The Role of Boron on Grain Refinement in Sterling Silver Alloy

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ABSTRACT

The role of boron on grain refinement in the Sterling silver alloys grade 950 containing 3.9%Cu, 0.08%Si, 0.11%Sn and 1%Zn without and with boron addition was studied. Microstructure of the silver alloys was investigated by light microscopy, electron probe microanalysis, scanning and transmission electron microscopy. To study microstructural phenomena at grain boundaries, thin foils for transmission electron microscopy were prepared by focused ion beam method, cross-sectional along the grain boundaries. The results revealed that addition of boron at less than 10 ppm level into the alloy reduced the grain size by a factor of about three. Nano-scale copper-rich particles were found at grain boundary vicinity in the silver alloy with boron addition. Enhancement of segregation ability of copper and a possibility of co-segregation of boron and carbon with copper to grain boundaries leading to precipitation of fine particles were therefore proposed. This supports the constitutionally-undercooled-zone mechanism of grain refinement.

Keywords: Grain Refinement, Sterling Silver, Boron, TEM.

1. INTRODUCTION

An understanding on the role of boron in some alloys has been well-established. Boron in steels has long been recognized mainly with respect to hardenability [1]. In ferritic steels, boron is added to increase the hardenability by segregating to prior austenite grain boundaries and thereby suppressing the nucleation of ferrite [2,3]. Boron segregation and precipitation of M23(B,C)6 at austenite grain
boundaries upon cooling from the austenitizing temperature have an influence on hardenability of boron steels [4]. Boron can substitute for carbon or nitrogen in MX compounds in some alloy and stainless steels [4]. In austenitic stainless steels, boron can be present either as a trace impurity or as an alloying addition in low concentration range (< 100 ppm by weight). The presence of Mo in austenitic stainless steel has a pronounced effect on the subsequent precipitation, giving Mo-rich borides of the M\textsubscript{2}B\textsubscript{5} and M\textsubscript{2}B\textsubscript{6} types and tetragonal M\textsubscript{2}B, whereas in Mo-free steels, the Cr-rich M\textsubscript{2}B generally forms with an orthorhombic structure [5]. Williams and Talks [6] suggested that B may stabilize M\textsubscript{23}C\textsubscript{6} and postpone the formation of sigma phase in 316 type steels. In HSLA steels, Sojka et al. [7] noted a synergistic effect of Cu and B on considerable increment in the yield strength of HSLA steels. In the nickel-base alloys, segregation of B to grain boundaries has also been reported [8,9] and Ni\textsubscript{3}B intermetallic increased wear resistance in nickel-based alloys [10]. In directionally solidified high chromium white irons, boron was observed to segregate mainly to the austenite/carbide interface, it was also detected within the eutectic carbide and rarely as a boron compound [11]. In Fe-Ni based alloys, appropriate boron addition, which affected the formation of h phase and boride precipitation, can be an effective way of lowering hydrogen embrittlement sensitivity of the alloys [12]. Grain refinement of aluminium and aluminium alloys by titanium-boride particles has been addressed [13]. The combined effect of increased undercooling of the eutectic reaction and the effective number density of eutectic nuclei in the presence of strontium and boron can be the refinement mechanism in near-eutectic Al-Si alloy [14]. In electrode alloys, boron strongly promotes the formation of the amorphous phase in the rapid-quenched alloy [15]. For titanium alloys, it has been reported recently that boron addition at ~ 0.1-0.2 wt% significantly refined the microstructure in the as-cast condition facilitating the subsequent processing and an improvement on mechanical properties from the presence of hard titanium boride particles [16-19]. Boron addition also affected microstructure and mechanical properties of Ti-based shape memory alloys [20].

However, the role of boron in silver alloys is not well-understood. Few literatures can be found regarding an addition of boron as a micro-alloying element in Sterling silver alloy grade 950, which contains 95wt%Ag. For silver alloys, grain refinement can lead to improvement of tensile strength and reduction of hot tearing crack [21]. Some patents [22,23] also indicate effects of boron on grain refinement in Sterling silver alloys, but the mechanism of boron on grain refinement has not been described. Because Sterling silver alloy grade 950 has been widely produced by the jewelry industry, the role of boron in grain refinement is therefore investigated in this study. Microstructural investigation was performed mainly by electron microscopy to study microstructural phenomena at grain boundaries. Focused ion beam method was utilized to prepare cross-sectional thin foils for transmission electron microscopy along the grain boundaries. Finally, the mechanism of B on grain refinement in these silver alloys was discussed.

2. MATERIALS AND METHODS
2.1 Materials Preparation and Chemical Analysis
The alloys were melted in a vacuum induction furnace at 1100°C and poured into plaster molds at 580°C. After complete solidification for ten minutes, the silver trees were washed without acid pickling. Table 1 shows the chemical composition of two Sterling silver alloys grade 950 prepared in this work, without and with boron addition. Inductively coupled plasma-optical emission spectroscopy (ICP-OES), Perkin Elmer Model ICP-Plasma-1000, was used for chemical analysis. Specimens were dissolved in an aqueous solution of 7 vol% nitric acid and 3 vol% hydrochloric acid.

Table 1. Chemical composition of the Sterling silver alloys determined by ICP-OES.

<table>
<thead>
<tr>
<th>Sterling Silver Alloys</th>
<th>Cu (%wt)</th>
<th>Zn (%wt)</th>
<th>Si (%wt)</th>
<th>Sn (%wt)</th>
<th>B (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>950A</td>
<td>3.85</td>
<td>0.96</td>
<td>0.077</td>
<td>0.112</td>
<td>0</td>
</tr>
<tr>
<td>950B</td>
<td>3.84</td>
<td>0.95</td>
<td>0.073</td>
<td>0.111</td>
<td>8.46</td>
</tr>
</tbody>
</table>

2.2 Light Microscopy (LM)

Specimens were etched by an aqueous solution of 3 wt% chromic acid and 5 vol% sulfuric acid. Etched specimens were characterized by Axio Lab.A1 Mat polarized light microscope. Grain size measurement was determined following the ASTM E112-96 (Reapproved 2004). A planimetric method was used by inscribing a circle of known area on a micrograph. The sum of all the grains included completely within the field plus one half the number of grains intersected by the circumference of the area gives the number of equivalent whole grains. This equivalent number should be in between 50-100 grains and is then multiplied by the Jeffries’ multiplier to obtain the number of grains per square millimeter. At least 3 fields were counted to obtain an average value.

2.3 Scanning Electron Microscopy (SEM)

Specimens were taken from the main sprue adhered to the riser of the cast trees and cut as slices with 4-5 mm in thickness. They were ground by silicon carbide papers down to 1200 grits, then polished down to ¼ µm diamond pastes. Polished specimens were investigated by a JEOL-JSM 5910LV scanning electron microscope in backscattered electron image (BEI) mode. The accelerating voltage was 15-20 kV.

2.4 Electron Probe Microanalysis (EPMA)

Polished specimens were also used for EPMA-1610 Shimadzu to determine elemental mapping. The accelerating voltage, beam current and beam diameter were 15 kV, 20 nA and 3 µm, respectively.

2.5 Focused Ion Beam (FIB)

Preparation of thin foils for transmission electron microscopy by twin-jet electro-polishing technique was tried, but did not give satisfactory results in these cast silver alloys. Firstly, solute segregation in the alloys led to local pitting during electropolishing. Secondly, it was very difficult to obtain thin areas at grain boundaries because of their relatively large grain sizes. Therefore, FIB method was chosen. A Quanta 200 3D FIB machine was utilized and operated at 30 kV with Ga+ ion beam. Firstly, 20 µm-thick specimens were mechanically polished and etched by an aqueous solution of 3 wt% chromic acid and 5 vol% sulfuric acid to reveal grain boundaries. They were mounted on copper grids, which were cut half. FIB milling was then performed cross-sectionally along grain boundaries as shown schematically in Figure 1. The procedure A started from using high current (20 to 10 nA) to reduce the thickness down to about 3 µm, following...
by medium current (1 to 0.1 nA) down to about 100 nm obtaining a wedge shape, and then by low current (0.05 to 0.01 nA) down to about 30 nm as shown in Figures 2(a-b). Alternatively, the procedure B started from high current followed by medium current.

**Figure 1.** Schematic illustration of specimen mounted on Cu grid, which is cut half, and FIB milled to prepare thin foils for transmission electron microscopy.

**Figure 2.** Two procedures for preparing thin foils for transmission electron microscopy by FIB. (a) Procedure A used low current Ga⁺ beam in the last stage to obtain thin wedge-shape areas. (b) Secondary ion image shows a thin area prepared by the procedure A. (c) Procedure B used medium current, tilted Ga⁺ beam in the last stage to obtain thin diamond-shape areas. (d) Secondary ion image shows a thin area prepared by the procedure B. (e) A plot between the beam current and the corresponding thickness of specimen in the procedures A and B.
to obtain a wedge shape but, instead of using low current, the medium current can be maintained and the Ga⁺ beam was glanced by ±1 degree forming a diamond shape as shown in Figures 2(c-d). It should be noted that grain boundaries were clearly revealed in secondary ion image, but not in secondary electron image. A plot between the Ga⁺ beam current and the specimen thickness is given in Figure 2(e).

2.6 Transmission Electron Microscopy (TEM)

After FIB preparation, thin foils were investigated by a JEM-2010 and a JEM-2010 transmission-scanning transmission electron microscopes (TEM/STEM), operated at 200 kV, for bright-field transmission electron microscopy (BF-TEM) image, selected area electron diffraction pattern (SADP) and energy dispersive x-ray spectrometry in transmission electron microscopy (TEM-EDS).

3. RESULTS

3.1 Macrostructure and Microstructure of the Alloys

Light micrographs of macrostructure showing grain size of both alloys are given in Figure 3. Average grain size of the alloys 950A and 950B is 1.85 mm and 0.64 mm, respectively. Addition of boron reduced the grain size of the Sterling silver alloy by a factor of approximately three. Figure 4 illustrates SEM-BEIs showing microstructure of the alloys 950A and 950B. Between dendritic arms, secondary phases were revealed with darker contrast. Although addition of boron affected the grain size, the distribution of secondary phases was not significantly affected. From elemental mapping by EPMA in Figure 5, the secondary phases contain mainly Cu and Si. On the other hand, Zn distribution is more uniform in the microstructure and B is uniformly distributed in dendritic areas.

Figure 3. Polarized light micrographs show macrostructure of the alloy 950A with the average grain size 1.85 mm (a) and the alloy 950B with the average grain size 0.64 mm (b).
Figure 4. SEM-BEIs show microstructure of the alloys 950A (a) and 950B (b), respectively.

Figure 5. BEI image (a) and elemental maps (b-e) in EPMA show the microstructure of the alloy 950B and distribution of Cu, Si, Zn and B, respectively.
3.2 Transmission Electron Microscopy

Figures 6(a-b) are BF-TEM micrographs comparing the structure of grain boundaries in the alloys 950A and 950B, respectively. Grain boundaries in the alloy 950A is less undulating and no particle is observed along. On the other hand, grain boundaries in the alloy 950B is obviously undulating (actually this can also be seen in FIB image in Figure 2). Fine particles are evidenced as indicated by arrows in Figure 6(b). Figure 6(c) is an enlargement of the area within the border in Figure 6(b), whereas fine particle at the grain boundaries is revealed by Moire’ fringes contrast. Size of these particles is about 10-20 nm. It is likely that grain boundaries in the alloy 950B were also pinned by these particles resulting in an undulating grain boundary structure. Figures 6(d-e) are corresponding selected area diffraction patterns (SADPs) from the two silver grains marked as ‘Ag(1)’ and ‘Ag(2)’ in Figures 6(b-c), indicating their structure as fcc-Ag, and their zone axes are close to [112]_{Ag(1)} and [011]_{Ag(2)}, respectively. Figures 6(f-g) are corresponding SADPs from the particle and the two surrounding matrix grains in Figure 6(c) and their indexing. Most strong reflections are from the silver grains constructing the grain boundary and from double diffraction by {hkl}_{Ag(i)} to {311}_{AgDy}, which arises from overlapping of the two silver grains at the grain boundary. One strong reflection from the particle is observed as marked by ‘A’ in Figure 6(g) and has a measured d-spacing of 2.08 close to {111}_{fcc-Cu} (2.088, JCPDS file No. 04-0836) or {137}_{copper boron} (2.08, JCPDS file No. 26-1111). This reflection occurs in the direction parallel to the {111}_{Ag(i)} reflection (2.354, JCPDS file No. 87-0720), resulting in parallel Moire’ fringes with a spacing of about 1.76 nm in Figure 6(c).

![Figure 6. BF-TEM micrographs show a grain boundary in the alloy 950A (a) and 950B (b), respectively. Fine particles can be observed as marked by arrows in (b). A particle within the border in (b) was enlarged in (c) and parallel Moire’ fringes are clearly seen. SADPs in (d-f) are corresponding to the Ag(1), the Ag(2) and the particle in (c), respectively. Indexing of the SADP in (f) is given in (g). The reflection marked ‘A’ is a strong reflection from the particle.](image-url)
Figure 7 are TEM-EDS spectra taken from the matrix and the particle, shown in Figure 6. Characteristic peak of Cu L\(\alpha\) at about 0.93 keV was clearly detected. The results suggest that these particles are Cu-rich and also contains high carbon content. Overlapping of the carbon K\(\alpha\) peak to the boron K\(\alpha\) peak leads to a difficulty in identifying boron in the particles by TEM-EDS. It is possible that, during solidification in the molds, these alloying elements, which had been segregated to edges of dendrites, precipitated as small particles obstructing migration of dendritic edges.

![TEM-EDS spectra](image)

**Figure 7.** TEM-EDS spectra taken from the Ag matrix and the Cu-rich particle in Figure 6(c).

By the use of FIB, the secondary phases occurred between dendritic arms have also been revealed. Figure 8(a) is a low magnification BF-TEM image from an area containing secondary phases connected to a grain boundary in the alloy 950B. Enlarged image of the area inside the border is given in Figure 8(b). Surprisingly, fine polycrystallines with the size less than 100 nm were observed, not as the typical structure as expected in the last stage of solidification e.g. eutectic or peritectic. This can be the effect of the focused ion beam preparation on inducing a change in microstructure of these secondary phases. The SADP as inset in Figure 8(b) can be indexed as a combined pattern of fcc-Cu and fcc-Si. This is in agreement to the results from elemental mapping from EPMA in Figure 5, in which high content of Si and Cu in the secondary phases was indicated.

4. **DISCUSSION**

Sterling silver alloys have been developed to improve their properties regarding tarnishing or sulphidation resistance, strength and productivity without embrittlement during solidification and hot working, so-called “hot tearing or hot shortness” [24,25]. Normally, Cu and Zn are two major elements used in Sterling silver. Cu acts as a strengthening element. Zn increases castability by decreasing the melting point and improving
Figure 8. BF-TEM micrograph at low magnification of an area of secondary phases connected to a grain boundary in the alloy 950B (a). Higher magnification of the area in the border is shown in (b) and the corresponding SADP as inset. The ring pattern in SADP indicated a mixture of fine polycrystallines of fcc Cu and Si. Two large light-grey areas in (a) are holes in the specimen created by ion beam.

the fluidity of the molten alloys, levels up whiteness, and also acts as a deoxidant [25]. Recently, the alloying development is focused on anti-tarnishing properties by alloying with Zn, Sn and Si. Tarnishing resistance can be promoted by Si and Sn. Si is not only known to perform deoxidization and brightening functions in the Sterling silver alloys grade 950 [26], but also has a major drawback on promoting large grain size which leads to brittle behavior, especially hot tearing [24,26]. Si content is consequently limited in the range of 0.01-2 wt% in cast silver alloys [23]. Grain refinement is an approach to improve strength and to reduce the detrimental effects of the Si-containing Sterling silver alloys. Many alloying elements as grain refiner are therefore added to reduce
susceptibility of the silver alloys to the formation of hot tearing crack, but the amount of usage is still ambiguous. Excessive addition will cause many intermetallic compounds and addition in a micro-alloying level is typically applied. Boron has been known [14] to inhibit grain growth in silver alloys, even at low concentration less than 20 ppm and at temperatures used for soldering in the jewelry trade. However, the mechanism has not been addressed.

How the solute elements affect grain refinement during solidification can be described by two mechanisms [27]. Firstly, the segregating elements cause restriction to grain growth in the melt, thereby the transformation process is slowed down and there is more time for nucleation events to occur. Secondly, segregation of the solute elements leads to a so-called “constitutionally undercooled zone” in front of the growing solid-liquid interface and nucleation can occur on nucleants, thereby interrupting the growth of previous grains. The role of boron on grain refinement in aluminium and titanium alloys has been explained by the boride-particle theory [13, 16-19], but the constitutionally undercooled zone has been addressed for the case of the near-eutectic Al-Si alloy [14]. In this work, the constitutionally-undercooled-zone mechanism can also be the case to explain effects of boron on grain refinement of the Sterling silver alloys. Cu-rich particles were observed at and nearby grain boundaries only in the alloy 950B with boron addition. Even though the presence of boron at grain boundaries has not been evidenced, it can be proposed that boron enhances segregating ability of Cu and C and may also co-segregate to grain boundaries. This can lead to a constitutionally undercooled zone, within which Cu-rich particles can precipitate. These precipitates can act as nucleants for nucleation or the solid-liquid interface in the melt can be pinned by these particles, as observed in the case of the solid-solid interface during grain growth in the solid state. The Cu-rich precipitate has also been found in Ag-Cu alloy with beryllium addition, which improved the modulus of resilience and spring property of the alloy [28]. In HSLA steels, Sojka et al. [7] noted a synergistic effect of Cu and B on considerable increment in the yield strength of HSLA steels, which effectively lowers the austenite-to-ferrite transformation and precipitation strengthening due to e-Cu particles. Even though the lattice spacing of the precipitate in this study can be indexed also as e-Cu, borides or borocarbides can also be the case as observed in other boron-containing steels. Therefore, synergistic effects of Cu and some other alloying elements on the microstructure and properties of Sterling silver alloys should be further investigated.

5. CONCLUSIONS

Addition of boron at less than 10 ppm level into the Sterling silver alloys grade 950 can cause grain refinement and the grain size was reduced by a factor of about three. Nanoscale Cu-rich particles were found at grain boundary vicinity in the boron-containing alloy. Therefore, it can be proposed that boron enhances segregation ability of Cu and perhaps co-segregates with Cu and carbon to grain boundaries leading to precipitation of Cu-rich precipitates. This supports the mechanism of grain refinement by a formation of nucleants within constitutionally undercooled zone in front of the growing solid-liquid interface leading to nucleation and interruption of growth of previous grains.

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REFERENCES


