

TARNISH-RESISTANT SILVER ALLOY

FIELD OF INVENTION

The invention relates to silver alloys, and in particular, to tarnish-resistant silver alloys.

BACKGROUND TO THE INVENTION

The following discussion of the background to the invention is intended to facilitate an understanding of the present invention. However, it should be appreciated that the discussion is not an acknowledgment or admission that any of the material referred to was published, known or part of the common general knowledge in any jurisdiction as at the priority date of the application.

Pure silver (99.99 wt%) is white in colour and gives a brilliant, shining luster. It also possesses a good tarnish resistance compared to other precious metals. Due to its brilliant luster appearance and good tarnish resistance, silver has often been used for jewellery, table wares, dental and other applications that desire aesthetic appeal. In a way similar to pure gold, pure silver is a much sought-after precious metal in the commercial world.

However, pure silver is ductile and soft, with a low hardness value in the region of 28 to 35 Vickers Hardness Number (VHN). This low hardness characteristic of pure silver limits its use in the form of pure silver in the jewellery, table wares, dental and other applications.

Due to the limitation of pure silver, the jewellery industry, for example, has adopted the use of silver alloys in place of pure silver in the making of jewellery. Sterling Silver (92.5 wt% Ag) and Britannia Silver (95.8 wt% Ag) are two common forms of silver alloy that are fast becoming more widely used than pure silver. This is due to the fact that Sterling Silver, for example, has a hardness value in the region of 80 to 100 VHN, which is significantly higher than that of pure silver. The higher hardness value translates to better workability and better machineability for wider range of applications.

Despite so, Sterling Silver and Britannia Silver face a significant drawback, which explains why pure silver has to-date not yet been completely replaced by Sterling Silver and Britannia Silver. Sterling Silver and Britannia Silver each has a poor tarnish resistance compared to pure silver, due to the lower silver content in the alloy. This renders the use of Sterling Silver and Britannia Silver in premium jewellery ornaments highly undesirable.

In attempts to provide silver alloys with good tarnish resistance and higher hardness compared to pure silver, many works were directed towards the prevention of formation of silver sulfides, which is the primary cause of silver tarnish. Tarnish is generally caused by a reaction of sulfur, either from the surrounding air or perspiration that reacts with silver to form silver sulfide. For example, silver alloys containing noble metals such as approximately 19 to 40 wt% Pd, or at least 70 wt% Au, or at least 60 wt% Pt have been proposed. And it has been found that among the silver alloys proposed thus far, silver alloys containing noble metal Pd provide the best protection against tarnishing of silver. As expected, many further works were directed towards silver alloys containing primarily noble metal Pd together with complex combinations of other elements such as Sn, Zn, In, Fe, Cr, Mn, Bi, B, Co, Ge, Ga, Ce, and Zr.

Although silver alloys containing noble metal Pd provide good tarnish resistance and higher hardness compared to pure silver, such silver alloys are expensive and therefore are not commercially attractive due to the use of expensive and rare noble metal Pd. Further, with the complex array of combinations of other elements, such silver alloys appear even less attractive commercially.

It is therefore desirable to provide silver alloys having hardness (VHN) higher than pure silver and yet possessing tarnish resistance comparable to pure silver.

SUMMARY OF THE INVENTION

Throughout this document, unless otherwise indicated to the contrary, the terms "comprising", "consisting of", and the like, are to be construed as non-exhaustive, or in other words, as meaning "including, but not limited to".

Where applicable, the weight percentage values of the various elements have an accuracy of up to two decimal places.

According to a first aspect of the present invention, there is provided a tarnish-resistant silver alloy having a composition comprising Ag, Be, Sr and Zn.

5 Preferably, the silver alloy comprises at least 92.0 wt% Ag.

Preferably, silver alloy comprises 92.0 to 99.0 wt% Ag.

Preferably, the silver alloy comprises 0.001 wt% to 0.2 wt% Be.

Preferably, the silver alloy comprises 0.002 wt% to 0.05 wt% Be.

Preferably, the silver alloy comprises 0.001 wt% to 0.2 wt% Sr.

10 Preferably, the silver alloy comprises 0.4 wt% to 7.5 wt% Zn.

Preferably, the silver alloy comprises 0.01 to 2 wt% Pd and/or 0.02 to 0.05 wt% Cr.

Preferably, the silver alloy possesses a higher tarnish resistance than 99.99 wt% silver.

15 Preferably, the silver alloy shows a hardness value of at least 46 VHN.

According to a second aspect of the present invention, there is provided a method for forming tarnish-resistant silver alloy comprising Ag, Be, Sr and Zn. The method comprises melting Ag, Be and Sr to first form a solid mixed alloy, re-melting the solid mixed alloy and bubbling Zn through the molten mixed alloy,
20 quenching the molten mixed alloy, and heat tempering at between 250 to 400 °C.

According to a third aspect of the present invention there is provided a use of the silver alloy as described in the first aspect in the making of jewellery, watches, table wares, dental and other applications.

BRIEF DESCRIPTION OF THE DRAWING

5 In the figure, which illustrate, by way of example only, embodiments of the present invention, in which:

FIG. 1 shows the comparison of tarnish-resistance test results between commercial silver alloys and silver alloys (for alloys 1-4) of the present invention 12 hours after suspending the silver alloys over a solution of ammonium polysulfide.

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DETAILED DESCRIPTION

The invention relates to silver alloys, and in particular, to tarnish-resistant silver alloys.

15 In accordance with a first embodiment of the invention, there is provided a tarnish-resistant silver alloy having a composition comprising Ag, Be, Sr and Zn. The inventor has found that by alloying Ag, Be, Sr and Zn, the resultant silver alloy possesses tarnish resistance that is better than or at least comparable to pure silver, and yet has hardness higher than pure silver such that the resultant silver alloy possesses better workability and more superior machineability than
20 pure silver.

Zn is added as an alloy component because of its deoxidizing ability. Commercially available pure silver contains small amount of silver oxide. Casting of silver alloys is preferably performed in a non-oxidizing environment; otherwise the silver will absorb more oxygen. Such silver oxide layer gives a dull appearance
25 to the silver alloy, thereby rendering the silver alloy losing its aesthetic appeal. Even if the casting is performed in a non-oxidizing environment, oxidation may inevitably occur. Zn helps to deoxidize or reduce the silver oxide. Further, with Zn present in the silver alloy, the likelihood of oxidation occurring is much reduced since Zn will suppress the formation of silver oxide.

Be is added as an alloy component to provide substantial hardening effect to the resultant silver alloy so that the resultant alloy possesses sufficient hardness for subsequent workability and machineability. In the present invention, the silver alloys possess a hardness value of at least 46 VHN.

5 Sr is added as an alloy component because Sr is an active oxide former that acts in synergy with Zn to provide an effective tight oxide layer on the resultant silver alloy surface. The oxide formed from these two elements does not affect its aesthetic appearance; in fact it gives the resultant silver alloy a brighter and shinier tone. The tight oxide layer acts as a barrier to the formation of silver sulfide,
10 thereby preventing the tarnishing of the silver alloy.

The silver alloy preferably comprises at least 92.0 wt% Ag, wherein the weight content is based upon the total weight of the silver alloy.

More preferably, the silver alloy comprises 92.0 to 99.0 wt% Ag, so that the amount of Ag content present in the silver alloy is comparable to the amount of Ag
15 content present in Hallmark Silvers such as Sterling Silver (92.5 wt% Ag) and Britannia Silver (95.8 wt% Ag). If the Ag content present in the silver alloy is below 92.0 wt%, the resultant silver alloy loses the Hallmark qualification. More importantly, the low Ag content in the resultant silver alloy gives a less brilliant, less shining lustre and therefore an inferior appearance compared to Hallmark
20 Silvers. On the other hand, if the Ag content present in the silver alloy is above 99.0 wt%, the resultant silver alloy may not possess sufficient hardness for workability and machineability useful for working into a wide range of silver components and articles. The tarnish resistance of the silver alloy having more than 99.0 wt% Ag is also lower.

25 The Be content present in the silver alloy is preferably between 0.001 to 0.2 wt%, wherein the weight content is based upon the total weight of the silver alloy. More preferably, the Be content present in the silver alloy is between 0.002 to 0.05 wt%. If the Be content is below 0.002 wt%, the resultant silver alloy may not possess sufficient hardness for workability and machineability. On the other hand,
30 if the Be content is above 0.2 wt%, the resultant silver alloy may possess extreme hardness that may cause problems for mechanical working. In extreme cases, embrittlement may occur after cold working and micro cracks may therefore occur.

The Sr content present in the silver alloy is preferably between 0.001 to 0.2 wt%, wherein the weight content is based upon the total weight of the silver alloy. If the Sr content is below 0.001 wt%, the Sr-Zn synergy effect described above may not be effective so as to form a tight oxide layer acting as a barrier against the formation of silver sulfide. On the other hand, if the Sr content is above 0.2 wt%, embrittlement may occur due to the relatively large amount of Sr-Ag compounds, for example SrAg_5 , being formed.

The Zn content present in the silver alloy is preferably between 0.4 to 7.5 wt%, wherein the weight content is based upon the total weight of the silver alloy. If the Zn content is below 0.4 wt%, the low Zn content may not have the effective deoxidizing effect. In addition, the low Zn content may not achieve the Sr-Zn synergy effect described above and tarnishing of the silver alloy may then occur. On the other hand, if the Zn content is above 7.5 wt% and therefore the Ag content will be below 92.5 wt%, the resultant silver alloy loses the Hallmark qualification. More importantly, the low Ag content in the resultant silver alloy gives a less brilliant, less shining lustre and therefore an inferior appearance compared to Hallmark Silvers.

Optionally, 0.01 to 2.0 wt% Pd may be added to improve the castability or metal forming of the resultant silver alloy.

Optionally, 0.02 to 0.05 wt% Chromium Cr may be added to improve the castability, hardness and oxidation resistance of the resultant silver alloy.

[Examples]

The silver alloys of the present invention are formed by alloying techniques using 100 g of 99.99 wt% Ag, which is first heated, followed shortly by the addition of Be, Sr and Zn in the following described manner.

Ag, Be and Sr are first melted in an inert arc or an induction furnace in a non-oxidizing environment. A reducing hydrogen torch is used to protect the silver from oxidizing to silver oxide. After melting of the Ag, Be and Sr mixture and proper agitation, Zn is then introduced from the bottom of the molten Ag, Be and Sr mixture. Zn, with its low melting point, melts quickly and bubbles upwards through

the molten mixture thereby providing a good mixing. This method of introducing Zn into the mixture minimizes the vapourization of Zn, thereby reducing losses of Zn.

The molten silver alloy is then cast into an ingot and rolled into sheet, normalized and cut to sample size for tarnish-resistance testing to be described later.

Table 1 illustrates the exemplary compositions (Alloy 1 to 5) of tarnish-resistant silver alloy suitable for the working of the present invention, where the silver alloy is formed by the method described above. The silver alloy comprises essentially the main elements Ag, Be, Zn and Sr. Optionally, 0.01 to 2.0 wt% noble metal Pd may also be added to improve the castability of the resultant silver alloy. Optionally, 0.02 wt% to 0.05 wt% Cr may also be added to improve the castability, hardness and oxidation resistance of the resultant silver alloy. Trace elements make up the balance of the silver alloy composition.

Element (wt%)	Alloy 1	Alloy 2	Alloy 3	Alloy 4	Alloy 5
Ag	92.5	95.0	98.0	92.5	92.5
Zn	7.15	4.66	1.8	4.57	4.57
Be	0.02	0.01	0.01	0.01	0.01
Sr	0.02	0.03	0.01	0.02	0.02
Pd				2.0	0.98
Cr					0.02
Trace Elements	0.31	0.3	0.18	0.9	1.9

TABLE 1: EXEMPLARY COMPOSITIONS OF SILVER ALLOY

[Tarnish-Resistance Tests]

Samples of the tarnish-resistant silver alloys of Examples 1 to 4 were used to evaluate the tarnish resistance in comparison with pure silver of 99.99 wt%, with a

tarnish-resistant Sterling Silver available commercially, and with a standard Sterling Silver of 92.5 wt% Ag and 7.5 wt% Cu.

One piece each of the samples of Examples 1 to 5, of the pure silver, of the tarnish-resistant Sterling Silver, and of the standard Sterling Silver were cut into 25
5 x 10 x 1 mm, normalized. All samples were polished and degreased in an ultrasonic bath using soap solution.

The cleaned samples were then suspended over ammonium polysulfide solution which contains 0.5 ml ammonium polysulfide in 200 ml distilled water. The samples were kept in a fume cupboard with an ammonium polysulfide vapour flow
10 rate of 0.75 m/s and in an ambient temperature of 24 °C. These samples were examined after one hour, two hours, 6 hours, 12 hours, and 24 hours respectively.

The comparison results for 12 hours duration are depicted in **Figure 1**. As clearly shown in the figure, silver alloys of the present invention, i.e. Alloys 1 to 4 show better tarnish resistance compared to pure silver, commercial tarnish-
15 resistant Sterling Silver and standard Sterling Silver. From **Figure 1**, it clearly illustrates that the standard and commercial tarnish-resistant Sterling Silver were severely blackened after 12 hours. Pure silver of 99.99% shows sign of moderate discoloration. Alloys 1 and 4 show little discoloration. Alloys 2 and 3 show signs of moderate discoloration comparable to that of pure silver. Overall, Alloys 1 to 4
20 demonstrated better tarnish resistance than standard and commercial tarnish-resistant Sterling Silver.

The tests illustrated that with the silver alloys of the present invention, the use of expensive noble metal Pd and other complex arrays of elements taught in the existing art may be minimized, if not eliminated, while the tarnish-resistance of the
25 silver alloys has improved. Noble metal Pd, if required, may be added in minute amount up to 2 wt% compared with existing art where approximately 19 to 40 wt% Pd is required.

The solubility of Zn in Ag at high temperature is more than 30 wt%, and its solubility falls rapidly as the temperature decreases. When the Ag-Zn alloy is
30 quenched, an ordered beta-Ag phase is formed with a FCC (Face-Centered-Cubic) structure or lattice. Upon heat tempering of the alloy, the silver alloy

transforms to a HCP (Hexagonal-Close-Packed) structure accompanied by a color change. Perhaps, this phenomenon might be the reason why silver gives off a better whitish tone when Zn is added. During the moment of the lattice transformation, Be, with its smaller variable atomic radii, may have caused lattice distortion. Though the present inventor did not study the actual phenomenon that is occurring, it is found that upon quenching of the silver alloys, the silver alloys becomes much softer. With a mild tempering heat treatment of 300 to 400 °C, the silver alloys subsequently become harder, giving sufficient hardness of at least 46 VHN for workability and machineability, which pure silver lacks.

The afore-described alloy composition provides silver alloys possessing high degree of tarnish-resistance compared to pure silver and existing tarnish-resistant Sterling Silver. The present silver alloys also give sufficient strength and hardness without the addition of expensive noble metal Pd or the complex array of elements as taught in the existing art.

Although the foregoing invention has been described in some detail by way of illustration and example, and with regard to one or more embodiments, for the purposes of clarity of understanding, it is readily apparent to those of ordinary skill in the art in light of the teachings of this invention that certain changes, variations and modifications may be made thereto without departing from the spirit or scope of the invention as described in the appended claims.

I CLAIM:

1. A tarnish-resistant silver alloy having a composition comprising Ag, Be, Sr and Zn.
2. The silver alloy of claim 1, wherein the silver alloy comprises at least 92.0 wt% Ag.
3. The silver alloy of claim 2, wherein the silver alloy comprises 92.0 to 99.0 wt% Ag.
4. The silver alloy of any one of claims 1 to 3, wherein the silver alloy comprises 0.001 to 0.2 wt% Be.
5. The silver alloy of claim 4, wherein the silver alloy comprises 0.002 to 0.05 wt% Be.
6. The silver alloy of any one of claims 1 to 5, wherein the silver alloy comprises 0.001 to 0.2 wt% Sr.
7. The silver alloy of any one of claims 1 to 6, wherein the silver alloy comprises 0.4 to 7.5 wt% Zn.
8. The silver alloy of any one of claims 1 to 7, wherein the silver alloy comprises 0.01 to 2.0 wt% Pd.
9. The silver alloy of any one of claims 1 to 8, wherein the silver alloy comprises 0.02 to 0.05 wt% Cr.
10. The silver alloy of any one of claims 1 to 9, wherein the silver alloy possesses a higher tarnish resistance than 99.99 wt% silver
11. The silver alloy of any one of claims 1 to 10, wherein the silver alloy shows a hardness value of at least 46 VHN.
12. A method for forming tarnish-resistant silver alloy comprising Ag, Be, Sr and Zn, the method comprising:
 - melting Ag, Be and Sr to first form a solid mixed alloy;

- re-melting the solid mixed alloy and bubbling Zn through the molten mixed alloy;
 - quenching the molten mixed alloy; and
 - heat tempering at between 250 to 400 °C.
- 5 13. Use of the silver alloy of any one of claims 1 to 11 in the making of jewellery, watches, table wares, dental and other applications.