindeman-like melting behaviors. When solutes were added to the lattice, the lattice distortion was inevitable. Once the distortion exceeded a certain threshold, the lattice collapsed and led to a local melting event. When comparing with the solute addition (at%) our findings confirmed the same trends for the supersaturation rate ( $dC_{\text{critical}}/d\chi$ ), the mean lattice distortion rate ( $dL_{\text{klh}}/d\chi$ ), the increase rate in microvickers hardness ( $dHv/d\chi$ ), and the Lindeman melting behavior particularly the rate of drop in solidus temperatures ( $dT_{\text{solidus}}/d\chi$ ).

### Introduction

Sterling silver is the workhorse alloy family in the jewelry industry. At 92.5 wt% silver content as standard, the alloying content is therefore limited to 7.5 wt%. In order to improve the multitude of desired properties, metallurgists only have little room to play with. For example, the targeted properties include better tarnishing resistance<sup>(1)</sup>, work-ability<sup>(2,3)</sup>, better casting-ability<sup>(1,4,5)</sup>, as well as high hardness values.<sup>(6)</sup> A conventional Ag – 7.5 wt% Cu alloy, also known as standard sterling silver, could be used for baseline in terms of mechanical and tarnishing properties. This Ag – 7.5 wt% Cu alloy could be age-hardened by homogenizing above the solvus temperature (1018 K)<sup>(7)</sup> to dissolve all copper atoms back into the silver matrix. The alloy is then rapidly quenched to room temperature and subsequently heated to aging temperature at typically 550 – 600 K<sup>(7)</sup> for 30 – 60 minutes. The kinetics of the nucleation and growth of Cu-rich  $\beta$  phase has been thoroughly investigated, however in order to put alloy to good use, all jewelry items must be subjected to heat treatment process.

In one particular example, Johns developed a Germanium containing sterling silver<sup>(8)</sup> that could achieve high tarnish resistance and good hardness of approximately 100 Hv after heat treatment which could be considered lengthy by jewelry manufacturers.

In order to speed up the production, manufacturers prefer to bypass the subsequent aging process. We report on the alternative to harden the alloys by supersaturating the matrix, while in many cases, these alloys could be age-hardened *in-situ* during the cooling of the alloys in the flask right after casting. Various ternary alloy systems are investigated for solid solubility. The combined solid solubility could be different from the binary system's solubility when each alloy element is investigated separately. Effectiveness of alloying elements could also be linked to other important properties such as tarnishing resistance. Copper is a wonderful addition to silver alloy in term of age-hardening. However, it is also known to have negative effect for tarnish resistance. To address the relationships, different combinations of the ternary silver alloys must be investigated.

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## Background and experimental procedures

In 1936, Hume-Rothery *et al* investigated silver alloys with alloying elements contents and the related broadening of lattice parameters. Careful measurements of lattice spacing ( $\pm 0.001$  Angstrom accuracy) were obtained by customized X-ray diffraction equipment using Cobalt  $K\alpha$  doublets.<sup>(9)</sup> Cadmium, Indium, antimony and tin were added to silver until the solid solubility range. The change in lattice spacing was monitored as a function of added alloying content in atomic percent. The “mean lattice distortions<sup>(9)</sup>” for all four alloys increased at four different rates. In this seminal finding, Hume-Rothery found the strong dependency of valency to the lattice distortions. In this paper, we extended Hume-Rothery’s study towards the relationship amongst lattice distortions, melting point via Lindeman-like<sup>(11)</sup> melting criteria, and intrinsic hardness increase due to distortion in the lattice.

There are several factors that could contribute to reduction or increase of solid solubility when two or more alloying elements were considered together. For example, atomic size, valency and the location where the alloying atoms are resided in the matrix, all could determine their ability and tendency to be dissolved in the silver. With help of thermodynamics modeling (ThermoCalc®) solid solubility of various systems could be predicted. However, because the production process is a complex problem that deals with thermodynamics, kinetics and heat transfer, we performed actual experiments to confirm our results from thermodynamics modeling in order to accurately access the tendency. To be specific, during casting, the liquid alloy solidifies and is left in a heated crucible before quenching or air-cooled in some ultimate cases. The solid jewelry could be involuntary subjected to subsequent “natural” aging process due to slow cooling of the flask. In such case, the precipitates could nucleate and continue to grow. This suggests that microstructure and mechanical properties could be heavily affected just by how the solid metal is cooled after casting.

It must also be noted that jewelry pieces of different thicknesses and different vicinities in the flask would experience varied temperature profiles and would subsequently result in cast pieces of different microstructures and therefore different mechanical properties. Amongst various mechanical properties, hardness values are of particular interest. Jewelry makers are especially interested in the hardness values as it is goldsmith’s traditional

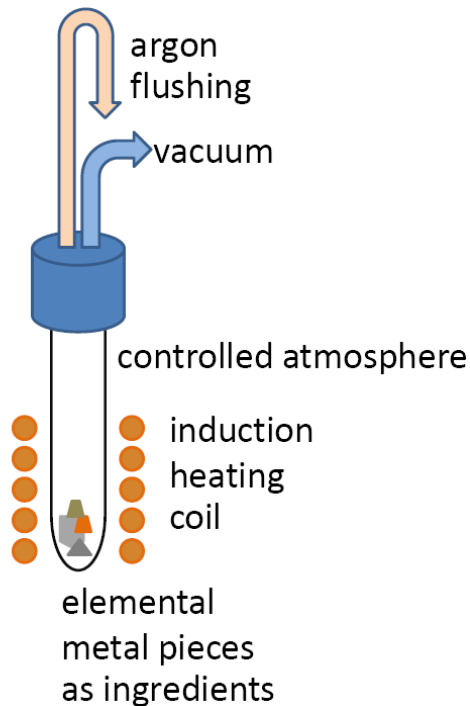
wisdom that “harder” jewelry alloys are typically *stronger*, *springier*, and more difficult to get scratched. Such wisdom is not entirely correct but at least the numbers agree with some common trend.

Another important aspect that we investigated was tarnish resistance. Chemical compositions and microstructures of the alloys could dictate of how “silvery” and “bright” the alloys looked after polishing and how the alloys resisted tarnishing. Tarnishing refers to the surface deterioration of the silver articles after a period of usage. In our test, we performed an accelerated tarnishing test by subjecting the alloys to controlled  $H_2S$  atmosphere. The brightness ( $L^*$ ) and colors ( $a^*$  and  $b^*$ ) of the silver articles were measured using Commission Internationale de l’éclairage’s  $L^*,a^*,b^*$  standard (or the better known CIELAB) which represented the color space visible to human eyes. The alloys were subjected to before- and after-tarnishing CIELAB tests.<sup>(10)</sup> Therefore time-dependent sets of  $L^*a^*b^*$  values were obtained and compared. The discoloration and deviation from original color could be calculated by the length of the color-shift vector in three-dimensional  $L^*,a^*,b^*$  space. Therefore the value, known as  $DE^*$ , could be calculated by the following equation:

$$DE^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2}$$

If the value was larger, suggesting the longer length of the shifting vector, the change in color or tarnishing was more significant. In particular if the  $DE^*$  values were less than 4, the changes would not be noticeable to human eyes.

Our alloys were prepared by induction melting high purity elements (99.9% or higher purity) in an argon-flushed atmosphere in a setup as shown in figure 1. The melted samples were left in copper crucible to immediately cool. X-ray diffraction (XRD), metallographic investigation and electron microscope’s energy dispersive spectrometry study were performed to understand the evolution of phases and to fine tune the alloys to be near the saturated solid-solution range. Microvickers hardness values were compared amongst the saturated alloys. The alloys were then subjected to accelerated tarnish tests in  $H_2S$  environment. CIELAB measurements were performed before and after the tarnishing tests.



**Figure 1.** The alloys were prepared by induction melting of pure elements in a special crucible under well-controlled vacuum environment.

## Results and discussions

In figure 2, the percent difference in metallic radii  $[(r - r_{Ag})/r_{Ag}]$  were compared amongst the alloying candidates added to silver. Hume-Rothery criteria were used to identify suitable alloying elements to achieve solid solubility with minimal amount of alloying addition. In figure 3, comparative study of Hume-Rothery's work on mean lattice distortion measurement was shown for four silver alloy systems.

The mean lattice distortions were measured by XRD technique to investigate the ability of four different alloying elements to distort the lattice. In the study, antimony (Sb) was the most effective solute to increase mean lattice distortion per atomic percent, tin (Sn) was second, indium (In) was third while cadmium (Cd) was the least effective. The results showed linear relationship between mean lattice distortion and atomic percent of solutes as shown in figure 3. The slopes represented the rate of lattice distortion change per atomic percent solute ( $d\epsilon/d\chi$ ). For Sb, the slope was the highest, at 0.00619 suggesting that Sb is the most effective in distorting lattice. For Sn, the slope was 0.00414. In, 0.0031 and Cd, 0.00209. When we compare these values with metallic radii, the numbers did not show any

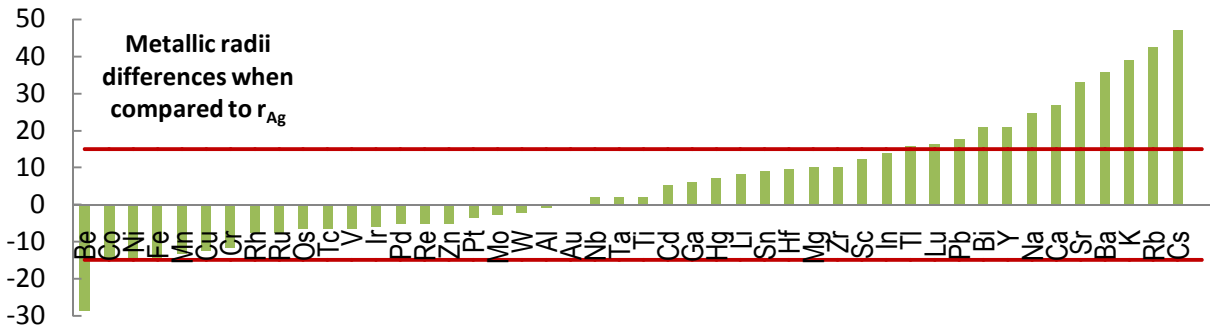
correlations. (Ag 144 pm, Cd 152 pm, Sn 158, Sb 159 pm and In 167) The results were compared with melting behaviors using Lindeman's melting criteria<sup>(11)</sup>.

When the mean lattice distortion was plotted with respect to the liquidus and solidus temperatures as well as Vickers hardness values, clear trends were observed as both relationships were linear. The finding suggested that the mean lattice distortion was by-far one of the most influential parameters in determining melting behaviors as well as hardness and related mechanical properties.

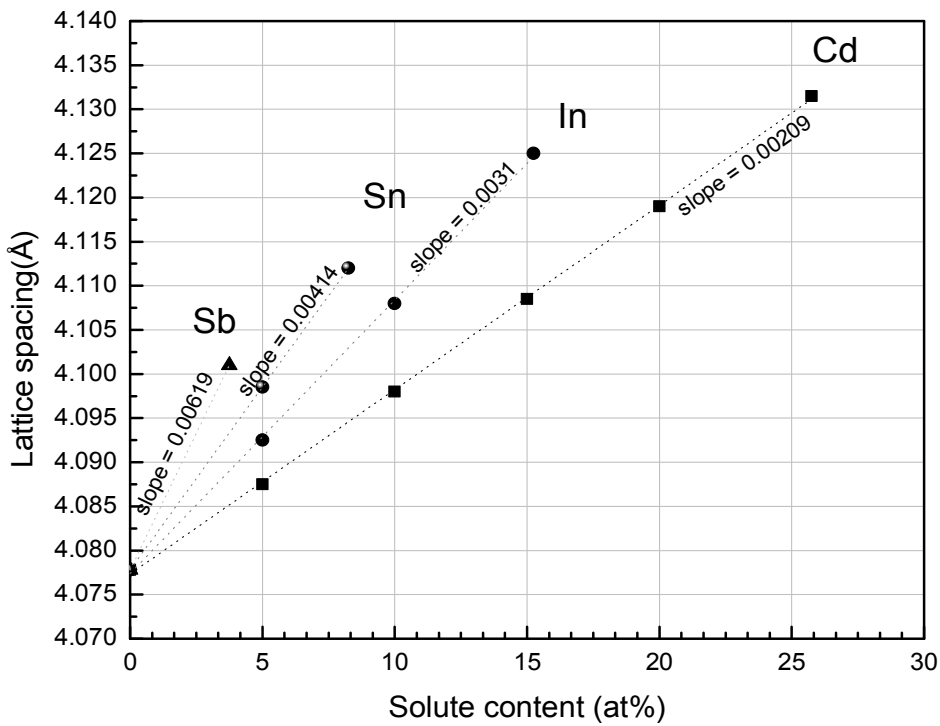
An example of a microstructural investigation of Ag-Mg-Sn ternary system was shown in figure 5 as to confirm that the microstructure had no obvious second phase. It may be deduced that the majority of the alloying elements remained inside the silver matrix. Similar observations were needed for all other alloy systems to confirm the supersaturation limit, at the cooling rate of the order of 20-200 K/sec. The range could be typically achieved in investment casting. The metallographic study was carried out for all examples which allowed us to fine tune the composition to be as close to the saturation point as possible.

By achieving the saturation limits through the controlling of microstructures and choosing the alloying elements that were most effective in increasing the hardness, in distorting the lattice, and in lowering the melting points, several alloy candidates were identified and their hardness values were found to be above 100 Hv in the as-cast state. In conventional sterling alloys, the values were of the order of 50-70 Hv in the as-cast state.

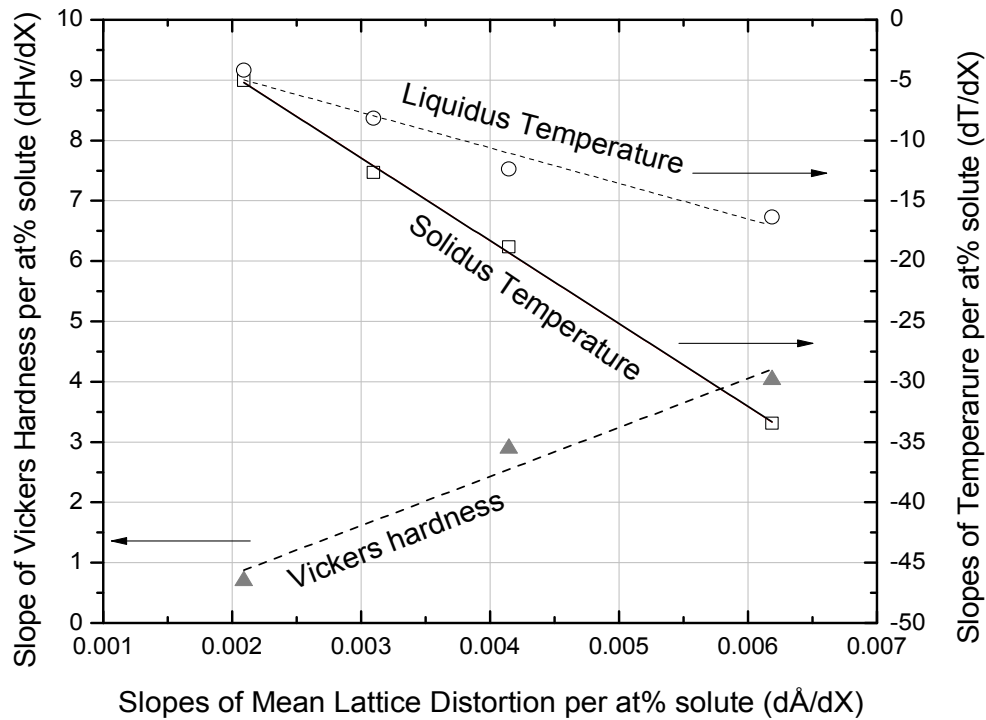




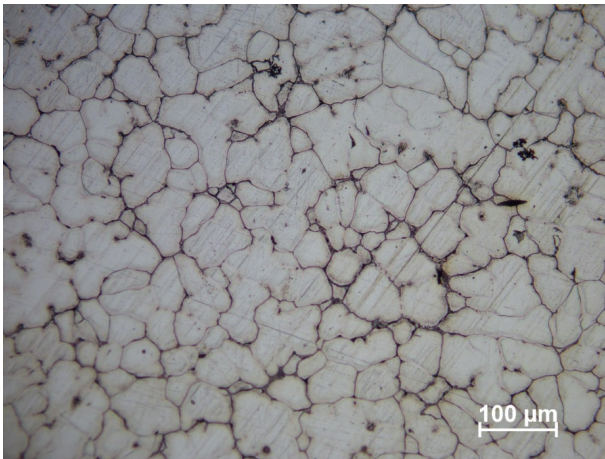
**Figure 2.** Hume-Rothery criteria was used to identify suitable alloying elements to achieve the highest solid solubility with minimal amount of alloying addition. Percentages of metallic radii differences compared to that of silver were plotted in order. Selections were made based on the 15% ratio as postulated by Hume-Rothery, as shown by two straight horizontal lines at +15% and -15%.



**Figure 3.** The shift in lattice spacing is known as mean lattice distortion. The lattice spacing was plotted as a function of solute content for four alloying elements, Sb, Sn, In and Cd. The slopes showed the effectiveness for the alloying elements to distort the lattice. Higher slope suggested that small amount of solute could significantly distort the lattice.



**Figure 4.** The slopes of graph in figure 3 were plotted against rates of change for both Vickers hardness and melting behaviors. The function  $df/dX$  showed strong correlations for both, suggesting that the mean lattice distortion played a very strong role in increasing the Vickers hardness values and the drop in solidus temperatures.



**Figure 5.** Microstructure of Ag-Mg-Sn system when the composition was near the saturation limit. The matrix was FCC silver, saturated with Mg and Sn.

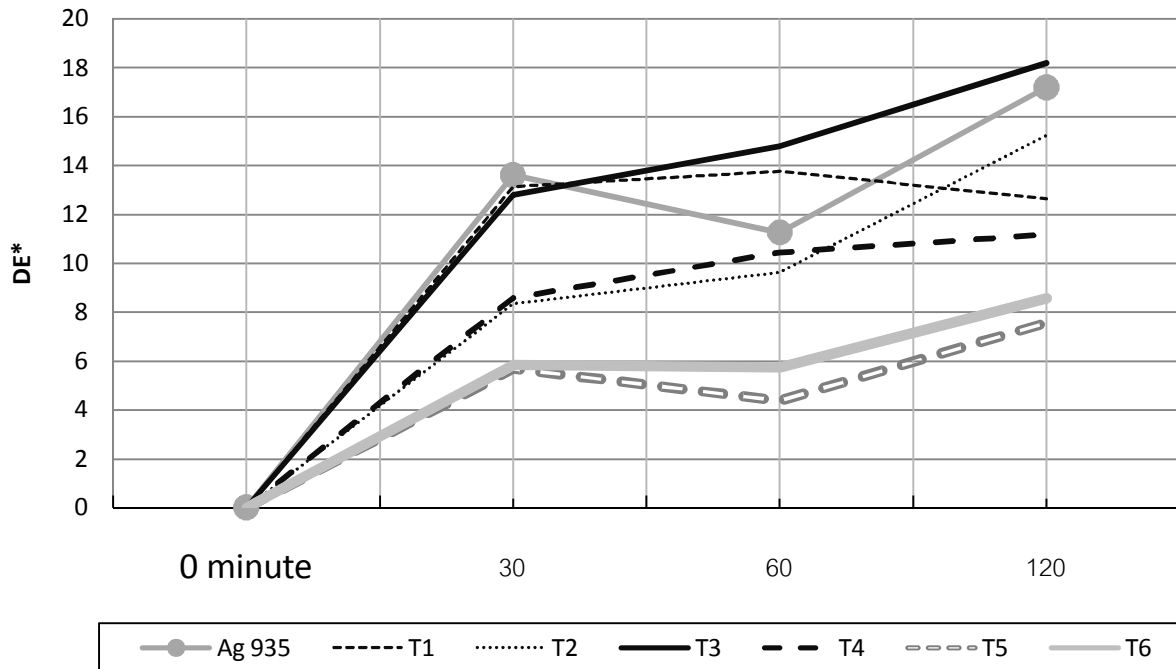
In the final test, the alloys were subjected to tarnishing test in  $H_2S$  environment. The color and brilliance of silver pieces were measured in both before- and after- states in 0 min, 30 mins, 60 mins and 120 mins interval. The  $DE^*$  values as the function of time were then compared for six alloy

candidates (T1-T6) and compared with 93.5 wt% silver which some used as industry standard for acceptable tarnish resistance alloy because of the added 1 wt% silver. The results were summarized in figure 6. Most of the silver alloys tested were comparable or better to 93.5 wt% silver used as standard. It must be noted that T5 and T6 silver alloys exhibited reasonably good tarnish resistance as their trends were near the detectable limit of human eyes in which the  $DE^*$  value is equal to 4.

In summary when ordinary metals are added to silver alloy systems, supersaturation condition demonstrated strong and direct correlation with the solute's ability to distort the mean lattice spacing. This relationship did not apply when the metallic sizes or atomic sizes were considered directly. In our finding, the four agreeable trends were the supersaturation rate ( $dC_{critical}/d\chi$ ), mean lattice distortion rate ( $dL_{khl}/d\chi$ ), increase in microvickers hardness ( $dHv/d\chi$ ), and the drop in Lindeman melting behavior ( $dT_{solidus}/d\chi$ ). The emphasis must be made on the alloy development in which hard sterling silver

could be quickly designed by investigating directly the ability for the alloying elements to reduce the solidus temperatures, and by the mean distortion of the lattice. Both methods allowed for quick survey

of the compositional sample space through Differential Scanning Calorimetry and X-Ray Diffraction Techniques, in conjunction with metallographic investigation.



**Figure 6.** Tarnishing was measured and compared using the DE\* values. DE\* could be calculated as the length of shifting of color and brilliance vectors in three-dimensional L, a\* and b\* space in CIELAB system. The six alloys were tested against Ag 93.5 wt% standard and found to be better or comparable. The DE\* value of approximately 4 or less suggested the change or tarnishing that could not be detected by naked eyes.

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