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[Continued on next page]

(54) **Title:** SILVER ALLOY COMPOSITIONS

Alloy No.	Ag	In	Sn	Zn	Cu	Ni	Al	B	Si	Li	Mg
1	92.500	-	-	-	7.500	-	-	-	-	-	-
2	93.000	1.000	3.600	2.235	0.115	0.050	-	-	-	-	-
3	93.000	1.000	2.900	2.935	0.115	0.050	-	-	-	-	-
4	93.000	1.000	4.500	1.335	0.115	0.050	-	-	-	-	-
5	93.000	1.000	3.600	-	2.350	0.050	-	-	-	-	-
6	93.000	1.000	3.600	1.235	0.115	0.050	1.000	-	-	-	-
7	93.000	1.000	3.000	2.235	0.115	0.050	0.600	-	-	-	-
8	93.000	1.000	3.000	2.235	-	0.050	0.600	0.115	-	-	-
9	93.000	1.000	3.000	2.235	-	0.050	0.600	-	0.115	-	-
10	93.000	1.000	3.000	2.035	-	0.050	0.600	0.115	-	0.200	-
11	93.000	1.000	3.000	2.035	-	0.050	0.600	0.115	-	-	0.200

(57) **Abstract:** Silver alloy compositions having reduced susceptibility to sulphidation and reduced susceptibility to fire stain relative to 92.5% silver 7.5% copper alloy, and having mechanical properties for casting and forming comparable to or better than 92.5% silver 7.5% copper alloy, and having an appearance similar to 92.5% silver 7.5% copper alloy. The silver alloy compositions include at least 92.5% silver 2.0% - 4.0% tin; 1.7% - 2.6% zinc and 0.50% - 1.5% indium.

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SILVER ALLOY COMPOSITIONS

Field of the Invention

The field of the invention relates to silver alloy compositions, and in particular to sterling silver alloy compositions that have an improved resistance to sulphidation and formation of fire stain.

Background to the Invention

Sterling silver alloys are widely used in jewellery and silverware because of their sparkling reflectivity, their artistic heritage, as well as their bactericidal properties. Jewellery includes items such as rings, earrings, necklaces, bracelets and so on. In the European Union, there are strict regulations governing the amount of nickel that can be present in jewellery and fine jewellery. Silverware includes items such as tableware (cutlery, trays, tea and coffee sets and so on), candlesticks, cigarette lighters, photograph frames, mirrors, coins, musical instruments and the like.

A requirement of sterling silver is that it must contain at least 92.5% silver in order to be entitled to be termed "sterling silver". Conventional sterling silver alloys comprise 92.5% silver and 7.5% copper.

Sulphidation

A problem of sterling silver alloys is that they suffer from sulphidation (also termed tarnishing). Silver alloys slowly react with sulphur compounds present in the air to form silver sulphide. Consequences of the silver sulphidation are that the surface of sterling silver products becomes an unattractive yellow colour or the surface darkens as silver-sulphur compounds such as silver sulphide are slowly deposited on the surface. This constitutes a problem for manufacturers of sterling silver articles whose products tend to get darker. Tarnishing is aesthetically unacceptable for most consumers, who must spend time polishing silverware products to remove the tarnish.

The most prevalent reaction that causes sulphidation is between silver and H_2S present in the air, as shown in equation 1:

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

The main factors that increase the degree of sulphidation of silver are:

1. Relative humidity: The higher the humidity, the higher the sulphidation rate. For the manufacturer of silverware, this factor cannot be altered.

2. Temperature: The higher the temperature, the higher the sulphidation rate. As for the humidity rate, for the manufacturer of silverware this factor cannot be altered.

3. Surface roughness: Rough surfaces react more readily with tarnishing compounds. Control of surface roughness can therefore be a factor in reducing sulphidation, especially for silverware.

4. Alloy composition: Alloying additions may have a beneficial or deleterious effect on sulphidation of silver. For example, copper (Cu) is often added to sterling silver items such as silver forks, knives, salvers and a whole range of silver tableware because of its beneficial effect on mechanical properties and the non-deleterious effect on the colour. 92.5% silver – 7.5% copper alloy is consequently very widely used in the silverware sector. However, copper enhances sulphidation. Therefore the addition of copper improves certain properties such as the 'workability' of the silver, but at the expense of increasing the susceptibility of the sterling silver alloy to sulphidation and fire stain (oxidation of alloying elements, especially copper).

Sulphidation of sterling silver leads to a graduate change of colour of the surface of the silver. Silver is a very white metal, with a high reflectivity. The first effect of sulphidation is to give a yellowish hue to the surface. As the degree of sulphidation increases, the colour changes from yellow to brown, and the reflectivity is strongly reduced. With further sulphidation, the colour changes to bluish and black. This effect can occur in different ways depending on the sulphur content in the atmosphere. For example, a piece of silverware can remain visibly unchanged over a period of one year in an environment with low pollution, such as the countryside, but the same piece of silverware can becomes dark brown in 3 months in an environment with higher pollution such as a city during winter.

Referring to Fig. 1 herein, there is illustrated a table showing the colour change of 92.5% Ag 7.5% Cu sterling silver when subject to a sulphidation test. It can be seen that the reflectivity L decreases with increasing time of exposure to sulphidation, and the colour change ΔLab increases with increasing time of exposure to sulphidation.

<u>Other properties in relation with alloying elements</u>:

Elements that are commonly alloyed with silver include:

Al, Au, Bi, Cu, Ge, In, Mg, Ni, Pb, Pd, Sb, Si, Sn, Te, Tl, Zn.

In jewellery and silverware applications, the alloys are mostly silver-copper alloys, with 80% or 92.5% of silver. Another common addition is germanium (2% - 6%). However, the germanium alloys also contain copper that is necessary for appropriate mechanical properties of the alloy and the sulphidation resistance is therefore lowered.

The criteria used for selection of an alloy in the fields of silverware and jewellery are:

- Alloy colour
- Ability to anneal and work harden
- Mechanical properties (strong enough for use, but easy to work into a desired shape). Generally, the mechanical properties referred to include Vickers hardness in the annealed and cold worked conditions. Vickers

hardness (Hv_{10}) values of 92.5% silver 7.5% copper alloys are around 60 in the annealed condition and 120-150 with 75% reduction.

- Resistance to sulphidation
- Weldability
- Polishability
- Easy to cast
- Low fire stain tendency (fire stain is a termed used to describe the discolouration due to oxidation of alloying elements, especially copper. See below).

Current ways of avoiding silver sulphidation

The current methods that are widely used to avoid the problem of sulphidation of silver alloys are a) the use of surface treatments or b) the direct manufacture of silver alloys more resistant to sulphidation.

a) Surface treatments

Metallic coatings

Extremely thin metal coatings of gold, palladium, platinum or rhodium can be used to reduce the degree of tarnishing of silver. Using these treatments, sulphidation resistance of silver alloys is said to be enhanced up to five times compared to pure silver (see Inder Singh, P. Sabita, V.A. Altekar, 'Silver Tarnishing and its Prevention – A Review', National Metallurgical Laboratory, India). These films are around 100-200 Å thick. Rhodium is the most commonly used metallic coating in jewellery.

Problems of thin metallic films include:

- Such metallic coatings are difficult and expensive to obtain.
- Any damage to the coating leaves the underlying silver alloy exposed, which can then react with sulphur.
- Metallic coatings modify the surface aspect, for example the colour, which is unsatisfactory for silverware articles.

Oxide coatings

Oxides coatings such as BeO, Al_2O_3, ZrO_2, MgO and TiO_2 can be produced by sputtering or by cathodic reduction of solutions containing soluble salts of the metallic ion. Sputtering requires expensive equipment and is complicated, as is cathodic reduction.

Anodic treatment of silver to form a tarnish preventive film on its surface has also been studied. Silver may be anodically passivated in chloride solution or in alkaline solutions by photoelectric polarisation. Oxidation of silver is quite complex and results in the formation of both AgO and Ag_2O that are resistant to sulphidation.

As for metallic coatings, oxide coatings are reported to increase the protection of the underneath silver alloy up to five times (see L. Gal-Or, '*Tarnishing and Corrosion of Silver and Gold Alloys*', Institute of Metals, TECHNION – Israel Institute of Technology).

Organic coatings / Lacquers

Varnishes or lacquers based on polymers dissolved in solvents can be used to reduce the degree of tarnishing of silver or silver alloys. Varnish or lacquer coatings protect silver by forming a physical barrier between the metal and its environment. They are very resistant against sulphidation.

However, these coatings are not really suitable for silverware products. Such coatings tend to modify the silver appearance by producing glittering reflections. Moreover, silver tableware (forks, knives, etc.) cannot be lacquered, as these organic products can be harmful and fall foul of health and safety regulations.

Organic coatings also exhibit poor wear resistance. Moreover, another drawback is their poor chemical resistance (against sweat, water, and detergents such as washing-up liquid). Organic coatings are therefore not suitable for silverware protection.

Chromatation / Passivation

Some chemical conversions treatments can be used on silver. They are called passivation or chromatation treatments and consist of a complex chromate layer on the surface. This layer is very sensitive to handling and is destroyed by rubbing. In addition, hexavalent chromium cannot be used for silverware used with food for health and safety reasons.

Limitations of surface treatments

Surface treatments introduced above are potential solutions to resist sulphidation but they exhibit major drawbacks that can be summarised as followed:

Accidental scratches issues:

Metal or oxide protective coatings exhibit good wear resistance. However, these surface treatments offer only superficial protection and therefore accidental scratches can lead to non-protected areas that will be tarnished. In the same way, complete removal of the protection leaves the surface unprotected and sulphidation occurs rapidly. Once the surface is scratched or damaged it is extremely difficult to remove discolouration caused by sulphidation, as the sulphide is disposed within the scratch and it is difficult to polish within the scratch.

Protective organic coatings can be used to increase the resistance to sulphidation, but they often do not last more than few months or years: They can be dissolved by washing products, sweat, or oral contact.

Poor Surface aspect

Some of the surface treatments (especially organic coatings) modify the appearance of silver products. So, even if they are efficient against sulphidation, the appearance is modified and that does not satisfy customers in the sector of silverware and jewellery.

Bio-compatibility

This is the case of lacquers and varnishes that do not fulfil health and safety requirements when applied to silverware such as cutlery, goblets, tankards, or to jewellery. Chromatation also involves hexavalent chromium that is harmful for health and polluting for the environment.

There is therefore a need to find sulphidation resistant sterling silver alloy compositions that do not require any protective coatings.

b) Sulphidation bulk resistant materials: Binary and Ternary silver alloys

Definitions

Binary Silver Alloy: This means an alloy such as Ag / X or [Ag / Cu] / X where 'X' is one additional element that should improve sulphidation resistance.

Ternary Silver Alloy: This is an alloy such as Ag / X / Y or [Ag / Cu] / X / Y, where 'X' and 'Y' are two additional elements used to improve sulphidation resistance.

Binary silver alloys

Ag / X (X = Cr, Ta, Al, Ti, or Th)

US 4,775,511 discloses that some binary alloys can improve sulphidation resistance of silver. This patent reported that small additions of chromium, tantalum, aluminium, titanium, and thallium in an amount that does not exceed 1.5% weight increases sulphidation resistance. A thin layer of oxide is formed (2-5 nm thick) and does not affect the properties of silver based-alloys. Furthermore, these binary alloys present the advantage of being resistant to scratches. Indeed, the added element, in the event of damage of the oxide layer, forms a new oxide film of the element before the formation of the silver sulphide, to thereby protect silver base alloys from tarnishing. However, the main disadvantage of these binary silver alloys is that the sulphidation resistance is not improved sufficiently to allow these alloys to be used commercially as silverware.

Furthermore, the addition of only these elements does not produce the required mechanical properties of the alloy to be comparable to those of 92.5% silver 75% copper alloy.

Ag / Ge – Ag / Cu / Ge

Germanium is one of the best currently known additional elements that increase sulphidation resistance of silver. M. RATEAU (Mateleurop Recherche,Trappes), 'Tarnishing Resistance of Silver – Germanium and Silver – Copper – Germanium', 1995, MATERIAUX & TECHNIQUES, N° 10 –11. reports the resistance to tarnishing of silver alloys under thioacetamid test ISO 4538 (90% humidity + H_2S vapours, T=25°C), shown in Fig. 2.

Addition of germanium delays the sulphidation up to 8 times (Ag – 4 % Ge) compared to pure silver. Indeed, germanium fixes oxygen and forms a protective layer of GeO_X. That is why germanium is currently used in very small amounts in dental alloys and high temperature brazing.

As shown in Fig. 2, the binary alloy Ag / Ge does not completely prevent tarnishing. Furthermore, germanium is expensive and increases the cost of silver alloy significantly. Germanium is added to a 92.5% silver 7.5% copper alloy and boron is added as a grain refiner. A grain refiner is required to maintain the mechanical properties of the alloy such as the "workability" or ease of processing. However, its "workability" is still not comparable to that of 92.5% silver 7.5% copper alloy, and therefore not suitable for normal processing. Furthermore, the inclusion of substantial amounts of copper reduces the effectiveness of the germanium in terms of its properties of reducing sulphidation.

Ag / Si

As with germanium, silicon is known for its deoxidising properties. As an additional element to silver to reduce tarnishing, silicon gives good results. However, it tends to make the material strongly brittle and prevents cold working.

There have been a lot of attempts to produce a "stainless" silver alloy that adequately resists tarnishing. However, these involved adding another metal in quantities of more than a few percentage. US 3,778,259 reports tarnish-inhibited silver made of (by weight):

- Tin 29 % - Silver 70 % (and some impurities of nickel)
- Tin 30 % -Silver 69 % (and some impurities of nickel)
- Tin 45 % -Silver 45 %

However, addition of large amount of metal changes other properties of the silver alloys in addition to tarnish resistance. In the field of jewellery and silverware, the carat composition, appearance and mechanical properties are also changed. Moreover, the standard composition of sterling silver includes a minimum of 92.5 % of silver. Therefore, adding more than 7.5 % of an element in silver to improve its sulphidation resistance is useless for silverware applications; the composition would lose its legal appellation 'silver' and could not be marketed under this name.

As a conclusion, binary silver alloys have not been successful candidates for sulphidation resistance because either large amounts of alloying elements are added (more than a few percent), which leads to good sulphidation resistance, but other properties (electrical, mechanical) are worsened and the standard appellation 'silver' is lost, or, small amounts of alloying elements are added (up to 1.5%), but sulphidation resistance is not enhanced in an optimal manner.

Ternary silver alloys and more than 2 additional elements

Some experiments have shown improvements in sulphidation resistance for ternary silver alloys. US 5,882,441 discloses improved tarnishing resistance of an alloy consisting of:

- 90% to 94% by weight silver
- 1% to 3% by weight copper
- 3.75% to 7.35% by weight zinc
- 0.1 % to 0.25 % by weight silicon

However, this alloy comprises a relatively high amount of copper to improve the mechanical properties of the alloy, and so would be susceptible to "fire stain" discussed below.

Oxidation

Another problem with 92.5% silver 7.5% copper alloy is the formation of "fire stain". Fire stain is caused by the oxidation of certain alloying elements, and especially copper in the 92.5% silver 7.5% copper alloy. If, for example, it is required to weld two pieces of 92.5% silver 7.5% copper alloy together, fire stain can form leading to an unsightly dark appearance on the surface of the silver object, which is difficult to remove.

It would be advantageous to have a silver alloy that has both improved tarnish resistance and improved fire stain resistance.

JP 62243725, JP 62010231 and JP 62054046 all disclose a silver alloy composition developed to exhibit sulphidation resistance. The principle components included within the alloys include silver, tin, zinc and indium. Whilst these documents do disclose a sulphidation resistant silver alloy, the alloys disclosed are disadvantageous for a number of reasons. In particular, the compositions are not optimised to reduce the amount of indium that is required to be incorporated within the alloy to achieve the desired sulphidation resistance.

Incorporation of excessive indium is disadvantageous due to its high cost which is typically four times that of silver.

What is required is a silver alloy composition that satisfies the following criteria:

- increased sulphidation resistance
- reduced fire stain
- the appropriate hardness
- the appropriate colour
- the appropriate mechanical properties including specifically the desired annealibility, ductility and malleability.

Summary of the Invention

The inventors have realized the problems associated with prior art sterling silver alloy compositions. It is desirable to reduce the susceptibility of a sterling silver alloy to tarnishing by the formation of silver sulphide, and also to reduce the susceptibility to fire stain of sterling silver alloy compositions, particularly those containing large quantities of copper. It is possible to achieve these properties with prior art alloys, but the prior art alloys do not give the required mechanical properties such as workability that can be obtained with 92.5% silver 7.5% copper alloy. Alternatively, the prior art alloys do not have the required appearance for silverware, but are dull and exhibit a poor reflectivity.

The inventors have developed range of sterling silver alloy compositions that have a reduced susceptibility to sulphidation and a reduced susceptibility to fire stain, whilst retaining the properties required for casting and mechanical properties required for various working operations. The alloy comprises at least 92.5% silver in order to be entitled to the term “sterling silver”. The alloy further comprises indium to improve the tarnish resistance and zinc and tin also to improve the tarnish resistance and to improve the mechanical properties of the alloy. Additionally, the alloy further comprises aluminum to provide the required colouration characteristics of the metal and magnesium so as to achieve the desired flowability of the material.

According to a first aspect of the present invention there is provided a sterling silver alloy composition comprising by weight: at least 92.5% silver; 3.0% - 4.0% tin; 1.7% – 2.6% zinc; 0.5% - 1.5% indium.

Preferably, the composition further comprises 0.1% - 1.5% aluminium and/or 0.01% - 0.15% magnesium.

Preferably, the composition further comprises one or more grain refiners, each grain refiner or the total amount of grain refiners representing 0.05% - 0.35% by weight and selected from the list of:

Copper; manganese; iron; nickel; silicon; boron; titanium; iridium and/or cobalt.

Alternatively, the composition may comprise copper, manganese and/or iron, each in the range 0.10% - 0.3% or 0.01% - 0.2% by weight. Additionally, the composition may comprise any one or a combination of the following:

Nickel, silicon, boron, titanium, iridium or cobalt, each within the range 0.05% - 0.2% by weight.

Optionally, the composition may comprise 0.01% - 0.1%; 0.05% - 0.35% or no more than 0.05% nickel.

Preferably, the composition comprises 0.05% - 0.25% lithium.

Preferably, the composition further comprises 0.02% - 0.3% phosphorous.

Alternatively, the composition may comprise 96.8% silver.

Preferably, the composition comprises 92.5% - 93.5% silver.

According to a second aspect of the present invention there is provided a silver alloy composition comprising by weight: at least 92.5% silver > 0% - 5% tin; > 0% - 5% zinc; > 0% - 2% indium; > 0% - 3% aluminum; > 0% - 2% magnesium; wherein any remaining weight % may be silver.

According to a third aspect of the present invention there is provided a silver alloy composition comprising by weight: at least 92.5% silver; > 0% - 5% tin; > 0% - 5% zinc; > 0% - 2% indium; > 0% - 3% aluminum; > 0% - 2% magnesium; wherein any remaining weight % is silver and/or any one or a combination of the following grain refiners: copper; manganese; iron; nickel; silicon; boron; titanium; iridium; cobalt.

Preferably, the composition comprises any one of the grain refiners wherein each or the total amount of grain refiners added is within the range 0.05% - 0.35% by weight.

According to a fourth aspect of the present invention, there is provided a sterling silver alloy composition comprising by weight: 92.5% - 93.5% silver; 2.5% - 3.5% tin; 2.0% - 3.0% zinc; 0.3% - 1.1% indium; 0.2% - 0.8% aluminum; 0.03% - 0.1% magnesium.

Brief Description of the Drawings

For a better understanding of the invention and to show how the same may be carried into effect, there will now be described by way of example only, specific embodiments, methods and processes according to the present invention with reference to the accompanying drawings in which:

Figure 1 illustrates a table showing the colour change of 92.5% Ag 7.5% Cu sterling silver when subject to a sulphidation test.

Figure 2 illustrates a table showing prior art data of the resistance to tarnishing of silver alloys under thioacetamid test ISO 4538 (90% humidity + H_2S vapours, T=25°C).

Figure 3 illustrates the processing steps of test samples.

Figure 4 illustrates a table showing the Vickers Hardness and colour change after a sulphidation test, and the average grain size of selected ternary silver alloys.

Figure 5 illustrates a table showing the compositions of a series of sterling silver alloys.

Figure 6 illustrates a table qualitatively rating the properties of the series of sterling silver alloys.

Figure 7 illustrates a table showing the effect of aluminium and germanium additions to sterling silver alloys on the reflectivity of the alloy.

Figure 8 illustrates a table showing the effect of tin and indium additions to sterling silver alloys on the reflectivity of the alloy.

Figure 9 illustrates a table showing the effect of indium and zinc additions to sterling silver alloys on the reflectivity of the alloy.

Figure 10 illustrates the variation of hardness with the annealing temperature and time for standard sterling silver (92.5% Ag, 7.5% Cu) and a sterling silver alloy of the present invention.

Detailed Description

There will now be described by way of example a specific mode contemplated by the inventors. In the following description numerous specific details are set forth in order to provide a thorough understanding. It will be apparent however, to one skilled in the art, that the present invention may be practiced without limitation to these specific details. In other instances, well known methods and structures have not been described in detail so as not to unnecessarily obscure the description.

Indium, zinc and tin are alloyed with silver to give an improved sterling silver alloy being less susceptible to tarnishing by sulphidation and formation of fire stain. Aluminium may be included within the present composition to achieve the desired colouration of the resulting silver alloy. The weight % of aluminium added may be adjusted to achieve the desired colouration of the resulting silver alloy. Aluminium is considered to be a 'brightener' that improves the lustre and reflectivity of the alloy.

Indium is added to reduce the susceptibility to sulphidation. It is suggested that the mechanism by which this works is that indium in the alloy forms a replenishable oxide layer on the surface of a product manufactured from the alloy. This surface oxide layer is extremely thin, of the order of nanometres. However, it protects the surface of the silver alloy object from sulphur in the atmosphere, or sulphur introduced by handling that would otherwise cause sulphidation and hence tarnishing. If the indium oxide surface layer is removed, for example by polishing or scratching, indium in the silver quickly reacts with oxygen in the atmosphere to form a new replenishable surface oxide layer. It is suggested that the presence of indium protects the silver alloy from tarnishing in this way, as indium has been found to reduce the degree of tarnishing. However, it may be that the indium is protecting the silver alloy from tarnishing by some other mechanism.

Magnesium, zinc and/or tin may be added for several reasons. In prior art sterling silver, copper is added to improve the mechanical properties of silver such as hardness, workability and so on. Zinc, tin and optionally magnesium have the same effect in the new alloy composition. Magneisum, zinc and tin improve the mechanical properties of the alloy without being detrimental to the distinctive colour of sterling silver. Magnesium and tin in particular has been found to improve the flowability of the molten alloy in processes such as spinning.

It is also thought that zinc and tin form replenishable oxides on the surface of the silver alloy, and hence protect the surface from sulphidation.

It is thought that the presence of significantly more than 3% tin can be detrimental to the final colour of a 92.5% Ag 7.5% Cu sterling silver alloy such that it would not have the brightness, lustre and reflectivity of a prior art 92.5% Ag 7.5% Cu sterling silver alloy. However, for some applications of sterling silver alloys, tin levels up to 3.6% by weight are acceptable.

A grain refiner may also added to refine the grain size of the alloy. Refining the grain size improves the mechanical properties of the alloy in addition to improving the resistance of the surface to tarnishing and the surface appearance of products manufactured from the alloy.

It is preferred to use nickel as the grain refiner, although it may be that other grain refiners can be used. Current legislation does not permit the presence of more than 0.05% nickel in silverware that may be used in prolonged contact with the skin, for example jewellery. However, this level of nickel provides adequate grain refinement to the alloy.

It is difficult to introduce nickel into a cast alloy on its own, as nickel does not readily form a solid solution with the other constituents of the alloy. However, it is known that nickel forms a good solid solution with a master alloy of copper-nickel in the ratio of 75/25 copper/nickel. There may therefore be a small quantity of copper added to the alloy, but the low levels of copper are insufficient for it to lead to problems with fire stain. However, it is not essential that nickel is added as a master alloy with copper, under certain conditions nickel can be added without copper.

It has also been found that the addition of phosphorous can improve the flowability of the molten metal and therefore improve the ease of casting the alloy. Phosphorous can be added in the range 0.02% - 0.3% by weight.

An alternative addition that can improve the flowability of the molten metal by reducing its viscosity, and hence improving the castability of the alloy, is lithium. Lithium may be added in the range 0.05% to 0.2% by weight to improve the castability of the alloy.

EXAMPLES

A series of alloys were prepared and cast. Each alloy was cast into a bar test sample. Referring to Figure 3 herein, there are illustrated the processing steps of test samples. The bar was milled 301 on its upper and lower surfaces to a thickness of approximately 15.24 mm. The bar was then rolled 302 to a thickness of 7.62 mm on the first run (approximately a 50% reduction). The bar was then annealed 303 in a retort furnace after the first rolling at 550°C for 20 hours in a 95% nitrogen 5% hydrogen atmosphere. A light abrasive clean 304 was then applied to the bar. A second rolling 305 to approximately 3.81 mm (a further 50% reduction) was then applied to each bar, followed by a second annealing 306 under the same conditions as the first annealing. A third rolling 307 to approximately 1.91 mm (a further 50% reduction) was applied to each bar followed by a third annealing 308. The third annealing 308 was performed in a belt furnace to 550°C under a 75% hydrogen, 25% nitrogen atmosphere. A fourth rolling 309 was then applied to a thickness of approximately 1 mm (approximately 50% reduction) and a fourth annealing 310 was carried out under the same conditions as the third annealing 308. A finished sheet of each alloy was then prepared by a performing a fifth rolling 311 to approximately a 50% reduction, such that the final sample thickness was approximately 0.5 mm.

The Vickers Hardness was measured for a sample of each as-cast alloy, and also measured after the first rolling, the first annealing, the second rolling, the second annealing, the third rolling, the third annealing, and for the finished sheet. Vickers Hardness was measured using a Vickers diamond indenter on a polished surface of each alloy sample. A load of 10 kg was applied and the indent size measured optically. The Vickers Hardness was calculated from tabulated figures for Vickers Hardness.

To obtain an indication of the susceptibility of an alloy composition to sulphidation, a colour change test was performed on each finished sheet before and after a sulphidation test. The sulphidation test was performed by placing the example in a closed container containing a tarnishing atmosphere. The tarnishing atmosphere was obtained using a solution of ammonium sulphide in water. 1 ml of ammonium sulphide 4% was added to 20 ml distilled water (giving a final concentration of ammonium sulphide as 0.2 g/l). The ammonium sulphide was prepared in a beaker having a diameter of 50 mm and a height of 70 mm. To obtain the atmosphere, the beaker containing the ammonium sulphide solution was placed in a dessicator having a volume of approximately 5 l. Each sample was placed in the dessicator for a period of 1 hour.

The colour of each sample was measured before placing in the dessicator and after removal from the dessicator using the Lab system of colour measurement, and the colour change from before the sulphidation test to after the sulphidation test was measured as ΔLab. Colour was measured using a spectrocalorimeter using a measurement area of 3 mm. A high value of ΔLab indicates a large colour change associated with sulphidation, and a low ΔLab indicates a small or negligible colour change. The lower the ΔLab value, the lower the degree of sulphidation undergone by the sample and therefore the greater the resistance of the alloy composition to sulphidation.

Referring to Figure 4 herein, there is illustrated a table showing the Vickers Hardness and colour change after a sulphidation test, and the average grain size of selected ternary silver alloys. For comparison, selected values for 92.5% silver 7.5% copper alloy and electroplated silver are included.

A 92.5% silver 7.5% copper prior art sterling silver alloy has a Vickers Hardness for finished sheet of around 133, and a colour change of ΔLab of 48.1, and an average grain size of 8 μm.

An alloy comprising 93% silver, 1% indium, 3.6% tin, 2.2% zinc, 0.1% iron and 0.1% manganese has an as-cast Vickers Hardness of 55, a Vickers Hardness of 129 after the first rolling, a Vickers Hardness of 44 after the first annealing, a Vickers Hardness of 129 after the second rolling, a Vickers Hardness of 47 after the second annealing, and a Vickers Hardness of 121 for the finished sheet. The average grain size is 33 μm.

An alloy comprising 93% silver, 1% indium, 3.6% tin, 2.2% copper, 0.1% iron and 0.1% manganese has an as-cast Vickers Hardness of 51, a Vickers Hardness of 113 after the first rolling, a Vickers Hardness of 48 after the first annealing, a Vickers Hardness of 115 after the second rolling, a Vickers Hardness of 47 after the second annealing, and a Vickers Hardness of 107 for the finished sheet. The average grain size is 12 μm. This alloy is provided by way of comparative example.

Adding grain refiners has been found to reduce the grain size allowing better workability and surface appearance of the finished alloy. Furthermore, a reduced grain size improves the sulphidation resistance of the alloy.

Through experimental investigation the inventors have developed an alloy composition particularly suitable for horizontal or vertical continuous casting that displays suitable properties of sulphidation resistance, fire stain resistance and mechanical properties suitable to allow the alloy to be used as a replacement for 92.5% silver 7.5% copper alloy is as follows:

93.0% silver;

0.115% copper;

3.6% tin;

2.2% zinc; and

1.0% indium.

In addition to the alloy mix, 0.05% nickel grain refiner is added. The alloy contains 93% silver, and so can still be classified as sterling silver. It has good tarnish resistance and exhibits good resistance to fire stain.

Additionally, through further experimental investigation, the inventors provide an alloy composition particularly suitable for lost wax precision casting that also displays suitable properties of sulphidation resistance, fire stain resistance and mechanical properties suitable to allow the alloy to be used as a replacement for 92.5% silver 7.5% copper alloy is as follows:

92.8% silver;

0.15% copper;

3.05% tin;

2.4% zinc;

1.0% indium;

0.05% nickel;

0.05% magnesium; and

0.5% aluminium.

Magnesium is added to refine the grain size, and hence the workability of the alloy, and also to improve the castability of the molten alloy. Boron is added as a grain refiner. Aluminium is added to brighten the colour of the alloy and as a grain refiner to improve the workability of the alloy. Nickel is added as a grain refiner. This alloy displays no fire stain and is resistant to sulphidation.

Figure 5 illustrates a table showing the compositions of a series of sterling silver alloys. These alloys have been produced and the workability through all forming processes, visible grain structure, presence of fire stain, final alloy colour, reflectivity after a final polish and sulphidation resistance have been compared. The forming processes mentioned include cold rolling, spinning, deep drawing and tube making. The properties of the sterling silver alloys listed in Figure 5 are given in Figure 6. The properties are defined qualitatively as a comparative score with that of 92.5% Ag 7.5% Cu sterling silver alloy.

Alloy 1 comprises a prior art 92.5% Ag 7.5% Cu sterling silver alloy. It has a small tight grain structure that provides good workability, has a bright reflective colour, but displays fire stain owing to the presence of copper, and has poor sulphidation resistance.

Alloy 2 comprises 93% Ag, 1% In, 3.6% Sn, 2.235% Zn, 0.115% Cu and 0.05% Ni. Because the alloy has over 92.5% Ag, it is entitled to use the legal appellation "sterling silver". It has improved workability compared to 92.5% Ag 7.5% Cu sterling silver alloy, does not exhibit fire stain and has a very good resistance to sulphidation. However, its final colour and reflectivity are not as good as that of 92.5% Ag 7.5% Cu sterling silver alloy.

Alloy 3 comprises 93% Ag, 1% indium, 2.9% tin, 2.935% zinc, 0.115% copper and 0.05% nickel. Compared to alloy 2, the tin levels of alloy 3 have been reduced and the zinc levels raised. This alloy had similar properties to alloy 2, but was less workable than alloy 2, and also less workable than 92.5% Ag 7.5% Cu sterling silver alloy.

Alloy 4 comprises 93% silver, 1% indium, 4.5% tin, 1.335% zinc, 0.115% copper and 0.05% nickel. This alloy is provided by way of comparative example only. It had poor colour, reflectivity, and workability, although no fire stain was evident and the sulphidation resistance was good compared to that of 92.5% Ag 7.5% Cu sterling silver alloy.

Alloy 5 comprises 93% silver, 1% indium, 3.6% tin, 2.35% copper and 0.05% nickel. This alloy is provided by way of comparative example. Despite the high levels of copper, alloy 5 did not exhibit fire stain. Its castability and workability are comparable to that of 92.5% Ag 7.5% Cu sterling silver alloy, although the colour and reflectivity were inadequate compared to that of 92.5% Ag 7.5% Cu sterling silver alloy. The sulphidation resistance was better than that of 92.5% Ag 7.5% Cu sterling silver alloy, but not so good as alloys 2 to 4.

Alloy 6 comprises 93% silver, 1% indium, 3.6% tin, 1.235% zinc, 0.115% copper, 0.05% nickel and 1% aluminium. Aluminium is added as a "brightener" to improve the appearance of the sterling silver alloy. The castability and workability of this alloy are not so good as that of 92.5% Ag 7.5% Cu sterling silver alloy, but the resistance to sulphidation is better than that of 92.5% Ag 7.5% Cu sterling silver alloy, and alloy 6 exhibits no fire stain. The final colour and reflectivity of alloy 6 are better than those of alloys 2 to 5.

Alloy 7 comprises 93% silver, 1% indium, 3% tin, 2.235% zinc, 0.115% copper, 0.05% nickel and 0.6% aluminium. The quantity of tin and aluminium has been lowered and the quantity of zinc has been raised compared to alloy 6. The sulphidation resistance was very good, and no fire stain was exhibited. The final alloy colour and reflectivity approaches that of 92.5% Ag 7.5% Cu sterling silver alloy. The workability is comparable to 92.5% Ag 7.5% Cu sterling silver alloy, and the castability is not quite so good as 92.5% Ag 7.5% Cu sterling silver alloy.

Alloy 8 comprises 93% silver, 1% indium, 3% tin, 2.235% zinc, 0.05% nickel, 0.6% aluminium and 0.115% boron. Boron is added as a grain refiner to improve the workability of the alloy. It can be seen that this alloy has similar properties to alloy 7, but with an improved workability.

Alloy 9 has the same composition as alloy 8, with the boron replaced by silicon. The properties of alloy 9 are substantially the same as those of alloy 8.

Alloy 10 comprises 93% silver, 1% indium, 3% tin, 2.035% zinc, 0.05% nickel, 0.6% aluminium, 0.115% boron and 0.2% lithium. Boron is added as a grain refiner to improve workability, lithium is added as a flow aid to reduce the viscosity of the molten alloy and improve castability. It can be seen that the castability and workability of alloy 10 are better than those of 92.5% Ag 7.5% Cu sterling silver alloy. There is no fire stain present and the alloy has a very good resistance to sulphidation. The final colour and reflectivity of the alloy approach those of 92.5% Ag 7.5% Cu sterling silver alloy.

Alloy 11 comprises 93% silver, 1% indium, 3% tin, 2.035% zinc, 0.05% nickel, 0.6% aluminium, 0.115% boron and 0.2% magnesium. Magnesium is added to reduce the viscosity of the molten alloy, and hence improve its castability. The properties of this alloy are very similar to those of alloy 10.

It can be seen that by careful use of additives to refine grain size (to improve workability), and reduce viscosity (to improve castability), an alloy having comparable properties to 92.5% Ag 7.5% Cu sterling silver alloy can be produced that does not exhibit fire stain and is resistant to sulphidation. Careful control of additions is also required to maintain an appearance similar to that of 92.5% Ag 7.5% Cu sterling silver alloy, in order that the alloy can be used in applications such as silverware and jewellery.

The appearance of the alloy can be in part measured by the reflectivity of the alloy, and studies have been made into the effect of additions of different elements to sterling silver alloys on the reflectivity of the alloy.

Referring to Figure 7 herein, there is illustrated a table showing the effect of aluminium and germanium additions to sterling silver alloys on the reflectivity of the alloy. These figures can be compared with those shown in figure 1 for 92.5% Ag 7.5% Cu sterling silver alloy. It can be seen that the reflectivity of the alloy goes down as the amount of silver in the alloy goes down.

Referring to Figure 8 herein, there is illustrated a table showing the effect of tin and indium additions to sterling silver alloys on the reflectivity of the alloy. It can be seen that increasing the amount of tin is detrimental to the appearance of the alloy. It is thought that tin forms an oxide around the surface of the alloy, which reduce the reflectivity and are detrimental to the appearance.

Referring to Figure 9 herein, there is illustrated a table showing the effect of indium and zinc additions to sterling silver alloys on the reflectivity of the alloy. High levels of zinc are not particularly detrimental to the appearance of the silver alloy. However, high levels of zinc cannot be used as problems with oxidation could arise.

A feature of alloys 2 to 11 is that they have a high resistance to sulphidation and do not exhibit fire stain under conditions such as soldering, annealing and casting.

The alloy compositions of the present invention are readily prepared using conventional techniques such as casting. Additionally, the alloys may also be prepared using other known techniques including vapour deposition, in particular, physical vapour deposition (PVD) or chemical vapour deposition (CVD).

Examples of master alloys that can be used to introduce a grain refiner include the following:

- 15 wt% manganese, 85 wt% copper
- 15 wt% silicon, 85 wt% copper;
- 10 wt% aluminium, 90 wt% copper;
- 6 wt% titanium, 94 wt% silver;
- 25 wt% nickel, 75 wt% copper

Iron can be added on its own, as it forms an adequate solid solution with silver. Other of the elements listed above may also be added on their own without the necessity of using a master alloy. This is useful to keep the levels of copper down in the sterling silver alloy to reduce the risk of fire stain.

It is desirable to keep the silver content of the alloy at least 92.5% by weight in order for the alloy to be entitled to the appellation "sterling silver". However, silver is one of the more expensive elements in the composition, and so it is also commercially desirable to keep the silver content of the alloy to no more than 93% silver. In some applications, the silver content of the alloy can be raised above 93% where necessary.

Mechanical Properties Comparison

Various mechanical properties of alloy No.2 of figure 5 where investigated and compared with standard sterling silver (92.5% Ag, 7.5% Cu).

The hardness of both alloys was measured after both alloys were annealed at 550°C for 20 minutes in air and after rolling of the alloys to reduce the sheet thickness 'cold worked condition' simulating the process of rolling the sterling silver alloy following continuous casting to produce the required sheet thickness. The results of the investigation are detailed in table 1.

	Cold Worked Condition HV (5kg Load)	Annealed 550°C for 20mins in air HV (5kg Load)
Alloy 2 of Fig 5	145	66
Standard Sterling (92.5% Ag, 7.5% Cu)	145	90

Table 1. Results from figures hardness test using a 5 kg load.

The results indicate that alloy 2 of figure 5 of the present invention exhibits similar mechanical properties to standard sterling confirming the suitability of the present alloy as a replacement for standard sterling.

The variation of hardness with annealing temperature and time was also investigated for the same two alloys. The results are presented in figure 10. The alloys were annealed in air at various temperatures and times. Figure 10 shows the hardness results for standard sterling annealed for 20 minutes 1000; 40 minutes 1001; and the alloy 2 of figure 5 annealed for 20 minutes 1002; and 40 minutes 1003.

As illustrated in figure 10, both alloys exhibit similar mechanical properties with the hardness decreasing with an increase in annealing temperature and time.

Following work hardening, both alloys were tensile tested and the results are indicated in table 2.

	Standard Sterling Silver	Alloy 2 of Fig.5
UTS (MPa)	476	495
% Elongation	6.71	6.14
HV5	145	145

Table 2. Strength results for alloy 2 of figure 5 and standard sterling.

The tensile tests were undertaken on both alloys in a work hardened state. Both alloys exhibited a very similar tensile strength (UTS) and elongation immediately prior to failure.

As confirmed by the mechanical properties investigation, that sterling silver alloy of the present invention does exhibit very similar mechanical properties to that of standard sterling silver. Accordingly, the change from standard sterling to the alloy of the present invention by manufacturers would not necessitate substantial revision of the manufacturing process given the similar mechanical behavior of the alloys. Moreover, the silver alloy of the present invention may be considered energy saving when compared with standard sterling to achieve a desired hardness given the required annealing temperature and time as illustrated in figure 10.

Claims:

1. A sterling silver alloy composition comprising by weight:

at least 92.5% silver

3.0% - 4.0% tin

1.7% – 2.6% zinc

0.5% - 1.5% indium.

2. The composition as claimed in claim 1 further comprising:

0.15% - 1.5% aluminium.

3. The composition as claimed in claims 1 or 2 further comprising:

0.01% – 0.15% magnesium.

4. The composition as claimed in any preceding claim further comprising:

0.01% - 0.1% nickel.

5. The composition as claimed in any one of claims 1 to 3 further comprising:

0.05% - 0.35% nickel.

6. The composition as claimed in any one of claims 1 to 3 further comprising:

less than 0.05% nickel.

7. The composition as claimed in any preceding claim further comprising:

0.05% - 0.35% copper.

8. The composition as claimed in any one of claims 1 to 6 further comprising:

0.01% - 0.2% copper.

9. The composition as claimed in any preceding claim further comprising:

0.05% – 0.35% manganese.

10. The composition as claimed in any preceding claim further comprising:

0.05% - 0.35% iron.

11. The composition as claimed in any preceding claim further comprising:

0.05% - 0.35% silicon.

12. The composition as claimed in any preceding claim further comprising:

0.05% - 0.35% boron.

13. The composition as claimed in any preceding claim further comprising:

0.05% - 0.35% titanium.

14. The composition as claimed in any preceding claim further comprising:

0.05% - 0.35% iridium.

15. The composition as claimed in any preceding claim further comprising:

0.05% - 0.35% cobalt.

16. The composition as claimed in any preceding claim further comprising:

0.05% - 0.25% lithium.

17. The composition as claimed in any preceding claim further comprising

0.02% - 0.3% phosphorous.

18. The composition as claimed in any preceding claim comprising:

92.5% - 93.5% silver.

19. The composition as claimed in any one of claims 1 to 17 comprising:

96.8% silver.

20. A silver alloy composition comprising by weight:

at least 92.5% silver

> 0% - 5% tin

> 0% - 5% zinc

> 0% - 2% indium

> 0% - 3% aluminum

> 0% - 2% magnesium.

21. The composition as claimed in claim 20 further comprising:

0.1% - 0.2% copper.

22. The composition as claimed in claim 21 further comprising:

0.01% - 0.1% nickel.

23. A silver alloy composition comprising by weight:

at least 92.5% silver

> 0% - 5% tin

> 0% - 5% zinc

> 0% - 2% indium

> 0% - 3% aluminum

> 0% - 2% magnesium

wherein any remaining weight % is silver and/or any one or a combination of the following grain refiners:

copper;

manganese;

iron;

nickel;

silicon;

boron;

titanium;

iridium;

cobalt.

24. The composition as claimed in claim 23 wherein said composition comprises any one of said grain refiners within the range 0.05% - 0.35% by weight.

25. The composition as claimed in claims 23 or 24 further comprising:

0.1% - 0.2% copper.

26. The composition as claimed in claim 25 further comprising:

0.01% - 0.1% nickel.

27. A sterling silver alloy composition comprising by weight:

92.5% - 93.5% silver

2.5% - 3.5% tin

2.0% - 3.0% zinc

0.3% - 1.1% indium

0.2% - 0.8% aluminium

0.03% - 0.1% magnesium.

28. The composition as claimed in claim 27 further comprising:

0.1% - 0.2% copper; and

0.01% - 0.1% nickel.

Time	L	Colour change, ΔLab
0min	97	0
10min	71	38
20min	50	52
30min	43	57

Fig. 1 (Prior Art)

Alloy	**Stains appearance time**	**Colour of the surface**
Ag 99,99 %	~ 2 hours	Uniformly black
Ag – 7,5 % Cu	~ 2 hours	Yellowish
Ag – 5,7 % Cu –1,8 % Ge	~ 6 hours	Yellowish
Ag – 4 % Ge	~ 16 hours	Grey / Yellowish

Fig. 2 (Prior Art)

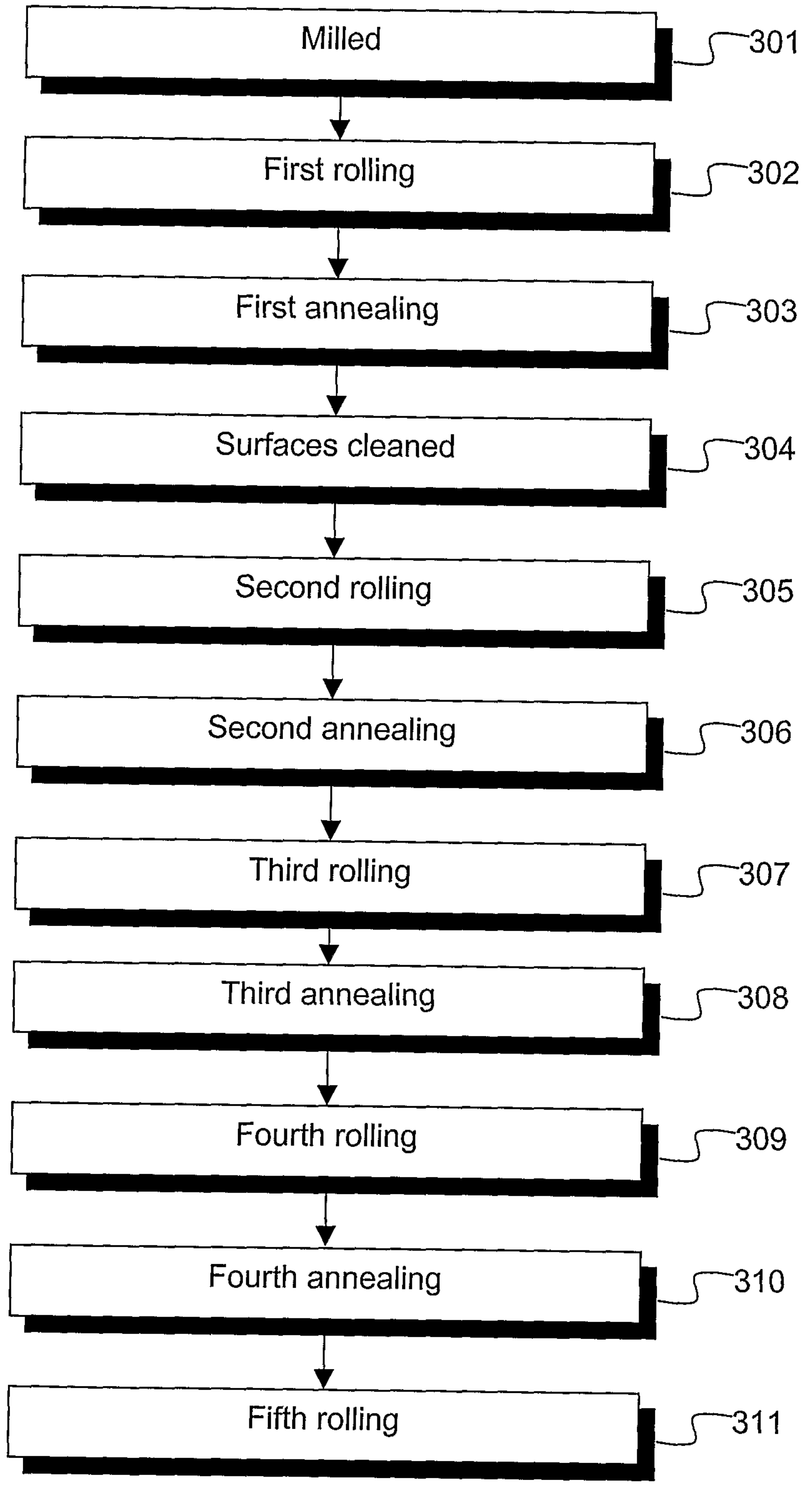

Milled
301
First rolling
302
First annealing
303
Surfaces cleaned
304
Second rolling
305
Second annealing
306
Third rolling
307
Third annealing
308
Fourth rolling
309
Fourth annealing
310
Fifth rolling
311

Fig. 3

Hardness after treatment	93% Ag 1% In 3.6% Sn 2.2% Zn 0.1% Fe 0.1% Mn	93% Ag 1% In 3.6% Sn 2.2% Cu 0.1% Fe 0.1% Mn	92.5% Ag 7.5% Cu (prior art sterling silver)	Electro-plated silver
as cast	55	51	77	
after 1st rolling	129	113	126	
after 1st annealing	44	48	67	
after 2nd rolling	129	115	130	
after 2nd annealing	47	47	68	
Finished sheet	121	107	133	
colour change after sulphidation test ΔLab			48.1	35.9
Grain size μm Average Std dev Std dev%	 33 12 38	 12 4 36	 8 2 31	

Fig. 4

Alloy No.	Ag	In	Sn	Zn	Cu	Ni	Al	B	Si	Li	Mg
1	92.500	-	-	-	7.500	-	-	-	-	-	-
2	93.000	1.000	3.600	2.235	0.115	0.050	-	-	-	-	-
3	93.000	1.000	2.900	2.935	0.115	0.050	-	-	-	-	-
4	93.000	1.000	4.500	1.335	0.115	0.050	-	-	-	-	-
5	93.000	1.000	3.600	-	2.350	0.050	-	-	-	-	-
6	93.000	1.000	3.600	1.235	0.115	0.050	1.000	-	-	-	-
7	93.000	1.000	3.000	2.235	0.115	0.050	0.600	-	-	-	-
8	93.000	1.000	3.000	2.235	-	0.050	0.600	0.115	-	-	-
9	93.000	1.000	3.000	2.235	-	0.050	0.600	-	0.115	-	-
10	93.000	1.000	3.000	2.035	-	0.050	0.600	0.115	-	0.200	-
11	93.000	1.000	3.000	2.035	-	0.050	0.600	0.115	-	-	0.200

Fig. 5

Alloy No.	Casting Ability	Workability Through All Forming Processes	Visible Grain Structure	Presence Of Fire stain	Final Alloy Colour	Reflectivity After Final Polish	Sulphidation Resistance
1	6	7	small, tight	Yes	9	9	0
2	5	8	medium, tight	No	6	6	9
3	5	4	medium	No	6	6	9
4	6	4	large	No	4	4	8
5	6	6	medium	No	5	5	7
6	5	4	medium	No	7	7	7
7	5	7	medium	No	8	8	9
8	5	8	small	No	8	8	9
9	5	8	small	No	8	8	9
10	7	8	small, tight	No	8	8	9
11	7	8	small, tight	No	8	8	9

Fig. 6

Ag	Total Alloying Elements	Al	Ge	Reflectivity L
98.81	1.19	0.22	0.96	97.26
97.72	2.28	0.23	2.06	96.55
98.16	1.84	1.05	0.79	95.89
98.8	1.20	0.53	0.67	95.15
96.03	3.97	1.21	2.76	94.18
96.02	3.98	3.23	0.75	92.65
95.01	4.99	0.42	4.56	91.34

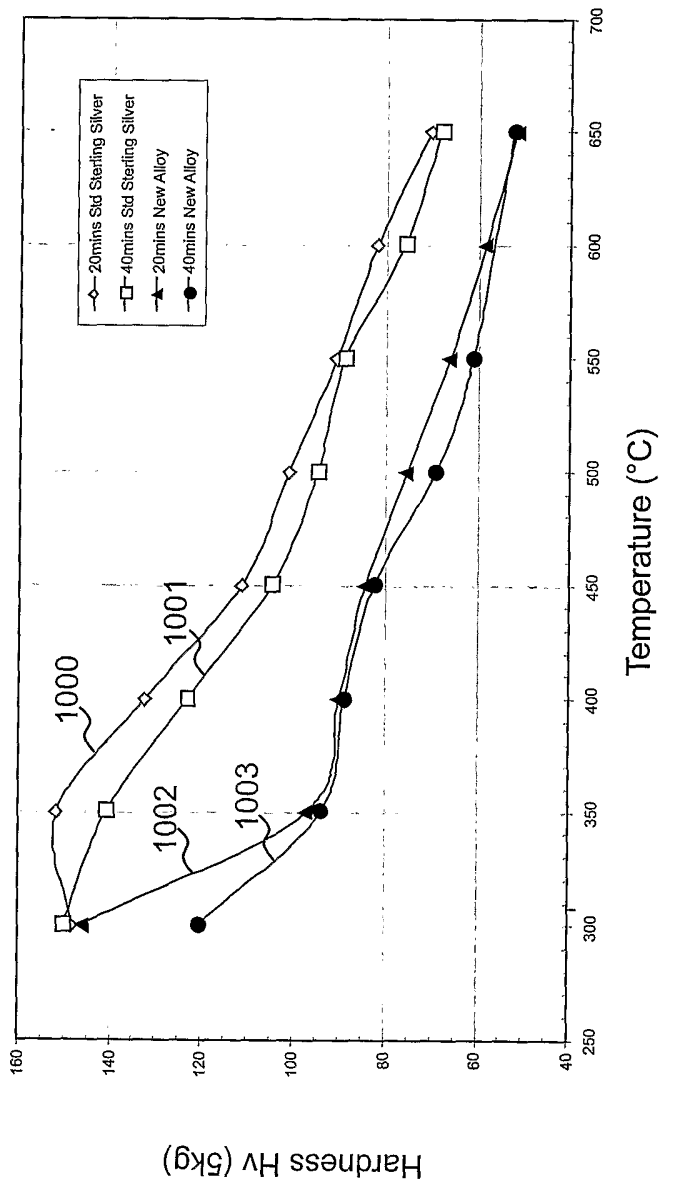
Fig. 7

Ag	Total Alloying Elements	Sn	In	Reflectivity L
99.39	0.61	0.43	0.18	97.41
94.73	5.27	0	5.27	95.89
94.24	5.76	4.6	1.16	95.66
95.74	4.26	2.97	1.29	93.99
84.22	15.78	0.51	15.27	92.56
85.83	14.17	7.45	6.72	91.56
86.56	13.44	11.61	1.84	89.92

Fig. 8

Ag	Total Alloying Elements	In	Zn	Reflectivity L
96.4	3.6	0.66	2.95	96.73
88.05	11.95	0	11.95	96.39
99.3	0.70	0.25	0.45	96.11
95.7	4.30	3.02	1.28	95.78
89.97	10.03	3.19	6.84	95.22
94	6.00	4.09	1.91	94.91
93.27	6.73	5	1.73	93.87

Fig. 9



20mins Std Sterling Silver
40mins Std Sterling Silver
20mins New Alloy
40mins New Alloy
1000
1001
1002
1003
Hardness Hv (5kg)
160
140
120
100
80
60
40
250
300
350
400
450
500
550
600
650
700
Temperature (°C)

Fig. 10

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2006/000363

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22C5/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 150 982 A (SHIBATA, AKIRA) 24 April 1979 (1979-04-24) example A	1,20,23
A	US 3 811 876 A (HARIGAYA H,JA ET AL) 21 May 1974 (1974-05-21) column 1, line 6 - column 2, line 49 tables 1-5 claim 7	
A	US 2004/219055 A1 (CROCE SCOTT M) 4 November 2004 (2004-11-04) the whole document	
A	US 4 973 446 A (BERNHARD ET AL) 27 November 1990 (1990-11-27) the whole document	
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 May 2006	11/05/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Zimmermann, F

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GAY P-A ET AL: "THE PROTECTION OF SILVER AGAINST ATMOSPHERIC ATTACK" PLATING AND SURFACE FINISHING, AMERICAN ELECTROPLATERS AND SURFACE FINISHERS SOCIETY, ORLANDO, US, vol. 91, no. 5, May 2004 (2004-05), pages 71-73, XP008048375 ISSN: 0360-3164 the whole document -----	
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INTERNATIONAL SEARCH REPORT

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