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(71) Applicant: **Argentium International Limited**
Haslemere
Surrey GU27 1NN (GB)

(72) Inventor: **Johns, Peter Gamon**
Watford, Hertfordshire WD17 3BQ (GB)

(74) Representative: **Lucas, Phillip Brian**
Lucas & Co.
135 Westhall Road
Warlingham, Surrey CR6 9HJ (GB)

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(54) **Alloy for investment casting**

(57) In an Ag, Cu, Ge alloy containing boron as grain refiner, investment castings of a clean bright silvery appearance and/or free from cracking defects are obtained by incorporation of silicon, in some embodiments in the absence of added zinc.

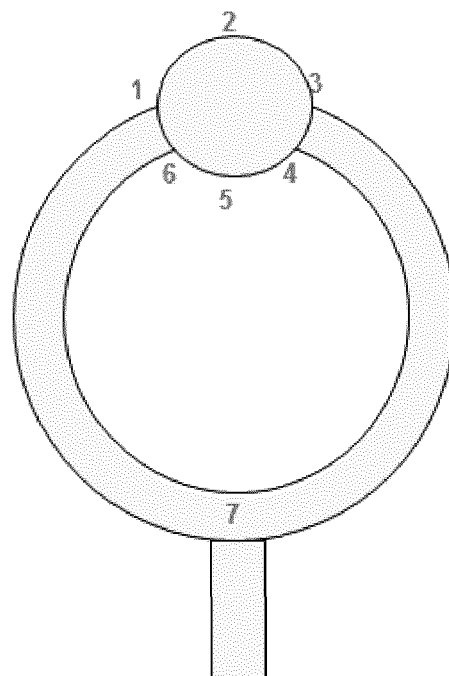


Fig. 1

Description**FIELD OF THE INVENTION**

5 **[0001]** The present invention relates to silver casting alloys, to investment casting using the alloys and to articles investment cast from the alloys.

BACKGROUND TO THE INVENTION

10 **[0002]** It has long been desired to produce investment castings in silver with a bright and shiny as-cast colour.

[0003] Investment casting of sterling silver and standard deox alloys is reviewed by Jörg Fischer-Bühner, *Advances in the Prevention of Investment Casting Defects Assisted by Computer Simulation*, The Santa-Fe Symposium on Jewellery manufacturing, 2010, the contents of which are incorporated herein by reference.

15 **[0004]** Various alloying ingredients are discussed by Fischer-Bühner. Copper remains the main addition in variations of standard sterling silver despite its many disadvantages. It accelerates tarnishing. It lowers the melting point of silver and leads to a broad melting range, making the alloy intrinsically prone to hot cracking. It oxidizes easily, leading to dark surface oxide layers on as-cast trees during cooling in air after pouring or during re-heating, e.g. for soldering. It also leads to internal or subsurface oxidation which can be revealed as "firestain" (grey, bluish or reddish areas) on finished surfaces. Zinc is used up to ~ 2.5 wt%. It decreases the surface tension of the melt, increases fluidity and form filling and reduces surface roughness. Together with silicon it helps to avoid the development of dark copper oxide layers and firestain. However, the high vapour pressure of zinc can lead to loss of Zn by evaporation depending on melting conditions and to fumes of zinc. Silicon is used up to ~ 0.2 wt%. It has a greater affinity for oxygen than silver, copper and zinc and therefore acts as deoxidizer of the molten alloy, but depending on equipment and process conditions it can also give rise to surface dross. It prevents the formation of dark copper oxide layers by preferential formation of bright and white silicon-oxide layers on as-cast trees. Like Zinc it increases fluidity and assists in form filling. It also widens the melting range and tends to segregate and form low-melting phases along grain boundaries, leading to increased risk of hot cracking. If used in high quantities, silicon and zinc may reduce the rate of tarnishing.

25 **[0005]** A bright and shiny as-cast tree colour is often a practical necessity, especially for companies carrying out stone-in-place casting. In such cases alloys with medium to high silicon level are at present considered by Fischer-Bühner the only safe choice. While the dark copper oxide layers on as-cast tree surfaces obtained for silicon-free alloys can be removed by pickling, they are sometimes difficult to remove completely below the stones. A high silicon-level provides the most bright as-cast tree colour under all manufacturing conditions and the most white metal colour after finishing, making it particularly attractive for stone-in-place casting. Furthermore the higher fluidity of such an alloy allows for lower flask temperatures, which reduces the risk of damage to the stones

30 **[0006]** Depending on alloy composition the brightness of as-cast trees also significantly depends on the cooling procedure of flasks after pouring. A common standard cooling procedure consists in removing the flask from the flask chamber ~ 1 min after pouring followed by cooling in air for another 10-20 min before quenching. For silicon-free alloys the surface of the as-cast tree then is covered by a grey to dark copper-oxide layer depending on flask temperature. The oxidation can be drastically reduced if a flask is kept for an extended time (e.g. 3-5 min) in the flask chamber under vacuum or protective gas which then is followed by removal of the flask from the machine and immediate quenching. In this case just a slight grey, sometimes yellowish discoloration is observed and internal (subsurface) oxidation of the copper in the alloy is avoided which eliminates firestain for Si-free alloys and significantly improves scrap metal quality. For Si-containing alloys such a process modification is not significant, since the brightness of the as-cast tree is not much affected by different flask cooling procedures. However, more protected cooling reduces consumption of silicon and also improves scrap metal quality.

35 **[0007]** Especially for alloys with a broad melting range, like all 925 silver alloys, "hot cracking" or "hot tearing" can be a problem. Hot cracking mainly occurs when mechanical stress is acting on the metal during the final stages of solidification, hence when there is only a small amount of liquid metal left between the growing grains. The thermal shrinkage of the solidifying metal coupled with the thermal expansion of the investment material (heating up when in contact with the hot metal) exerts local stresses and tears the metal apart. Fischer-Bühner explains that silicon-containing alloys are more prone to hot-cracking than silicon-free alloys. The somewhat increased risk for hot cracking of silicon-containing alloys as compared to silicon-free alloys can be theoretically understood. Silicon tends to segregate to grain boundary areas during solidification where it eventually forms low melting phases. This broadens the melting range, from a width of typically ~120°C for silicon-free alloys to ~150-170°C for medium-to-high silicon levels and also increases solidification time. For example an item that would need 1.5 min for completion of solidification if cast in a silicon-free alloy at a flask temperature of 500°C needs around 2.5 min if cast in an alloy with medium-to-high silicon-content. Hence the danger zone (temperature and time range) during which hot cracking may occur is broadened for silicon-containing alloys.

50 **[0008]** So-called "de-ox" sterling silver alloys are available *inter alia* from United Precious Metal Refining, Inc. ("UPM")

which claims on its website to have the only available silicon-deoxidized sterling silver casting grains and which are said to have the advantages of castability, reduced porosity, absence of firescale and tarnish resistance. De-ox alloys are described in two US patents of UPM. US-A-4793446 (Bernhard I) describes a silver alloy composition which consists essentially of the elements set out in the table below. A typical composition comprises 92.5 wt% silver, about 0.5 wt% copper, about 4.25 wt% zinc, about 0.48 wt% tin, about 0.02 wt% indium, about 1.25 wt% of a boron-copper alloy containing 2% boron and 98% copper, and 1% of a silicon-copper alloy containing about 10% silicon and about 90% copper. Silver is present in the necessary minimal percentage to qualify as either coin silver or sterling silver, as appropriate. Copper (2.625 wt%) is added as a conventional hardening agent for silver as well as the main carrying agent for the other materials. Zinc is added to reduce the melting point of the alloy, to add whiteness, to act as a copper substitute, as a deoxidant, and to improve fluidity of the alloy. Tin is added to provide tarnish resistance, and for its hardening effect. Indium is added as a grain refining agent and to improve the wettability of the alloy. Silicon (0.1 wt%) acts as a deoxidant that reduces the porosity of the recast alloy and has a slight hardening effect. Boron is added to reduce the surface tension of the molten alloy and to allow it to blend homogeneously.

[0009] US-A-5039479 (Bernhard II) describes a master metal composition for making alloys of the above type, tin apparently being optional. An alloy used as a reference example in EP-B-0752014 (Eccles I) and said to be made in accordance with Bernhard II consists of silver 92.5 wt%, copper 3.29 wt%, zinc 3.75 wt%, indium 0.25 wt%, boron 0.01 wt% and silicon 0.2 wt%; it is reasonable to conclude that this is an analysis of a commercial alloy of UPM.

[0010] As a result of discussions with Melvin Bernhard of UPM, Anthony Eccles of Apecs Investment Castings Pty Ltd developed alloys disclosed in EP-B-0752014 (Eccles I) is set out in the table below. Zinc is said to influence the colour of the alloy and to act as a reducing agent for silver and copper oxides. Silicon is said to provide firescale resistance and to maintain good colour. Germanium is said to provide firescale resistance and work hardening properties and indium and boron may be provided for modification of rheology, reduction in surface tension and grain refinement. In Eccles I a disadvantage of the alloys in Bernhard I and Bernhard II is said to be that they exhibit poor work hardening properties and do not achieve the mechanical strength of worked goods in traditional sterling silver. Many silver findings e.g. beads, links, charms, endbars and the like are made by investment casting, and are not intended to be worked after they have been cast, so that the reference to work hardening in Eccles I teaches away from the use of the disclosed alloys for investment casting. The same is true for many finished jewellery products made by investment casting e.g. rings and bracelets.

[0011] WO 96/22400 (Eccles II) discloses that in some deox alloys a high copper content is desired for the ability of copper to impart hardness, and aims to produce high copper alloys that exhibit reduced firescale, reduced porosity and oxide formation and reduced grain size relative to standard sterling silver. The disclosed solution is to provide alloys having the general composition set out in the table below, optional constituents being in brackets. It will be noted that the essential novelty over Eccles I is the absence of zinc, although high tin contents are considered acceptable. The specification explains that high copper alloys are inherently firescale prone and that to create a high copper content, firescale-free sterling silver was unexpected. In particular it was unexpectedly found that the choice of deoxidizing additive (silicon) provided the facility of high copper content without significant firescale production, whereas the more common aggressive deoxidizers such as zinc did not. Firescale resistance was considered to be of particular importance for hot working to impart hardness and the use of germanium as an alloying agent provided alloys which are both firescale resistant and work hardenable and which were harder than prior art alloys due to their elevated copper content. Rheology-modifying additives such as indium and boron are optional ingredients but the ability of boron to act as a grain refiner was not noted. Disclosed embodiments were Ag-Cu-Ge-Si and Ag-Cu-Ge-Si-In alloys and there was no boron-containing embodiment. However, the Eccles II alloys were never developed into a commercial product despite their apparently desirable properties, and it is believed that a main reason is a propensity for crack development which would have precluded their use for investment casting and for which none of Bernhard I, Bernhard II, Eccles I and Eccles II discloses a solution. Furthermore, there is no disclosure or suggestion that the alloys should be used for investment casting and the repeated mention of platework, rolling and work hardening teaches away from the use of these alloys for that purpose.

Element	Bernhard I	Eccles 1	Eccles II
	wt%	wt%	wt%
Silver	89-93.5	>90	To 100%
Copper	0.5-6	0.5-6	2.5-19.5
Germanium	N/A	0.01-1	0.01-3.3
Zinc	0.5-5	2-4	
Tin	0.25-2	0-6	(0-6)

(continued)

Element	Bernhard I	Eccles 1	Eccles II
	wt%	wt%	wt%
Indium	0.01-1.25	0-1.5	(0-1.5)
Silicon	0.01-2	0.02-2	0.02-2
Boron	0.01-2	0-2	(0-2)

[0012] Patent GB-B-2255348 (Rateau, Albert and Johns; Metaleurop Recherche) discloses a silver alloy that maintains the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of the copper content to oxidise. The alloys are ternary Ag-Cu-Ge alloys containing at least 92.5 wt% Ag, 0.5-3 wt% Ge and the balance, apart from impurities, copper. The alloys are stainless in ambient air during conventional production, transformation and finishing operations, are easily deformable when cold, easily brazed and are said not give rise to significant shrinkage on casting. They also exhibit superior ductility and tensile strength. Germanium exerts a protective function that is responsible for the advantageous combination of properties exhibited by the new alloys, and is in solid solution in both the silver and the copper phases. The microstructure of the alloy is said to be constituted by two phases, a solid solution of germanium and copper in silver surrounded by a filamentous solid solution of germanium and silver and copper which itself contains a few intermetallic Cu-Ge dispersoids. The germanium in the copper-rich phase inhibits surface oxidation of that phase by forming a thin GeO and/or GeO₂ protective coating that prevents firestain during brazing and flame annealing. Furthermore the development of tarnish is appreciably delayed by the addition of germanium, the surface turning slightly yellow rather than black and tarnish products being easily removed by ordinary tap water. The alloy is useful *inter alia* in jewellery and silversmithing. Conventional grain-refining agents were tested, the specific materials evaluated or suggested being gold, nickel, manganese or platinum. Investment casting of the alloy was not reported.

[0013] US-A-6168071 (Johns) describes and claims *inter alia* a silver/germanium alloy having an Ag content of at least 77% by weight, a Ge content of between 0.5 and 3% by weight, the remainder being copper apart from any impurities, which alloy contains boron as a grain refiner at a concentration of up to about 20 parts per million. The boron is provided as a copper-boron alloy e.g. containing 2 wt% boron and imparts greater strength and ductility to the alloy and permitting strong and aesthetically pleasing joints to be obtained using resistance or laser welding. It was explained that grain refining silver alloys had proved difficult and that a person of ordinary skill in the art would not previously have considered boron for this purpose, and that it is effective in inhibiting grain growth even at soldering temperatures. Again investment casting of the alloy was not reported.

[0014] EP-B- 1631692 discloses firestain and tarnish-resistant ternary alloy of silver, copper and germanium containing from more than 93.5 wt% to 95.5 wt% Ag, from 0.5 to 3 wt% Ge and the remainder, apart from incidental ingredients (if any), impurities and grain refiner, copper. Investment casting of strip is reported and the strip is said to be free of hot short (cracking) defects. The appearance of the strip as cast was not evaluated.

SUMMARY OF THE INVENTION

[0015] AgCuGe alloys of the kind described above have been useful in continuous casting and for the production of wrought objects from the resulting sheet, strip, tube or the like, but their performance as investment casting alloys has been less good owing to discoloration arising during investment casting. Articles of these alloys when removed from the investment have exhibited significant discoloration which has required extended processing to remove.

[0016] It has now been found that addition of silicon to the alloys largely or completely avoids such discoloration and also cracking defects and does not give rise to the cracking and other processing problems associated with conventional silicon-containing alloys when used in investment casting.

[0017] Embodiments of the invention provides casting grain comprising at least 77 wt% silver, 0.2-3 wt% germanium, copper and boron as grain refiner, said casting grain further comprising silicon in an amount effective to inhibit discoloration and/or cracking during investment casting.

[0018] Embodiments of the invention relate to the use of silicon in a silver-copper germanium alloy for investment castings, said alloy comprising at least 77 wt% silver, 0.2-3 wt% germanium, copper and boron as grain refiner, and said investment castings being free from discoloration arising in the casting process and exhibiting a clean silvery appearance.

[0019] Embodiments of the invention relate to the use of silicon in a silver-copper germanium alloy for investment castings, said alloy comprising at least 77 wt% silver, 0.2-3 wt% germanium, copper and boron as grain refiner, and said investment castings exhibiting reduced or eliminated cracking defects.

[0020] Further embodiments of the invention provide a process for the investment casting of a silver-copper germanium alloy comprising at least 77 wt% silver and 0.2-3 wt% germanium to provide a casting having a clean silvery appearance when removed from the investment, said process comprising using an alloy containing silicon in an amount effective to impart said clean silvery appearance to the casting and boron in an amount effective to impart grain refinement.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] Tests for cracking during investment casting are illustrated in the accompanying drawings, in which Fig 1 is a diagram representing an alloy test casting for showing the performance of the alloy in investment casting of rings, and Figs 2-4 are micrographs showing sections of cast ring at position 7 in Fig. 1.

DESCRIPTION OF PREFERRED EMBODIMENTS

Investment casting

[0022] The general procedure for making solid investment moulds in the jewellery industry involves attaching patterns having configurations of the desired metal castings to a runner system to form a set-up or "tree". The patterns and runner system may be made of wax, plastics or other expendable material. To form the mould, the set-up or tree consisting of the pattern or patterns attached to the runner system are placed into a flask which is filled with a refractory investment slurry that is allowed to harden in the flask around the tree or set-up to form the mould. After the investment slurry is hardened, the patterns are melted out of the mould by heating in an oven, furnace or autoclave. The mould is then fired to an elevated temperature to remove water and burn off any residual pattern material in the casting cavities.

[0023] Specific reactions take place with a calcium sulphate-bonded investment during burnout. After de-waxing, when the temperature of the flask rises above 100°C (212°F), free water evaporates and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) begins to lose its water of hydration. However the complete transformation of gypsum into the anhydrous form of calcium sulphate (anhydrite) occurs over a wide temperature range, through complex transformations of the crystal lattice. These transformations take place with a considerable volume contraction, which is particularly severe at 300-450°C (572-842°F). If gypsum alone were used to produce investment for lost wax casting, the moulds would crack in service and would also produce castings a great deal smaller than the original patterns. Silica is used to compensate for this gypsum shrinkage and to regulate the thermal expansion of the mould. Silica exists in several crystalline forms, and two of them are used in the production of investment powders. Quartz is the most readily available form and its conversion from a to b crystal forms is accompanied by an increase in volume at around 570°C (1058°F). Cristobalite is the other major constituent of investment powder and this form of silica also undergoes a significant increase in volume as it transforms from its a to b crystal structure at around 270°C (518°F). Thus, these two allotropic forms of silica are used to override the shrinkage effect of the gypsum binder.

[0024] Conventional investment formulations used for non-ferrous molds are comprised of a binder and a refractory made up of a blend of fine and coarse particles. A typical refractory usually is wholly or at least in part silica, such as quartz, cristobalite or tridymite. Other refractories such as calcined mullite and pyrophyllite also can be used as part of the refractory. Gypsum powder (calcium sulfate hemihydrate) is almost universally used as a binder for molds intended for casting gold, silver and other metals and alloys having relatively low melting points. The state of the art prior to this invention is reviewed in the paper by Jörg Fischer-Bühner discussed above. It will be appreciated that conditions for investment casting differ significantly from conditions for continuous casting e.g. for the manufacture of rods, bars, tubes, strips and sections where no investment is used and casting is followed rapidly by quenching with water. An indication in a prior art reference that an alloy is suitable for casting should not be taken to mean that it is suitable for all forms of casting. In particular, as discussed above, the alloy may perform well in continuous casting but may perform poorly in investment casting, as indicated above.

Silver

[0025] Embodiments of the present alloy have silver contents complying with the Sterling and Britannia standards.

[0026] Sterling silver has a minimum silver content of 92.5 wt%. However, embodiments have silver contents of 93 - 95.5wt% e.g. about 93.5 wt% or above, the onset of reduction in copper elution compared to that with 925 alloys being believed to be in the range 93.0-93.5 wt% Ag..

[0027] A reason why it is feasible to reduce the copper content of the alloy to improve physical properties and reduce copper elution compared to standard 925 Argentium alloys is because of the unique hardening properties of the AgCuGe system. Hardening can occur either by slow cooling alone or by low temperature baking which is advantageous because quenching any red hot silver alloy into cold water will always lead to cracking and solder joint failure. We have observed a surprising difference in properties between conventional sterling silver alloys and other silver alloys of the Ag-Cu family

on the one hand and silver alloys of the Ag-Cu-Ge family on the other hand. Gradual cooling of e.g. the binary Sterling-type alloys results in coarse precipitates and little precipitation hardening, whereas gradual cooling of Ag-Cu-Ge alloys optionally containing incidental ingredients results in fine precipitates and useful precipitation hardening, especially in those embodiments where the silver alloy contains an effective amount of grain refiner e.g. boron.

[0028] Experimental evidence has shown that Ag-Cu-Ge alloys of Ag content 93.5 wt% and above become precipitation hardened following cooling from a melting or annealing temperature by baking at e.g. 200°C-400°C and that baking the alloy can achieve a hardness of 65 or above, preferably 70 HV or above and still more preferably 75 HV or above which is equal to or above the hardness of standard sterling silver used to make jewellery and other silverware. These advantageous properties are believed to be the result of the combination of Cu and Ge in the silver alloy and are independent of the presence and amounts of Zn or other incidental alloying ingredients.

[0029] Addition of germanium to sterling silver changes the thermal conductivity of the alloy compared to standard sterling silver. The International Annealed Copper Scale (IACS) is a measure of conductivity in metals. On this scale the value of copper is 100%, pure silver is 106%, and standard sterling silver 96%, while a sterling alloy containing 1.1% germanium has a conductivity of 65%. The significance is that the Argentium sterling and other germanium-containing silver alloys do not dissipate heat as quickly as standard sterling silver or their non-germanium-containing equivalents, a piece will take longer to cool, and precipitation hardening to a commercially useful level (e.g. to about Vickers hardness 70 or above, preferably to Vickers hardness 110 or above, more preferably to 115 or above) can take place during natural air cooling or during slow controlled air cooling. Silver alloy of Ag 973 parts per thousand and containing about 1.0 wt% Ge, balance copper, has been successfully precipitation hardened by gradual air cooling from an annealing temperature, and it is believed that Ag-Cu-Ge alloys with silver content above this level are also precipitation hardenable, and this property is retained on incorporation of silicon.

[0030] The benefit of not having to quench to achieve the hardening effect is a major advantage of the present silver alloys. There are very few times in practical production that a silversmith can safely quench a piece of nearly finished work. The risk of distortion and damage to soldered joints when quenching from a high temperature would make the process not commercially viable. In fact standard sterling can also be precipitation hardened but only with quenching from the annealing temperature and this is one reason why precipitation hardening is not used for sterling silver.

[0031] In order to distinguish the operations of annealing and precipitation hardening (which are regarded as distinct by silversmiths) annealing temperatures may be defined to be temperatures above 500°C, whereas precipitation hardening temperatures may be defined to be in the range 150°C - 400°C, the lower value of 150°C permitting embodiments of the alloys of the invention to be precipitation hardened in a domestic oven. Annealing generally takes place for a relatively short time (approximately 45 minutes maximum, at temperatures above 500°C) and is designed to re-crystallise the worked metal alloy structure to enable further working operations to take place. Precipitation hardening takes place for longer times (2-3 hours at the lower temperature) and is designed to increase the hardness of the metal alloy by altering the solid solubility of a secondary phase present in the alloy.

[0032] Further embodiments of the present alloy are of Britannia silver which has a minimum silver content of 95.84 wt%, and will typically have a silver content of 96 wt%. Such alloys retain the ability to precipitation harden as described above. Silver contents in the range 96 - 97.2 wt% are also contemplated.

Germanium

[0033] Embodiments of the present alloy have germanium content of 0.2-3 wt%. Embodiments of the 935 alloy and 960 alloy may have a germanium content of 0.7 wt%, but improved performance and tarnish resistance may be obtained e.g. in the 935 alloy at a germanium content of 1.0-1.2 wt% e.g. 1.1 wt%.

Silicon

[0034] Silicon may be added in amounts of e.g. 10 ppm up to 0.2 wt% and may be added as a CuSi alloy containing e.g. 10-30wt% Si. In an alloy in which germanium is present e.g. in at least equal amounts it is fully compatible with the germanium so that the two elements (which are both metalloids in Group IV of the periodic table) form single phase(s) and the tendency of the silicon to migrate to grain boundaries is reduced or eliminated. In consequence the advantages flowing from incorporation of silicon in terms of deoxidation and forming bright castings can be obtained and cracking and other problems associated with conventional silicon-containing silver alloys do not appear or are significantly alleviated. Amounts of silicon in embodiments of the alloy may be 0.01-0.1 wt% e.g. 0.05 - 0.08 wt% with a reference value of 0.07 wt% (700 ppm). In embodiments the wt% silicon is $\leq 20\%$ of the weight% of germanium, e.g. $\leq 10\%$ of the weight of the silicon e.g. about 10% of the weight of the silicon..

Boron

[0035] The use of boron as grain refiner is a practical necessity when investment casting silver having an appreciable content of germanium. It is advantageously introduced at the time of manufacture of casting grain which then has the boron content needed for grain refinement on re-melting and investment casting.

[0036] A conventional method of introducing boron into a precious metal alloy or master alloy is through the use of 98 wt% Cu, 2 wt% B master alloy. Many manufacturers have been able to use that alloy without difficulty but others have reported that it introduces hard spots into the products. These hard spots are believed to be non-equilibrium phase CuB_{22} particles that form in copper saturated with boron when cooled from the liquid phase to the solid phase. The hard spots may not be detected until after the precious metal jewellery alloy is polished and inspected resulting in needless expense for the processing of ultimately unsatisfactory product.

[0037] A boron compound may be introduced into molten silver alloy in the gas phase, advantageously mixed with a carrier gas, which assists in creating a stirring action in the molten alloy and dispersing the boron content of the gas mixture into said alloy. Suitable carrier gases include, for example, hydrogen, nitrogen and argon. The gaseous boron compound and the carrier gas may be introduced from above into a vessel containing molten silver e.g. a crucible in a silver-melting furnace, a casting ladle or a tundish using a metallurgical lance which may be a elongated tubular body of refractory material e.g. graphite or may be a metal tube clad in refractory material and is immersed at its lower end in the molten metal. The lance is preferably of sufficient length to permit injection of the gaseous boron compound and carrier gas deep into the molten silver alloy. Alternatively the boron-containing gas may be introduced into the molten silver from the side or from below e.g. using a gas-permeable bubbling plug or a submerged injection nozzle.

[0038] The alloy to be heated may be placed in a solid graphite crucible, protected by an inert gas atmosphere which may for example be oxygen-free nitrogen containing <5 ppm oxygen and <2 ppm moisture and is heated by electrical resistance heating using graphite blocks. Such furnaces have a built-in facility for bubbling inert gas through the melt. Addition of small quantities of thermally decomposable boron-containing gas to the inert gas being bubbled through the melt readily provides a desired few ppm or few tens of ppm boron content. The introduction of the boron compound into the alloy as a dilute gas stream over an period of time, the carrier gas of the gas stream serving to stir the molten metal or alloy, rather than in one or more relatively large quantities, is believed to be favourable from the standpoint of avoiding development in the metal or alloy of boron hard spots. Compounds which may be introduced into molten silver or gold or alloys thereof in this way include boron trifluoride, diborane or trimethylboron which are available in pressurised cylinders diluted with hydrogen, argon, nitrogen or helium, diborane being preferred because apart from the boron, the only other element is introduced into the alloy is hydrogen. A yet further possibility is to bubble carrier gas through the molten silver to effect stirring thereof and to add a solid boron compound e.g. NaBH_4 or NaBF_4 into the fluidized gas stream as a finely divided powder which forms an aerosol.

[0039] A boron compound may also be introduced into the molten silver or gold alloy in the liquid phase, either as such or in an inert organic solvent. Compounds which may be introduced in this way include alkylboranes or alkoxy-alkyl boranes such as triethylborane, tripropylborane, tri-*n*-butylborane and methoxydiethylborane which for safe handling may be dissolved in hexane or THF. The liquid boron compound may be filled and sealed into containers of silver or of copper foil resembling a capsule or sachet using known liquid/capsule or liquid/sachet filling machinery and using a protective atmosphere to give filled capsules sachets or other small containers typically of capacity 0.5-5 ml, more typically about 1-1.5 ml. The filled capsules or sachets in appropriate number may then be plunged individually or as one or more groups into the molten silver alloy. A yet further possibility is to atomize the liquid boron-containing compound into a stream of carrier gas which is used to stir the molten silver as described above. The droplets may take the form of an aerosol in the carrier gas stream, or they may become vaporised therein.

[0040] Conveniently the boron compound is introduced into the molten silver alloy in the solid phase, e.g. using a solid borane e.g. decaborane $\text{B}_{10}\text{H}_{14}$ (m.p. 100°C , b.p. 213°C). However, the boron is conveniently added in the form of either a boron containing metal hydride or a boron containing metal fluoride. When a boron containing metal hydride is used, suitable metals include sodium, lithium, potassium, calcium, zinc and mixtures thereof. When a boron containing metal fluoride is used, sodium is the preferred metal. Most preferred is sodium borohydride, NaBH_4 which has a molecular weight of 37.85 and contains 28.75% boron.

[0041] Boron can be added to the other molten components both on first melting and at intervals during casting to make up for boron loss if the alloy is held in the molten state for a period of time, as in a continuous casting process for grain. This facility is not available when using a copper/boron master alloy because adding boron changes the copper content and hence the overall proportions of the various constituents in the alloy.

[0042] It has been found that when adding a borane or borohydride that more than 20 ppm can be incorporated into a silver alloy without the development of boron hard spots. This is advantageous because boron is rapidly lost from molten silver: according to one experiment the content of boron in molten silver decays with a half-life of about 2 minutes. The mechanism for this decay is not clear, but it may be an oxidative process. It is therefore desirable to incorporate more than 20 ppm boron into an alloy as first cast i.e. before investment casting or before rolling into strip, and amounts

of e.g. up to 50 ppm, typically up to 80 ppm, and in some instances up to 800 or even 1000 ppm may be incorporated. Thus there could be produced according to the present method silver casting grain containing about 40 ppm. boron. Owing to boron loss during subsequent re-melting and investment casting, the boron content of finished pieces may be closer to the 1-20 ppm of the prior art, but the ability to achieve relatively high initial boron concentrations means that improved consistency may be achieved during the manufacturing stages and in the final finished products. Furthermore higher boron content is desirable for master alloys which will be melted with precious metal to make casting grain and then further melted for investment casting.

Incidental ingredients

[0043] Embodiments of the present alloys are free from added zinc or other added metals save copper, germanium, boron and silicon and have the advantage *inter alia* of simplicity of formulation and of production. At higher silver contents and at relatively low germanium contents, addition of zinc in other embodiments may be desirable e.g. in amounts of 0.2-1 wt% e.g. about 0.4 wt%. Other metals may be added in small amounts e.g. up to 0.2 wt% provided that they do not interfere with the overall properties of the alloy, and such metals include e.g. gallium which in some embodiments may further decrease cracking defects. In embodiments small amounts of indium may also be present, so that a 960 alloy may comprise boron in ppm amounts as grain refiner, indium, gallium, zinc, silicon, germanium, copper and silver,

Exemplified alloys

[0044] An embodiment of a 935 alloy has 93.5 wt% Ag, 1.1 wt% Ge, 700 ppm Si, 3-60 e.g. 10 ppm B, the balance being copper. An embodiment of a 960 alloy has 96 wt% Ag, 0.65 wt% zinc 0.7 wt% Ge, 700 ppm silicon, 3-60 e.g. 10 ppm boron, balance copper. The above alloys exhibit bright stain-free castings following investment casting and are either substantially crack and void-free or are significantly lower in voids, see Fig. 1 which shows a standard test casting for a ring exhibiting gross porosity and Figs 2-7 which are micrographs of the illustrated alloys in the vicinity of position 7 where the body of the ring joins the sprue and which show little or no porosity. It will be appreciated since molten metal contracts on cooling, a sprue should solidify last to allow molten metal to be fed to the cooling casting, as the metal contracts on cooling and to minimise development of shrinkage porosity. Therefore the most sensitive area to display shrinkage porosity (or the potential for cracking due to hot cracking or hot tearing) is the area where the sprue and item to be cast join. This is why P7 was chosen, as the region at which there was the greatest possibility of shrinkage porosity being present.

Claims

1. Use in investment casting of a silver-copper germanium alloy comprising 92.5-96 wt% silver, 0.2-1.2 wt% germanium, 0.01-0.2 wt% silicon, optionally 0.2-1.0 wt% zinc when the silver content is about 96 wt%, up to 0.2 wt% of metals selected from indium and gallium, boron in an amount effective to impart grain refinement, the balance being copper and the wt% silicon being $\leq 20\%$ of the wt% of germanium to give castings at risk of shrinkage porosity or cracking but having a stain-free silvery appearance and reduced or eliminated shrinkage porosity or cracking defects.
2. Use as in claim 1, wherein the wt% silicon in said alloy is $\leq 10\%$ of the weight% of germanium.
3. Use as in claim 1 or 2, wherein silver is 93.5 or 96 wt% and germanium is about 0.7 wt%.
4. Use as in claim 3, wherein silicon is about 0.07 wt%
5. Use as in any preceding claim, wherein silver is 93.0-95.5 wt%.
6. Use as in any of claims 1-4, wherein silver is about 93.5 wt%.
7. Use as in claim 5 or 6, wherein the alloy is free of added zinc, indium or gallium.
8. Use as in claim 1, the alloy comprising about 0.7 wt% zinc.
9. A process for the investment casting of a silver-copper germanium alloy comprising at least 77 wt% silver and 0.2-3 wt% germanium to provide a casting having a clean silvery appearance when removed from the investment, said process comprising using an alloy containing silicon in an amount effective to impart said clean silvery appearance

to the casting and boron in an amount effective to impart grain refinement.

10. The process of claim 1, wherein either

- (i) (a) silver is 93.0-95.5 wt%. e.g. about 93.5 wt%; and/or (b) the alloy is free of added zinc; and/or (c) germanium is 0.5-1.5 wt% e.g. 1.0-1.2 wt% e.g. about 1.1 wt%, or
- (ii) (a) silver is about 96 wt%; and/or (b) germanium is 0.8-1.1 wt% e.g. about 0.9 wt%; and/or (c) the alloy further comprises 0.2-1.0 wt% zinc e.g. about 0.4 wt% or 0.7 wt% zinc; and/or (d) silicon is present in an amount of 10ppm-0.2wt%; and/or (e) silicon is present in an amount (wt%) ≤ 20 % of the amount (wt%) of germanium e.g. ≤ 10 % of the amount (wt%) of germanium; and
- (iii) boron is present in the alloy in an amount of ≤ 40 ppm e.g. 10ppm.

11. Use of silicon in a a silver-copper germanium alloy for investment castings, said alloy comprising at least 77 wt% silver, 0.2-3 wt% germanium, copper and boron as grain refiner, and said castings being free from discoloration arising in the casting process and exhibiting a clean silvery appearance.

12. Use of silicon in a a silver-copper germanium alloy for investment castings, said alloy comprising at least 77 wt% silver, 0.2-3 wt% germanium, copper and boron as grain refiner, and said castings exhibiting reduced or eliminated cracking defects..

13. Casting grain comprising at least 77 wt% silver, 0.2-3 wt% germanium, copper and boron as grain refiner, said casting grain further comprising silicon in an amount effective to inhibit discoloration and/or cracking during molding.

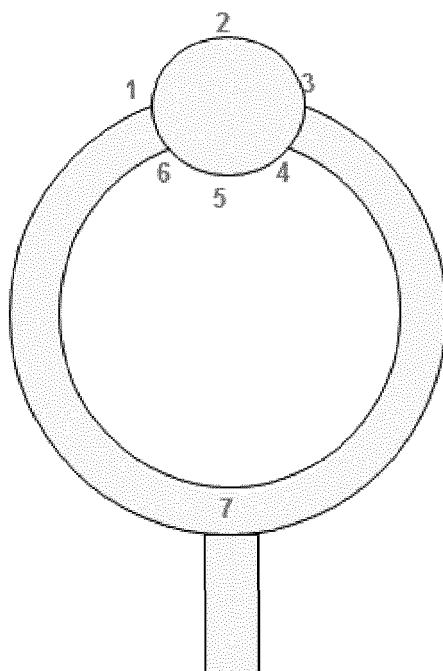
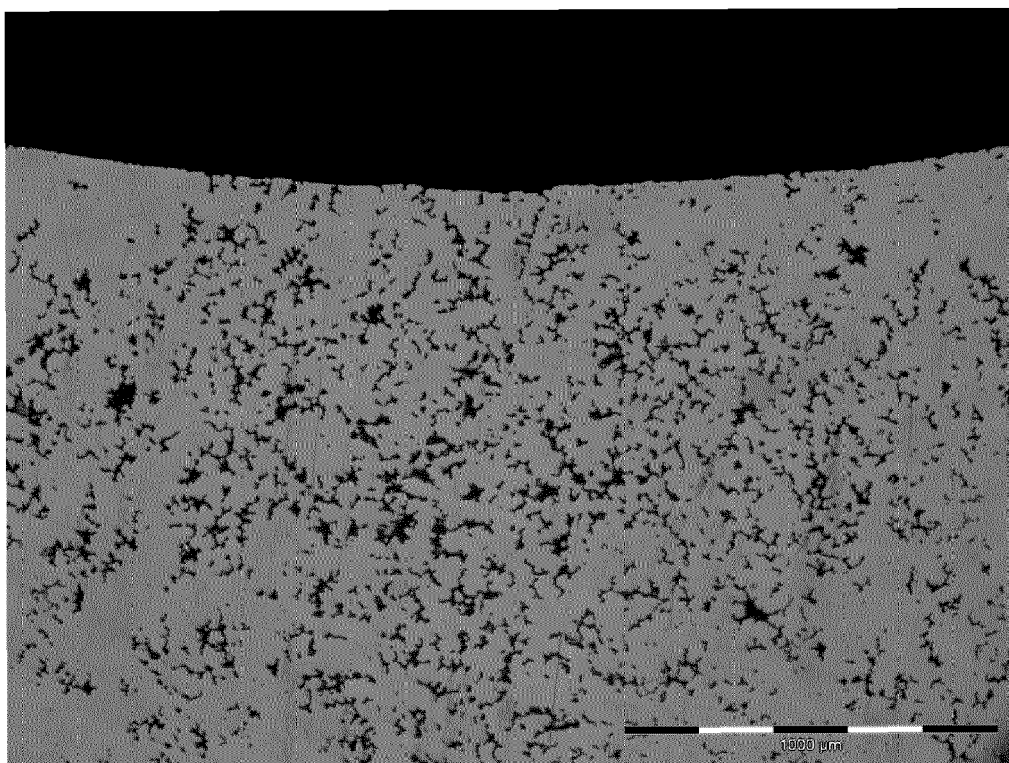
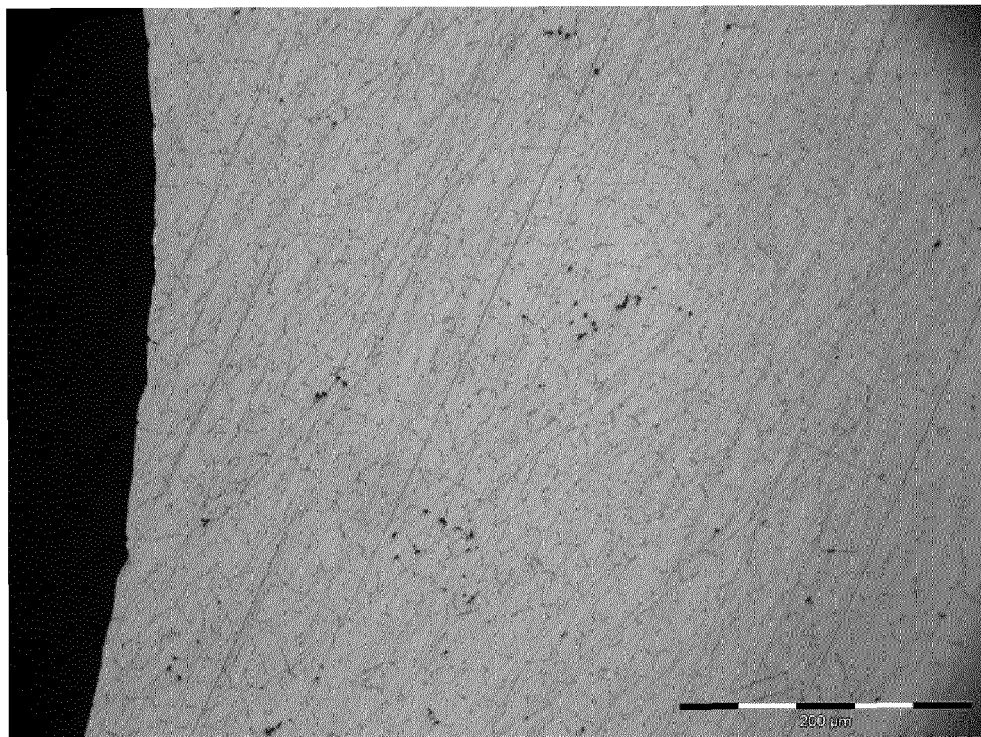


Fig. 1

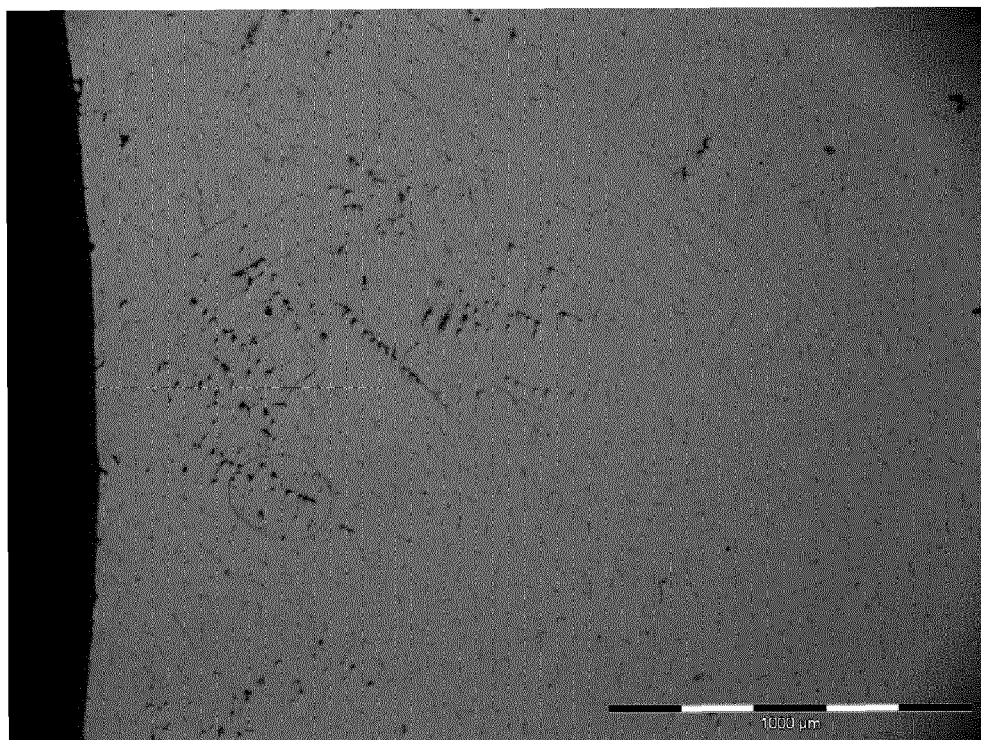


Standard Si-containing silver alloy @ p7

Fig. 2



935 Ag Cu Ge Si alloy @ p7; Fig. 3



960 Ag Cu Ge Si Zn alloy @ p7; Fig. 4

REFERENCES CITED IN THE DESCRIPTION

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