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[54] SILVER ALLOYS HAVING HIGH SULPHURATION RESISTANCE


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[63] Continuation of Ser. No. 5,917, Jan. 26, 1970, abandoned.

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[58] **Field of Search** ........... 75/173 R, 173 C, 134 T



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[57] **ABSTRACT**

Tarnish-resistant silver alloys which retain the malleability and silver-white appearance of the pure metal containing tin, indium and zinc in specified concentration ranges. These elements are synergistic in their effects. Small quantities of Ti, Zn, Be, Cr, Si, Al, Ge and Sb when used in addition to Sn, In and Zn further increase resistance to tarnishing by sulphur-containing materials.

**7 Claims, No Drawings**

# SILVER ALLOYS HAVING HIGH SULPHURATION RESISTANCE

This is a continuation of application Ser. No. 5,917, filed Jan. 26, 1970 now abandoned.

The present invention relates to silver alloys for ornaments and industrial art products, comprising Sn of 4–10 percent, In of 0.5–12 percent, Zn of 0.1–5 percent and substantially Ag of the remainder by weight wherein noble bright white color of silver alloys is maintained and resistance against discoloration into black, due to sulphuration, is greatly improved by the synergism (effect) which is caused from the addition of such elements as Sn, In and Zn into Ag at a time.

As is well known, Ag having its own bright white color and soft color tone is valued as a precious metal; for example, it is widely applied to some ornaments such as rings, silver tablewares, watch cases or to dentistry.

Silver, however, has defects that if it reacts with a small amount of sulfide in the air or sweat, silver sulfide is produced instantly and thus discoloration from silver white to black is brought about. It is also a well-known fact that it is restricted in its usage.

Silver alloys that do not change to black by silver sulfide have been widely sought. However, satisfactory silver alloys have not been obtained. But as the alloy making up these defects, silver alloys, including Pd and Au etc., are commonly known, for example, the alloys being employed by dentists.

These alloys are improved in their sulphuration resistance, while the bright white color of Ag own, as mentioned above, is tinged with grey and is too expensive. Most articles, such as watch cases, etc., for practical use or industrial products, are commonly plated with Rh, etc., to protect their surfaces, so that the natural color of Ag cannot be seen.

The purpose of the present invention is to eliminate the above defects and to provide silver alloys which can retain the natural silver white color of Ag and prevent the discoloration to black due to sulphuration during their use, and also the costs must be either the same as that of Ag or lower than Ag.

Many experiments have been carried out to obtain such alloys. As a result of such experiments, it was proved that proper addition of Sn to Ag increases the sulphuration resistance and the mechanical strength, and the effect of In in improving sulphuration resistance to a great degree together with Sn, and further addition of Zn with Sn and In makes it possible to realize the alloys according to the present ivention.

The effect of each additional element of the alloys according to the invention and the reason for restricting the amount of the element will be described hereinafter.

Sn becomes oxide preferably in the oxygen gas and becomes stable, thus protecting the surface of the alloy and prevents silver sulfide from growing. The additional amount of 4 percent (Sn) begins to show the desirable effect on the sulphuration resistance. As the amount is increased, the effect and the mechanical strength also increase. However, if the additional amount exceeds 10 percent, the color of silver proper turns to gray. In addition, the silver alloys including Sn become brittle and the workings, such as drawing and rolling would become enveloped in difficulties. Thus it could be found that Sn of 4–10 percent is sufficient.



In is very soluble in Ag, the elements however having poor corrosion resistance. If In of more than 10 percent is added singly to Ag, it has only some sulphuration resistance.

The inventor of the present invention found that In is far more effective in preventing Ag from sulphurating if it is added to a mixture of Ag with Sn. Further, after the various experiments and the examinations, it was found that the addition of Sn makes it possible to renew the color tinged with gray of the alloy to the vivid color of pure silver.

If a large amount of Sn is added, addition of 0.5 percent In shows a favorable effect on the sulphuration resistance, and as the additional amount of In is increased the effect is also increased. However, if the additional amount of In exceeds 12 percent, the alloys become tinged with yellow and their malleability is decreased. Therefore, the additional amount of In must not exceed 12 percent.

Zn has deoxidizing action on the alloys when they are melting. Generally Zn shows a favorable corrosion resistance in the air. In the solution, including salts, it also prevents the alloys from being corroded, that is, corrosion resistance of the alloys is highly increased. Even with a comparatively small amount of Zn to be added, it is effective as deoxidizing agents. In order to increase the corrosion resistance and the sulphuration resistance, an amount of more than 0.1 percent is needed. If the additional amount of Zn exceeds 5 percent, the alloys become tinged with gray and become brittle, which has a deleterious effect on their malleability and ductility. Therefore it is fixed in the amount of 0.1–5 percent.

According to the invention, as can be understood from the additional elements and their amount above stated, good properties of Ag proper can be maintained for a long time and the discoloration to black, due to sulphuration, which is the largest defect in Ag, can be prevented by adding some elements, mixed together, the prices of which are approximately the same as Ag or lower than Ag. Furthermore, the addition of Sn and In permits the mechanical strength of the alloys to increase greatly. Thus, the alloys, according to the present invention, can be applied not only to ornaments or technical products but also to various industrial uses.

The present invention will be disclosed in detail with the explanation of the following embodiments.

## EXAMPLE 1

The alloy comprising Sn of 8.2 percent, In of 2.1 percent, Zn of 1.2 percent and Ag of the remainder by weight, this alloy being called "the alloy No. 1" according to the invention hereinafter, was melted and founded. After being subjected to repeated heat treatment and rolling process, it was formed into the plates having a thickness of 2 mm. Further a test piece 30 mm by 30 mm was cut off from the plate. After the surface of the test piece was mirror polished by emery papers and a buff polishing machine, it was washed out to remove oils and fats and was kept in a sealed container, in which 6N (normal) potassium sulfide of 100 cc and 2N. potassium sulfide of 200 cc were poured and hydrosulfide gas was generated. After keeping the test piece in the hydrosulfide gas for 6 hours, the surface discoloration due to silver sulfide was examined.

As a result, no discoloration was found and the initial surface luster and tone could be maintained in the alloy No. 1 according to the present invention.

Moreover three kinds of alloys — the one comprising Sn of 8.9 percent and Ag of the remainder (Sn is added singly), the one comprising In of 9.7 percent and Ag of the remainder, and the one comprising Sn of 8.7 percent, In of 4.7 percent and Ag of the remainder (a mixture of Sn and In is added) were respectively melted and founded. They were then formed into the same test pieces as beforementioned. Thereafter, they were placed in hydrosulfide gas and examined. The result was as follows: The alloy including Sn added singly and the alloy including In added singly were discolored respectively within 5 minutes, while the alloy including Sn and In, mixed together, began to discolor to light brown in its surface after six (6) hours.

From the above experiment, it was found that the sulphuration resistance of Ag would be more highly increased by the synergism caused by the mixed addition of Sn, In and Zn at a time.

The alloy including Sn added singly shows white gray tone, and the alloy including In added singly shows silver color tinged with light yellow. On the other hand, the alloy No. 1, according to the invention can maintain soft silver white tone of Ag proper.

## EXAMPLE 2

Table 1 shows the chemical compositions of the alloys according to the present invention and the conventional silver alloys.

Table 1

| Alloy No. according to the invention | | Sn | In | Zn | Ag |
|---|---|---|---|---|---|
| Alloy No. | 2 | 5.2% | 2.2% | 0.4% | remainder |
| do. | 3 | 4.4 | 10.5 | 0.8 | do. |
| do. | 4 | 9.2 | 9.6 | 2.2 | do. |
| do. | 5 | 7.9 | 4.3 | 1.2 | do. |
| do. | 6 | 7.8 | 0.9 | 4.1 | do. |
| do. | 7 | 8.4 | 0.6 | 3.1 | do. |
| do. | 8 | 5.7 | 7.2 | 1.3 | do. |
| do. | 9 | 6.2 | 3.1 | 0.9 | do. |
| do. | 10 | 8.2 | 1.9 | 3.3 | do. |
| do. | 11 | 8.1 | 2.6 | 1.0 | do. |
| Pure silver | | — | — | — | 99.9% up |
| Sterling silver | | — | — | — | 92.5% (Cu 7.5%) |
| Au-Pd-alloy | | — | — | — | 70% (Pd 25% Au 5%) |

The melting process of the alloy according to the present invention can also be conducted by using the carbon crucible in the same manner as that of conventional silver alloys. But it is desirable to add Zn before founding into ingot in order to fully display its deoxidizing effect. It is especially desirable to reduce the amount of oxygen absorbed under high temperature.

The conventionally used phosphoric fluxes etc. as deoxidizing agents have an extremely deleterious effect on the sulphuration resistance in the alloys according to the present invention. Thus they must not be used. Similarly S must also be prevented from being mixed in by accident at melting. The founding is carried out by a melt mold etc. After face scraping, the alloys are subjected to the hot or cold rolling. The workability is very high. The heat treatment during processing is between 500° and 650° C. As for the cooling method, a quick cooling is more effective than a slow one from the point of view of workability or sulphuration resistance.

The alloys shown in the example were produced in the same manner as mentioned above. The final reduction rate was 30 percent (cold rolling) and the alloys were formed into the plates having a thickness of 2 mm, after which test pieces were cut off from them respectively for examination of their properties. The result is shown in Table 2.

Table 2

| Alloy No. according to the invention | | sulphuration range: hydro sulfide gas | sulphuration range: artificial sweat | Hv after 30% cold rolling | color tone |
|---|---|---|---|---|---|
| Alloy no. | 2 | ○ | ○ | 118 | silver white |
| do. | 3 | ○ | ◎ | 147 | semi yellow white |
| do. | 4 | ◎ | ◎ | 165 | silver white |
| do. | 5 | ◎ | ◎ | 155 | do. |
| do. | 6 | ◎ | ◎ | 148 | do. |
| do. | 7 | ◎ | ◎ | 148 | do. |
| do. | 8 | ◎ | ◎ | 152 | do. |
| do. | 9 | ◎ | ◎ | 153 | do. |
| do. | 10 | ◎ | ◎ | 165 | do. |
| do. | 11 | ◎ | ◎ | 142 | do. |
| Pure silver | | x | x | 77 | pure silver |
| Sterling silver | | x | x | 98 | semi yellow white |
| Au-Pd-alloy | | ○ | ◎ | 142 | gray |

In the sulphuration resistance test, the alloys were kept in the hydro sulfide gas in the same manner as shown in the Example 1. The surface condition of the test pieces was then examined after 6 hours. The result is shown by the following signs. The sign of ◎ shows "no discoloration." The sign of ○ shows "a little discoloration," the sign of "x" shows "discoloration to black," while the pure silver and the Sterling Silver discolored to black within 5 minutes.

Furthermore, the sulphuration resistance test was carried out in the artificial sweat as follows:

The half portion of the test piece was immersed in the sweat which was compounded artificially. After keeping it in the sweat at 36° C for 48 hours, it was examined. The result is also shown in Table 2. The signs have the same meaning as mentioned above.

The composition of the artificial sweat is as follows. This is the same as that of the normal sweat of man.

| COMPOSITION OF ARTIFICIAL SWEAT | |
|---|---|
| NaCl | 0.648 – 0.987% |
| $Na_2S$ | 0.006 – 0.025% |
| $(NH_2)_2Co$ | 0.086 – 0.173% |
| $NH_4OH$ | 0.010 – 0.018% |
| Saccharose | 0.006 – 0.022% |
| Lactic acid | 0.034 – 0.107% |
| $H_2O$ | remainder |

It can be understood from the above examples that the alloys according to the present invention have a high sulphuration resistance. As for the hardness, the alloys showed about 160 Hv by a 30 percent cold rolling. It was found that the alloys according to the invention have approximately the same mechanical properties as brass.

After various experiments, the inventors also found that the mechanical strength and the sulphuration resistance could be increased still higher by minimizing crystal grains and making the quality uniform by adding a very small amount of sub-additional elements such as Ti, Zr, Be, Cr, Si, Al, Ge and Sb. These elements are alloyed and act to make the Ag atom stable and at the same time act to protect the surfaces of the alloys by oxidizing themselves preferentially, all of these elements making the very stable oxides. Therefore, the sulphuration resistance can be further increased by making the oxidized film intentionally to protect the surface of the silver alloy.

In other words, the alloys can be heated up to 100° – 300° C in the atmosphere where oxygen is moderately rare (or in a vacuum) to make a stronger oxidized film than that in a room temperature. In this case, however, it is important to select the conditions such as atmosphere, temperature, etc. so the luster of the alloy surface by the oxidized film is not lost. If the additional amount of sub-additional element is less than 0.001 percent the favorable effect cannot be obtained. If Ti, Zr, Be, Cr and Si of more than 1 percent is added respectively, the alloy becomes extremely brittle and hardened, and further since insoluble elements are yielded, a fine luster of the alloy surface cannot be obtained at the mirror-polishing. The additional amount is, therefore, suitable in the range of 0.001–1 percent.



Further, respective additions of Al, Ge and Sb of 5 percent at the maximum does not diminish the workability and surely have favorable effects on the sulphuration resistance and the mechanical property. The additional amount is fixed in the range of 0.001– 5 percent.

These sub-additional elements have the same action. If more than two kinds of these elements are added as a mixture they do not diminish the effect of their own actions. Therefore, these sub-additional elements can be added not only singly but mixed together (more than two kinds). The latter is more effective than the former.

The effects of the sub-additional elements will be explained by way of the following embodiment.

## EXAMPLE 3

Table 3 shows the chemical composition of the alloys shown in the example. Table 4 shows the properties of the alloys above. These are the result of the examination in the same manner as shown in example 2. However, the keeping periods at the sulphuration resistance tests in hydrosulfide gas and in artificial sweat are 10 hours and 60 hours respectively.

As is apparent from Table 4, the sulphuration resistance and the mechanical property are greatly increased by adding the sub-additional elements. The alloy No. 15 according to the invention, for example, shows 50–52 kg/mm² in its tensile strength. This can compare with a brass in hardness. As Ti, Zr, Cr, Be and Si among these elements have high melting points, they are formed into mother alloys with Ag at melting and then added in the form of mother alloys. Further, they are easy to oxydize under a high temperature. Thus it is desirable to use some suitable fluxes or otherwise to melt in an inactive gas in order to prevent the loss of the melt due to oxydization at melting.

In the alloys, according to the present invention, the workings such as melting, founding and rolling, etc., are easily carried out, but if a relatively large amount of Sn and In are added, or the oxides are mixed in when a melting process is not carried out successfully, the workability (malleability and ductility) may be slightly decreased.

As to the above, various experiments and examinations were repeated. The inventor found that it is effective to add a little amount of Cu. Cu is soluble in the alloys and greatly improves foundability, malleability and ductility of the alloys. Further, it acts to avoid segregation of the other additional elements. When Sn and In are added in great amounts, while Zn in small amount, the effect mentioned above is especially large.

Table 3

| Alloy No. according to the invention | | Sn | In | Zn | Ag | Sub-additional element | |
|---|---|---|---|---|---|---|---|
| Alloy No. | 12 | 8.3 | 2.1 | 1.0 | remainder | | non |
| do. | 13 | 8.2 | 2.0 | 0.9 | do. | Ti | 0.2 |
| do. | 14 | 8.3 | 1.9 | 1.0 | do. | Zr | 0.9 |
| do. | 15 | 8.2 | 1.9 | 1.2 | do. | Be | 0.1 |
| do. | 16 | 8.2 | 2.0 | 1.0 | do. | Cr | 0.2 |
| do. | 17 | 8.3 | 2.1 | 1.1 | do. | Si | 0.05 |
| do. | 18 | 8.1 | 2.3 | 1.1 | do. | Al | 1.1 |
| do. | 19 | 8.0 | 1.9 | 1.2 | do. | Ge | 3.0 |
| do. | 20 | 8.2 | 2.2 | 1.0 | do. | Sb | 1.3 |
| do. | 21 | 8.2 | 2.1 | 0.9 | do. | Ti 0.1, | Al 1.3 |
| do. | 22 | 8.3 | 2.0 | 0.9 | do. | Be 0.2, | Cr 0.1 |
| do. | 23 | 8.3 | 2.0 | 1.1 | do. | Ti 0.03, Ge 13 | Zr 0.5 |

Table 4

| Alloy No. according to the invention | | sulphuration range hydro sulfide gas | artificial sweat | Hv. after 30% cold rolling | color tone |
|---|---|---|---|---|---|
| Alloy No. | 12 | ○ | ○ | 139 | silver white |
| do. | 13 | ○ | ○ | 155 | do. |
| do. | 14 | ○ | ○ | 163 | do. |
| do. | 15 | ○ | ○ | 153 | do. |
| do. | 16 | ○ | ○ | 165 | do. |
| do. | 17 | ○ | ○ | 151 | do. |
| do. | 18 | ○ | ○ | 163 | do. |
| do. | 19 | ○ | ○ | 168 | do. |
| do. | 20 | ○ | ○ | 159 | do. |
| do. | 21 | ○ | ○ | 170 | do. |
| do. | 22 | ○ | ○ | 162 | do. |
| do. | 23 | ○ | ○ | 175 | do. |

With the additional amount of more than 0.001 percent, the effect is shown. However, if it exceeds the solution limit, the sulphuration resistance of Ag is at times decreased. Thus it is fixed in the range of 0.001–10 percent.

The effects in improving workability and foundability by addition of Cu will be disclosed with the explanation of the following embodiment.

## EXAMPLE 4

Table 5 shows the chemical composition of the alloys — one with Cu added, the other without Cu.

Table 5

| Alloy No. according to the invention | | Sn | In | Zn | Ag | Cu |
|---|---|---|---|---|---|---|
| Alloy No. | 24 | 6.7% | 3.4% | 1.8% | remainder | 20% |
| | 25 | 7.2 | 1.5 | 1.4 | do. | 0.4% |
| | 26 | 6.7 | 3.5 | 1.8 | do. | 0 |
| | 27 | 7.4 | 1.6 | 1.5 | do. | 0 |

Table 6 shows the properties of the alloys shown in Table 5. Namely, the yields for face scraping to remove the surface roughness, workability in rolling process, etc., and the sulphuration resistance (keeping in hydrosulfide gas — in the same manner as shown in example 1) are shown. It can be understood from table 5 that Cu has a favorable effect on foundability and workability.

Table 6

| Alloy No. according to the invention | | Ingot Surface | Yield Rate By Face Scraping | Workability | Sulphuration resistance |
|---|---|---|---|---|---|
| Alloy No. | 24 | good | 79% | good | ○ |
| do. | 25 | good | 77 | extremely good | ○ |
| do. | 26 | average | 67 | average | ○ |
| do. | 27 | average | 64 | good | ○ |

As described above, the alloys according to the present invention comprise Ag, Sn, In and Zn as main elements. Ti, Be etc. as sub-additional elements for improving the sulphuration resistance and the mechanical property, and Cu for improving foundability and the workability. The addition of Cu and that of sub-additional elements show entirely different effects respectively. Thus even if these elements are added as a mixture, their own effects are not spoiled.

As can be understood from the above description, the silver alloys according to the invention have extremely high sulphuration resistance compared with that of the conventional silver alloys.

The inventors confirm "the superiority" of the alloys according to the invention not only by the experiments in the laboratory, but also by actually producing and using the ornaments, tablewares or watch cases, etc. Furthermore, since the silver alloy according to the invention has a mechanical property as high as brass, high plasticity and higher free cutting property than that of a free cutting brass, it can be widely applied to practical uses and industrial uses.

What is claimed is:

**1.** A tarnish-resistant, easily workable silver-base alloy having the characteristic appearance of pure silver consisting essentially of 4–10% of Sn, 0.5–12% of In, and 0.1–5% of Zn by weight, the remainder being silver.

**2.** A tarnish-resistant, easily workable silver-base alloy having the characteristic appearance of pure silver consisting essentially of 4–10% of Sn, 0.5–12% of In, 0.1–5% of Zn by weight and at least one member of the group consisting of Ti, Zr, Be and Cr wherein the total quantity of said member or members is in the range of .001 to 1 percent by weight, the remainder of said silver-base alloy being silver.

**3.** A tarnish-resistant, easily workable silver-base alloy having the characteristic appearance of pure silver consisting essentially of 4–10% of Sn, 0.5–12% of In, 0.1–5% of Zn by weight, and at least one member of the group consisting of Sb, Al and Ge, wherein the total quantity of said member or members is in the range of 0.001–5 percent by weight, the remainder of said silver-base alloy being silver.

**4.** A tarnish-resistant, easily workable silver-base alloy having the characteristic appearance of pure silver consisting essentially of 4–10% of Sn, 0.5–12% of In, 0.1–5% of Zn by weight, at least one member of the group consisting of Sb, Al and Ge, wherein the total quantity of said member or members is in the range of 0.001–5 percent by weight, and at least one member of the group consisting of Ti, Zr, Be and Cr wherein the total quantity of said member or members is in the range of .001–1 percent by weight, the remainder of said silver-base alloy being silver.

5. a tarnish-resistant, easily workable silver-base alloy having the characteristic appearance of pure silver consisting essentially of 4–10% of Sn, 0.5–12% of In, 0.1–5% of Zn by weight, containing 0.001–10% of Cu by weight and at least one member of the group consisting of Ti, Zr, Be and Cr wherein the total quantity of said member or members is in the range of .001–1 percent by weight, the remainder of said silver-base alloy being silver.

6. A tarnish-resistant, easily workable silver-base alloy having the characteristic appearance of pure silver consisting essentially of 4–10% of Sn, 0.5–12% of In, 0.1–5% of Zn by weight, containing 0.001–10% of Cu by weight, and at least one member of the group consisting of Sb, Al and Ge, wherein the total quantity of said member or members is in the range of 0.001–5 percent by weight, the remainder being silver.

7. A tarnish-resistant, easily workable silver-base alloy having the characteristic appearance of pure silver consisting essentially of 4–10% of Sn, 0.5–12% of In, 0.1–5% of Zn by weight, containing 0.001–10% of Cu by weight and at least one member of the group consisting of Sb, Al and Ge wherein the total quantity of said member or members is in the range of 0.001–5 percent by weight, and at least one member of the group consisting of Ti, Zr, Be and Cr, wherein the total quantity of said member or members is in the range of .001 to 1 percent by weight, the remainder being silver.

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