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(54) **Copper-zinc-manganese alloy for the production of articles coming into direct and prolonged contact with the human skin.**

(57) An alloy suitable for replacing Cu-Ni-Zn alloys for use in spectacles and other opticians' products, jewellery and cutlery, with substantially the same aesthetic characteristics and workability but without the risk of the release of noxious elements; the alloy has the following nominal composition by weight: from 50% - 70% Cu; from 8% - 25% Mn, from 0.05% - 1% Sn, the rest being Zn with possible small additions of Mg (from 0.01 - 0.1% by weight).

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The present invention relates to a copper-based metal alloy suitable for replacing copper-zinc-nickel alloys (so called nickel silvers) with the same aesthetic characteristics (particularly as regards their silvery-white colour) and workability for uses in which the alloy is intended to come into direct and prolonged contact with the human skin.

It is known that European legislation which is about to come into force prohibits the use of metal alloys containing metals considered harmful to health in all applications in which the alloy may or must come into direct contact with a human being. In particular Cu-Zn-Ni alloys (so-called nickel silvers) commonly used for cutlery and for the manufacture for articles intended to come into direct and prolonged contact with the skin of the user, such as zip fasteners , metal articles applied to clothing, spectacles (or parts thereof) and costume jewellery, fall within this category. In fact nickel is one of the metal elements which it has been found can migrate from an alloy into the human skin because of its reaction with the sweat produced thereby and can give rise to sensitisation with the development of allergies (so-called allergic contact dermatosis or dermatitis).

There are already numerous alloys which do not contain nickel on the market and which are suitably formulated to replace nickel silvers in such applications. The main ones are special bronzes (Cu-Sn-based alloys) containing manganese and zinc as additional alloying elements, brasses (Cu-Zn alloys) containing manganese and aluminium in addition, or Cu-Mn alloys (so-called manganins) with additions of aluminium and iron. These alloys have totally unsatisfactory aesthetic characteristics however since they either do not have a colour comparable with that of nickel silvers or it is difficult to give them a good surface finish.

Ternary Cu-Zn-Mn alloys (so-called DAVIS alloys) have also been known for some time (since 1944) and have a colour which is fairly close to that of nickel silver but which are difficult to cold-work and which can thus not be worked by the same tools currently used for nickel silvers; their use would therefore involve very high costs for the complete re-equipment of production lines for making the finished products and/or the semi-finished products (mainly wire).

The object of the present invention is to provide a metal alloy which does not include nickel and which, more generally, does not contain other elements harmful to human health (for example lead, antimony, arsenic, etc) which are capable of replacing nickel silvers in all applications in which the alloy is intended to come into direct and prolonged contact with the human skin and which will give aesthetic results and work ability not inferior to those obtainable with nickel silvers.

On this basis the invention therefore provides a copper-based "white" metal alloy for the production of articles intended to come into direct and prolonged contact with the human skin, including copper (Cu), zinc (Zn) and manganese (Mn) in quantities such that it has an alpha-brass metallographic structure, characterised in that it further includes tin (Sn) in quantities by weight variable between 0.05% and 1%, the tin being present mainly in solid solution so as to give a substantially homogeneous quaternary alloy.

In particular, the alloy according to the invention has the following composition in percentages by weight: from 50% to 70% copper; from 8% to 25% manganese; from 0.05% to 1% tin; the rest being zinc but not in any case more than 39%.

Thus a homogeneous alpha-phase alloy is obtained which may be considered, formally, as forming part of the family of brasses of the first title, but which, due to the presence of manganese and tin, has practically the same colour and aesthetic appearance as nickel silvers both in the rough state and after surface finishing. The alloy of the invention, moreover, on the contrary to known DAVIS alloys, from which it is evolved, is surprisingly workable, both by cold drawing/rolling and by extrusion: for example, the alloy of the invention may be hot-extruded over a very wide temperature range, of about 60°, that is about twice the normal range of workability for conventional DAVIS alloys (that is without tin) of equivalent composition. The alloy of the invention may also be cold-worked not only better than known DAVIS alloys but even better than nickel silvers, whereby the alloy of the invention may be used to produce semi-finished products (for example wires for spectacles and jewellery) or finished articles (for example cutlery) with the use of the same plants and processes as those used at present for nickel silvers, with the resulting real possibility of replacing of these latter alloys at low cost.

Between one cold deformation process (drawing or rolling) and another, the semi-finished product must be annealed to eliminate work-hardening. This annealing may be carried out in the air or in a controlled atmosphere or in a salt bath.

The alloy of the invention may further preferably include from 0.01% by weight to 0.1% by weight of magnesium which acts as a deoxidant for the manganese and may optionally include from 0.2% to 0.4% by weight of aluminium (Al), even though the addition of aluminium may give rise to undesirable colour problems because of the formation of alumina on the surface.

Finally it is preferred for the alloy of the invention to include no more than 0.4% by weight of tin, since higher percentages may give rise to the formation of low-melting phases at the edges of the alpha-phase crystals with the consequent need to reheat the alloy to high temperatures (about 800 °C) to enable the low-melting phases to be reabsorbed into the homogeneous matrix.

The metal alloy of the invention thus has the following nominal composition by weight: 60% copper, 20% manganese, 0.2% tin, 0.05% magnesium, 19.75% zinc.

Further characteristics and advantages of the invention will become clearer from the specific, non-limitative embodiments which follow and which refer to the figures of the appended drawing, in which:

Figure 1 is a photomicrograph of the alloy of the invention as seen by SEM at 1300 enlargement; and

Figure 2 is a graph showing the changes in the Sn content in the alpha phase of the photomicrograph of Figure 1, at the points indicated.

Example 1

An alloy (1) was prepared with the use of an induction furnace having a capacity of 4000kg and operated under a cover of chlorine at a temperature of 1140 °C, the alloy having the following percentage composition by weight: 60% Cu, 20% Mn, 0.2% Sn, 19.75% Zn, 0.05% Mg. This alloy was obtained by fusing 532 kg of ETP copper in the oven and then adding 2.668 kg of a Cu-Mn pre-alloy containing 30% by weight of Mn and finally 8kg of tin bars, 790 kg of zinc and 2 kg of magnesium; the alloy thus obtained was then scorified and poured in successive stages into a 1500 kg furnace kept at 1150 °C,from which it was cast semi-continuously, in a manner known, by copper ingot molds,which are cooled by water circulation and provided with secondary cooling at the outlet; round-section, 7-metre long bars having a diameter of 220 mm and 6 - 7 metre long plates of rectangular section, 1000 mm x 252 mm,were obtained; the casting speed used was between 180 and 200 mm/minutes.

The same method was used to prepare a ternary Cu-Zn-Mn alloy (2) with a composition by weight similar to that of the alloy (1) but without Sn (60% Cu, 20% Zn, 20% Mn) and an 18-18 nickel silver (18% Ni, 18% Zn, the rest being Cu - alloy (3)).Samples were taken from all three alloys prepared and compared visually, a high comparability being found in colour both in the crude and in the polished samples; in particular, after metallographic etching, the sample of the Cu-Mn-Zn-Sn alloy (1) had the appearance shown in the photomicrograph of Figure 1, being substantially homogeneous, with alpha-phase crystalline grains having an average diameter of 70-80 µm and a silvery white colour, entirely identical to that of the 18-18 nickel silver alloy (3).

Example 2

Workability tests were carried out on the alloys of Example 1 to test their mechanical deformability when hot and cold.

The round bars were hot extruded,after heating to a temperature of about 800 °C for two hours,to reduce their section from a diameter of 220mm to 21mm; the bars of alloy (1) could be extruded to give exactly the same good results over the entire temperature range between 740 and 800 °C; the bars of alloy (2), without Sn, however could be extruded without the appearance of defects only in a much narrower temperature range between 780 °C and 750 °C.

The round bars were then rolled to change their section from a 21mm-diameter round section to a 12x12mm square section and they were then annealed at 650 °C for 3 hours; a second rolling step was then carried out to reduce the section to 8x8 mm followed by annealing as above and the square, 8x8 mm bars were then drawn into wires 5.4 mm in diameter; subsequently the wire was scraped with a tool to give a final diameter of 5.1 mm after which it was drawn in a plurality of steps, with intermediate annealing to a diameter of 2.08 mm,annealed as above and drawn to a final diameter of 1.8 mm.

The plates, on the other hand, were hot-rolled at a temperature within the said range (740-800 °C) to obtain a reduction in thickness from 252 to 12 mm then milled to a thickness of 11.2 mm and finally cold-rolled in a plurality of steps, with intermediate annealing as indicated above, up to 3 mm (annealed material) and up to 1 mm (the material being left work-hardened). In this case the alloy (1) was again seen to behave noticeably better; the results of the tests are summarised in Table 1 where the extensibility values (A%) relate to the annealed materials.

Alloy	A%	Max. reduction by cold working
Nickel silver(3)	35-40	45 (drawn) 80 (rolled)
Cu-Zn-Mn (2)	30	30-35 (drawn)
Cu-Zn-Mn-Sn (1)	40	55-65 (drawn) 90 (rolled)

Example 3

Experiments were carried out as in Examples 1 and 2 to prepare alloys of the type (1) but with varying percentages of the alloy elements; more particularly, twelve alloys were prepared with copper contents varying between 50% and 70% by weight, manganese contents between 8% and 25% by weight, and tin contents between 0.05 and 1% by weight, the zinc content making up the difference. Four alloys were also prepared with compositions identical to that of the alloy (1) except for the fact that no magnesium was included in two alloys (this was compensated for by zinc) and aluminium was added to the other two in quantities of 0.2 and 0.4% by weight respectively (at the expense of zinc). Results similar to those for Examples 1 and 2 were found, the results worsening slightly and gradually as the tin content fell below 0.1%; below 0.05% by weight of tin, no appreciable differences in behaviour were found compared with those of the alloys (2), of DAVIS type. Above 0.4% of tin, a low-melting phase formed at the edges of the granules on solidification and this had to be reabsorbed before the heat treatments by a heat treatment at 800°C for 3 hours; above 1% of tin, the formation of the low-melting phase was too prevalent and the homogeneity of the matrix was lost. The absence of magnesium meant that the manganese in the alloy could oxidise more easily with the consequent migration thereof to the surface and the appearance of an opaque coloration; the presence of aluminium also resulted in a more opaque colour.

Example 4

The samples of the alloy (1) of Example 1 were analysed by SEM with several analysis points at the edges of the grains and within the grains themselves, as illustrated in Figure 1; the results are given in the graph of Figure 2 which shows that, at all the points analysed, the nominal tin content of the alloy is present almost exclusively in solid solution in the matrix instead of as a precipitate as would be presumed from the data in literature, whereby, within the limits of the compositions tested, a true quaternary phase Zn-Cu-Mn-Sn alloy is formed.

Claims

1. A copper-based "white" metal alloy for the production of articles intended to come into direct and prolonged contact with the human skin, including Cu, Zn, and Mn in quantities such that it has an alpha-brass metallographic structure, characterised in that it further includes tin in quantities by weight variable between 0.05% and 1%, the tin being present mainly in solid solution so as to give a substantially homogeneous quaternary alloy.

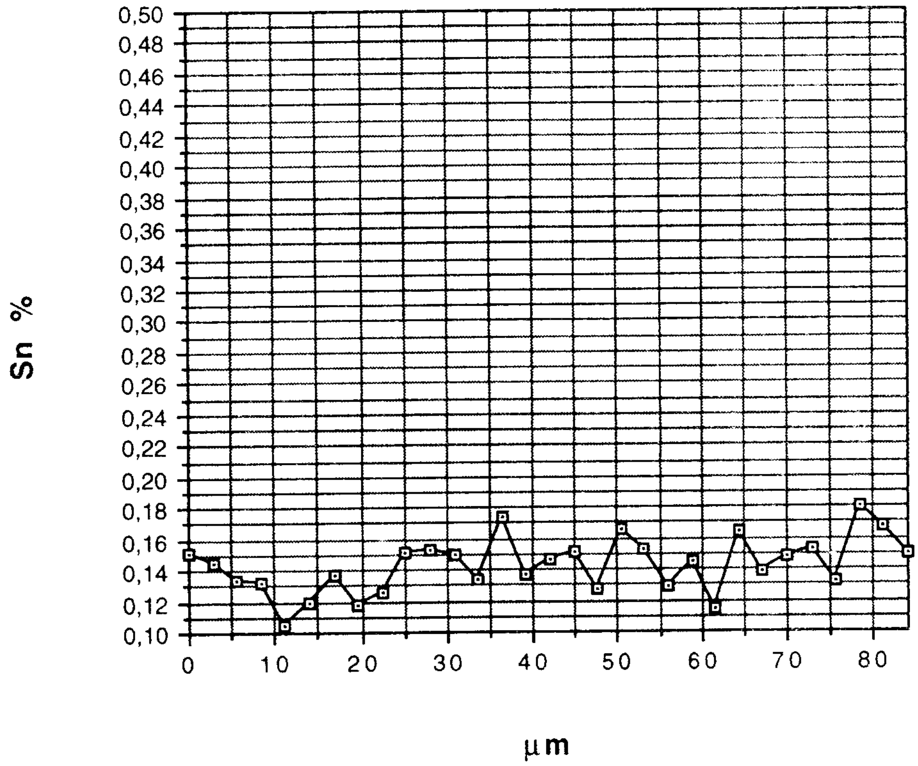
2. A metal alloy according to Claim 1, characterised in that it has the following percentage composition by weight: from 50% to 70% copper; from 8% to 25% manganese; from 0.05% to 1% tin; the rest being zinc but not in any case more than 39%.

3. A metal alloy according to Claim 1 or Claim 2, characterised in that it further includes from 0.01% to 0.1% by weight of magnesium.

4. A metal alloy according to any one of the preceding claims, characterised in that it contains not more than 0.4% by weight of tin.

5. A metal alloy according to Claim 3 or Claim 4, characterised in that it has the following nominal composition by weight: 60% copper, 20% manganese, 0.2% tin, 0.05% magnesium, 19.75% zinc.

6. A metal alloy according to any one of the preceding claims, characterised in that it optionally includes from 0.2% to 0.4% by weight of aluminium (Al).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Sn %
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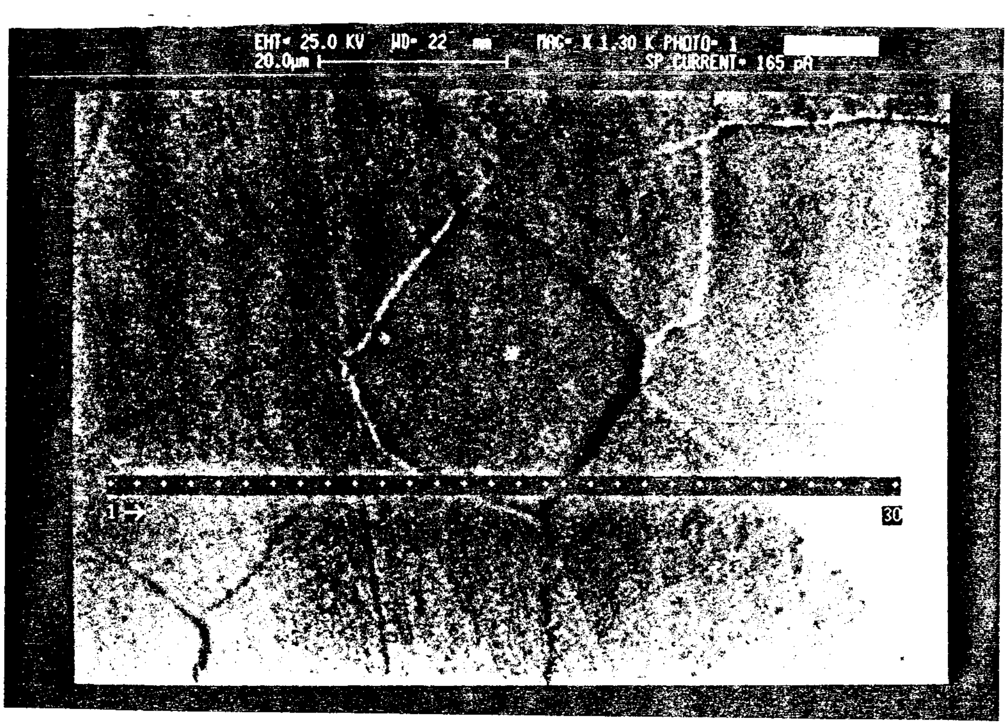
40
50
60
70
80
µm

Fig. 2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20.0µm
SP CURRENT= 165 pA
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Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 94 83 0269

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	DAVIS ET AL. 'METALS HANDBOOK' 1990 , A.S.M. , METALS PARK, OHIO, US *10th Edition, Volume 2, page 390, Alloy C99700*	1	C22C1/00 C22C9/04 C22C9/05
A	US-A-3 516 825 (SHASHKOV ET AL.) * the whole document *	2,6	
A	US-A-2 195 435 (SILLIMAN) * the whole document *	2	
A	EP-A-0 399 658 (GOMEZ) *Claims 1-3, 6-11*	2,6	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C22C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 October 1994	Lippens, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons

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