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(54) **METAL ALLOY AND RELATIVE LOST-WAX CASTING PROCESS**

(57) Metal alloy containing:

- a weight percentage of aluminium greater than or equal to 7,5% and less than or equal to 10,0%;
- a weight percentage of manganese greater than or equal to 12,0% and less than or equal to 18,0%;
- a weight percentage of iron greater than or equal to 2,5% and less than or equal to 6,0%;
- a weight percentage of silver greater than 0,4% and less than or equal to 2,0%;

- possibly an overall weight percentage of zinc and tin greater than or equal to 0% and less than or equal to 2,0%;
- possibly an overall weight percentage of further impurity elements greater than or equal to 0% and less than 0,4%;
- a weight percentage of copper such that a sum of said weight percentages of aluminium, manganese, iron, silver, zinc, tin, further impurity elements and copper is equal to 100%.

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**Description**

**[0001]** The present invention relates to a copper-based metal alloy and a lost-wax casting process for the production of objects (for example glasses parts) made of this metal alloy.

**[0002]** The lost-wax casting process is widely used for the production of small objects made of metal alloys. Such objects can for example be parts or components (e.g., frames, hinges, oval lenses, nose pads, temples, etc.) of wearable accessories such as costume jewellery or glasses.

**[0003]** For example, the lost-wax casting process can involve the making of a mould (e.g., in silicone or steel) for moulding (typically in series) wax models (e.g., beeswax or silicone wax, or similar material) of the objects which are to be made. Typically, the wax models are joined together in a "tree-like" structure that will allow the flowing of the melted alloy.

**[0004]** Subsequently, a plaster mould is made around the wax model (or the tree-like structure) which is placed in oven (e.g., at a temperature of about 600°C) for allowing the melting/evaporation and the consequent spill of the wax through appropriate channels.

**[0005]** At this point, through appropriate channels, the molten metal alloy is casted into the mould, which fills all the interstices of the mould, possibly also thanks to the action of a depression (e.g., in case of vacuum lost-wax casting) or of a centrifugal force (e.g., in case of centrifugal lost-wax casting). Finally, the plaster mould is completely removed (e.g., through water bath operations and preferably pickling operations for removing the plaster residues from the finished object). At this point, it is possible obtaining the finished objects (e.g., separating them from the tree-like structure and/or from the channels), which can undergo further surface treatments and/or heat treatments.

**[0006]** In the field of making objects by lost-wax casting, copper-based metal alloys are commonly used. Copper is in fact a common, cheap, non-toxic, recyclable metal and it has advantageous technological properties (for example a high castability and drawability).

**[0007]** In particular, copper-based metal alloys containing beryllium and/or cobalt are typically used for the making of objects by lost wax casting. These alloys, in addition to showing a colour and a gloss appreciated in the wearable accessories market, have characteristics suitable for their treatment (e.g., melting, casting, welding and tools working).

**[0008]** Furthermore, these alloys have excellent corrosion resistance.

**[0009]** The Italian patent 102017000005383, of the same Applicant of the present application, describes metal alloys substitutive of the alloys containing beryllium and/or cobalt for the lost-wax casting.

**[0010]** Typically, the known alloys require, after the lost-wax casting, a heat treatment (e.g., tempering, which includes a solubilization and an aging, and/or hardening), for improving their hardness and the fatigue resistance.

**[0011]** The Applicant has found that the copper-based metal alloys notoriously used for the lost-wax casting have some drawbacks and/or can be improved in some aspects.

**[0012]** For example, despite the aforesaid qualities, the alloys containing beryllium and/or cobalt have serious toxicity and/or carcinogenicity problems, in particular during the processing cycle for the production of the alloy and/or the subsequent lost-wax casting for the making of the objects destined to the market. Common processes such as melting, casting, welding, high temperature heat treatments, cutting, polishing and processing by electrochemical methods are subject to the emission of vapours and fumes, which if inhaled can cause serious diseases of the respiratory apparatus. For limiting the health risk, it is therefore necessary implementing machinery and/or production procedures that increase the cost and the complexity of the processing of the alloy and/or of the finished products.

**[0013]** For example, for ensuring mechanical properties, such as tensile strength and/or yield stress and/or breaking stress, suitable for their final application, the objects notoriously made by lost-wax casting with the aforesaid copper-based alloys containing beryllium and/or cobalt, after the lost-wax casting process typically require a heat treatment which by heating and cooling cycles, leads the alloy to assume a crystalline structure which gives the desired mechanical properties. The need to carry out these heat treatments entails an increase in the complexity of the production process and/or of the production times and/or of the production costs of the object to be destined to the market.

**[0014]** The Applicant has therefore faced the problem of making, or selecting, a metal alloy which has physical qualities and/or mechanical properties suitable for the making of objects by lost-wax casting, for example for eyewear and costume jewellery, and at the same time entailing little or no risks for the health and hygiene of the man and/or of the environment.

**[0015]** The Applicant has faced the problem of making, or selecting, a copper-based metal alloy, free from beryllium and/or cobalt, which has mechanical properties suitable for making objects by lost-wax casting even without heat treatment after the lost-wax casting process, for limiting the complexity of the production process and/or saving in terms of both production times and production costs.

**[0016]** Furthermore, thinking about the use of the metal alloys for making wearable objects, the

**[0017]** Applicant has faced the problem of making a metal alloy having low specific weight, for example lower than that of the copper-based alloys containing beryllium and/or cobalt.

**[0018]** One or more of the aforesaid problems are solved by a metallic alloy according to the attached claims and/or having the following features.

**[0019]** According to an aspect the invention relates to a metal alloy containing:

- a weight percentage of aluminium greater than or equal to 7,5% and less than or equal to 10,0%;
- a weight percentage of manganese greater than or equal to 12,0% and less than or equal to 18,0%;
- a weight percentage of iron greater than or equal to 2,5% and less than or equal to 6,0%;
- a weight percentage of silver greater than 0,4% and less than or equal to 2,0%;
- possibly an overall weight percentage of zinc and tin greater than or equal to 0% and less than or equal to 2,0%;
- possibly an overall weight percentage of further impurity elements greater than or equal to 0% and less than 0,4%;
- a weight percentage of copper such that a sum of said weight percentages of aluminium, manganese, iron, silver, zinc, tin, further impurity elements and copper is equal to 100%.

10 **[0020]** According to an aspect the invention relates to a lost-wax casting process for the production of objects in the metal alloy according to the present invention.

**[0021]** Preferably said lost-wax casting process comprises:

- melting said metal alloy;
- 15 - filling said mould (preferably made of plaster) with said melted metal alloy;
- solidifying said metal alloy inside said mould;
- removing said mould from said solidified metal alloy for obtaining said objects.

**[0022]** Preferably said filling said mould is made with a pressure gradient and/or with a centrifugal force.

20 **[0023]** Preferably said filling said mould is made at a casting temperature of said metal alloy, greater (e.g., greater than 50-150°C) than a melting temperature of said metal alloy.

**[0024]** Preferably it is provided making a wax model of said objects, making said mould around said model and removing said wax from said mould.

25 **[0025]** According to an aspect the invention relates to a production process of objects comprising the lost-wax casting process according to the present invention.

**[0026]** Preferably said objects are parts of wearable accessories, for example glasses parts or costume jewellery.

**[0027]** Exemplarily said objects do not undergo heat treatments for enhancing their hardness.

30 **[0028]** According to the Applicant, the aforesaid features of the alloy allow obtaining a metal alloy easily castable, tough, elastic, weldable (for example by TIG welding and flame and/or induction soldering) and easily workable: this makes the alloy particularly suitable for producing for example objects by lost-wax casting, in particular parts of wearable accessories.

35 **[0029]** Furthermore, the metals that make up the alloy have, to current knowledge, limited or no toxicity, and also entail a reduced release of fumes during the casting, helping to make their processing healthier. This entails that no special machinery and/or safety devices are required for the processing of described and claimed the metal alloy, with consequent increase of the production process simplicity and/or reduction of the production times and costs with respect to the known copper-based alloys containing beryllium and/or cobalt.

40 **[0030]** According to the Applicant, the aforesaid features allow obtaining alloys having mechanical properties (e.g., tensile strength, yield stress, breaking strength) comparable to the aforesaid copper-based alloys notoriously used for the lost-wax casting, even without undergoing heat treatments at the end of the manufacturing process, with consequent savings of manufacturing times and of production costs. In fact, the Applicant has verified that the main physical and mechanical properties of the described and claimed metal alloy are comparable, if not even superior, to the aforesaid copper-based alloys notoriously used for the lost-wax casting, which are subjected to heat treatments (e.g., tempering and/or hardening), consequently making the heat treatment unnecessary, and thus simplifying the production process of objects made with the described and claimed alloys.

45 **[0031]** Furthermore, the alloys of the present invention maintain their high mechanical properties even after surface treatments and/or manufacturing processes (e.g., welding) which can subject the alloy to high temperatures. In fact, unlike the aforesaid copper-based metal alloys notoriously used for the lost-wax casting, the alloys of the present invention, since they do not require heat treatments for obtaining the desired mechanical properties, can undergo high-temperature surface treatments and/or high-temperature manufacturing processes without undergoing a loss of mechanical properties due to remelting. On the contrary, in the aforesaid copper-based metal alloys notoriously used for the lost-wax casting, the high-temperature processing can entail, in the points subjected to processing, a localized loss of the mechanical properties gained after heat treatment, since the remelting of the material cancels out the effects of the heat treatment.

50 **[0032]** The Applicant considers advantageous the composition of the alloy according to the aforesaid features for making parts of wearable accessories, since it contains low-density materials, such as aluminum, in a percentage such as to make the objects comfortable to be wore.

55 **[0033]** According to the Applicant, the aforesaid features finally allow obtaining metal alloys having aesthetic properties, such as for example colour and/or gloss and/or brilliance (e.g., after polishing and/or brushing), such as to be particularly

attractive to the market for the production of wearable accessories, such as eyewear and costume jewellery.

**[0034]** The present invention in one or more of the aforesaid aspects can have one or more of the following preferred features.

**[0035]** Preferably said weight percentage of copper (Cu) is greater than or equal to 62,0%, more preferably greater than or equal to 65,0%, even more preferably greater than or equal to 68,0%. In this way the embrittlement of the alloy is kept limited.

**[0036]** Preferably said weight percentage of copper (Cu) is less than or equal to 77,0%, more preferably less than or equal to 75,0%, even more preferably less than or equal to 73,0%. In this way the malleability of the alloy is kept limited.

**[0037]** Preferably said weight percentage of aluminium (Al) is greater than or equal to 8,0%, more preferably greater than or equal to 8,4%, even more preferably greater than or equal to 8,8%, and/or less than or equal to 9,8%, more preferably less than or equal to 9,5%, even more preferably less than or equal to 9,2%.

**[0038]** The Applicant has found that for weight percentages of aluminum greater than or equal to 8,0% (and less than or equal to 10,0%), it is obtained a hardness comparable to that of the aforesaid copper-based metal alloys notoriously used for the lost-wax casting, even without any heat treatment, allowing obtaining alloys having both good malleability (for alloys with low content of aluminum within the above-described ranges) and alloys with good toughness (for alloys with high content of aluminum within the above-described ranges). Furthermore, the Applicant has found that by increasing the weight percentage of aluminum, within the above-described ranges, the hardness of the alloy is increased, regardless of possible heat treatment. The preferred above-described ranges of content of aluminum therefore represent for the Applicant an optimal selection with respect to the hardness of the resulting alloy, for the purpose of the lost-wax casting for wearable accessories. Aluminum also creates a passivating layer on the surface of objects made of the alloy, making them resistant to oxidation and to atmospheric agents. In addition, aluminum helps making the alloy lighter.

**[0039]** Incidentally, the Applicant has observed that when the alloy is subjected to remelting it can happen that a certain weight percentage of aluminum (e.g., around 0,3-0,4% of the overall weight of the alloy) is lost (e.g., by oxidation). For example, it can happen that by subjecting to lost-wax casting an alloy initially having a weight percentage of aluminum of 7,8%, the percentage of aluminum in the finished product drops to 7,4%.

**[0040]** Preferably said weight percentage of manganese (Mn) is greater than or equal to 13,0%, more preferably greater than or equal to 14,0%, even more preferably greater than or equal to 14,4%, and/or less than or equal to 17,0%, more preferably less than or equal to 16,0%, even more preferably less than or equal to 15,0%. Manganese, in the above-described ranges, is soluble in the alloy, it improves the grain fineness of the alloy (e.g., it contributes to the formation of the crystalline structure) contributing to give the desired mechanical properties to the alloy, it improves the fluidity of the alloy in the molten state and it acts as deoxidizer in the molten alloy. The Applicant has found that by increasing the weight percentage of manganese (within the above-described preferred ranges), a progressive increase of the deoxidation degree (e.g., absence of oxygen and hydrogen) in the molten alloy is obtained, with consequent decrease of the occurrence of the oxidation phenomenon of the molten alloy. The above-described preferred ranges of content of manganese, in combination with the content of the other elements, therefore represent for the Applicant an optimal selection with respect to the deoxidation degree of the molten alloy.

**[0041]** Preferably said weight percentage of iron (Fe) is greater than or equal to 3,0%, more preferably greater than or equal to 3,5%, even more preferably greater than or equal to 3,8%, and/or less than or equal to 5,0%, more preferably less than or equal to 4,5%, even more preferably less than or equal to 4,2%. Iron, in the above-described ranges, gives the alloy high mechanical strength and good workability (given its high ductility), it is a low-cost material and moreover it is a refiner of the crystalline structure, helping ensuring the desired mechanical properties to the alloy. The Applicant has found that by increasing the weight percentage of iron (within the above-described preferred ranges), a progressive increase in the refinement degree of the alloy is obtained (e.g., progressive increase in the crystallinity percentage of the resulting alloy) with a consequent increase in the mechanical properties of the alloy. The above-described preferred ranges of content of iron, in combination with the content of the other elements, therefore represent for the Applicant an optimal selection with respect to the refinement degree of the metal alloy.

**[0042]** Preferably said weight percentage of silver (Ag) is greater than or equal to 0,6%, more preferably greater than or equal to 0,7%, even more preferably greater than or equal to 0,8%, and/or less than or equal to 1,7%, more preferably less than or equal to 1,5%, even more preferably less than or equal to 1,3%. Silver, in the above-described ranges, gives the alloy a white-like colour and, possibly following polishing and/or brushing of the surface, excellent gloss and/or brilliance properties which makes it particularly attractive for applications such as the eyewear and the costume jewellery.

**[0043]** By "impurity element" it is meant any element not belonging to the group: copper, aluminum, manganese, iron and silver. According to the Applicant, the alloy of the present invention ideally contains all and only the elements of this group in the aforesaid weight percentages. However, it is possible that inside the alloy there are one or more elements which constitute unavoidable or tolerable impurities, for example due to the intrinsic impurity of the raw materials used for the making of the alloy and/or due to impurities deriving from the use of tools or machinery for the production and/or the treatment of the metal alloy.

**[0044]** For the purposes of the present invention, with the expressions "substantially absent" or "alloy substantially

not containing" referred to an element or to a system of elements, it is meant that said element or system of elements is absent or at most present in traces, for example in weight percentage lower than 0,01%, typically lower than 0,005%.

[0045] Among the possible impurities, the Applicants consider zinc and tin. Preferably said overall weight percentage of zinc (Zn) and tin (Sn) is less than or equal to 1,0%, more preferably less than or equal to 0,5%. Typically, tin and zinc are substantially absent.

[0046] However, according to the Applicant, the possible presence of tin and zinc in quantities such that the overall weight percentage remains less than or equal to 2% does not substantially change the physical and/or mechanical properties of the alloy.

[0047] According to the Applicant, the alloy can contain further impurity elements, for example one or more of the following elements: silicon (Si), nickel (Ni) and lead (Pb). Preferably said overall weight percentage of further impurity elements is less than or equal to 0,2%, more preferably less than or equal to 0,1%, even more preferably less than or equal to 0,08%.

[0048] Preferably said metal alloy contains a weight percentage of nickel (included in said overall weight percentage of further impurity elements) less than or equal to 0,05%, more preferably less than or equal to 0,03%. Typically, nickel is substantially absent. The very low or null content of nickel in the alloy eliminates toxicity and/or allergy problems from the objects made with the alloy.

[0049] Preferably said metal alloy does not substantially contain beryllium and/or cobalt (e.g., a weight percentage of one or both beryllium and cobalt is less than 0,01%).

[0050] The features and advantages of the present invention will be further clarified by the following description of some examples, presented by way of non-limiting example of the present invention.

[0051] The Applicant has made some samples of the alloy according to the present invention, as shown in table 1, wherein the measured weight percentages of the elements are shown.

[0052] The Applicant has estimated that in all the produced samples the overall weight percentage of all the impurity elements is less than or equal to 0,04% (with beryllium, nickel and cobalt substantially absent). This overall weight percentage will be neglected in the following.

Table 1

Alloy	Cu (%)	Fe (%)	Mn (%)	Al (%)	Ag (%)
Example 1	71,7	3,9	14,4	9,0	1,0
Example 2	71,6	4,1	14,6	8,6	1,1
Example 3	71,0	4,2	14,7	9,1	1,0
Example 4	71,3	4,3	14,4	9,1	1,1
Example 5	72,7	3,7	14,0	8,7	0,9

[0053] For all the examples 1-5 the casting temperature (i.e., the optimal temperature for casting the alloy under gravity) is comprised in a temperature range greater than or equal to 1050°C and/or less than or equal to 1100°C, the hardness is equal to 300 Vickers (hardness value obtained without heat treatments on the samples), the linear shrinkage (i.e., the percentage decrease in the linear length of the sample following cooling) is equal to about 2%, the specific weight is equal to 7,17 g/cm<sup>3</sup>, and finally the elastic modulus (E) is equal to about 90-100 GPa.

[0054] These values of the physical properties are comparable to those of the copper-based metal alloys notoriously used for the lost-wax casting, exemplarily shown in tables 2 and 3 relating to comparative examples of commercially available alloys containing beryllium and not containing beryllium, respectively:

Table 2

Alloy	Cu (%)	Be (%)	Co (%)	Other (Fe, Ni, ecc.) (%)	Casting Temp (°C)	Hardness (HV)	Specific Weight (g/cm <sup>3</sup> )
Com parative Example 1 (Tempered)	97	2	0,3	0,7	900	350	8,36

Table 3

Alloy	Cu (%)	Be (%)	Co (%)	Other (Fe, Ni, ecc.) (%)	Casting Temp (°C)	Hardness (HV)	Specific Weight (g/cm <sup>3</sup> )
Comparative Example 2 (Hardened)	79	3	8	10	1170	320	6,71

**[0055]** Table 4 shows the measured values of yield stress (Rp), breaking stress (Rm) (both expressed in MPa (N/mm<sup>2</sup>)) and elongation percentage (A) for a tensile test performed on a sample (having area equal to 11,4 mm<sup>2</sup> and length equal to 25 mm) of the alloy according to the aforesaid example 5.

Table 4

Alloy	Rp (MPa)	Rm (MPa)	A (%)
Example 5	662	809	4

**[0056]** These values of the mechanical properties are comparable to those of the aforesaid copper-based metal alloys notoriously used for the lost-wax casting after having being subjected to heat treatments, exemplarily shown in table 5 relating to the aforesaid examples of commercially available alloys:

Table 5

Alloy	Rp (MPa)	Rm (MPa)	A (%)
Comparative Example 1 (Tempered)	650	830	4
Comparative Example 2 (Hardened)	630	711	3,2

**[0057]** The Applicant has also verified that the alloys object of the present invention have low or null emission of fumes during casting, few residues in the melting crucible (index of low stickiness and good fluidity), excellent weldability (with TIG technology and flame and/or induction soldering), excellent tools workability, as well as not being subjected to loss of mechanical properties following remelting due to high temperature processing (e.g., welding). Moreover, these alloys have a white-like colour and an excellent gloss following polishing and/or brushing.

**[0058]** Furthermore, the described and claimed alloys can be subjected to electrochemical processes (e.g., galvanization) with the aim of making a passivating layer with function of both protection (e.g., antioxidant) from external agents and providing the appropriate aesthetic characteristics (e.g., colouring), resulting to be furtherly attractive for the making of objects for wearable accessories.

**[0059]** Therefore, the described and claimed alloys are particularly suitable for their use in lost-wax casting processes, and show advantages in terms of health and safety for the man and/or the environment (e.g., absence of beryllium and cobalt which are carcinogenic and/or mutagenic materials, and absence of nickel which is allergenic), in terms of process simplicity (e.g., no heat treatments are required), and in terms of aesthetic characteristics (given by the silver content) with respect to copper-based alloys notoriously used for the lost-wax casting.

## Claims

### 1. Metal alloy containing:

- a weight percentage of aluminium greater than or equal to 7,5% and less than or equal to 10,0%;
- a weight percentage of manganese greater than or equal to 12,0% and less than or equal to 18,0%;
- a weight percentage of iron greater than or equal to 2,5% and less than or equal to 6,0%;
- a weight percentage of silver greater than 0,4% and less than or equal to 2,0%;
- possibly an overall weight percentage of zinc and tin greater than or equal to 0% and less than or equal to 2,0%;
- possibly an overall weight percentage of further impurity elements greater than or equal to 0% and less than 0,4%;
- a weight percentage of copper such that a sum of said weight percentages of aluminium, manganese, iron, silver, zinc, tin, further impurity elements and copper is equal to 100%.

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2. Metal alloy according to claim 1, wherein said weight percentage of copper is greater than or equal to 62,0%, preferably greater than or equal to 68,0%, and/or less than or equal to 77,0%, preferably less than or equal to 73,0%.
- 5 3. Metal alloy according to anyone of the previous claims, wherein said weight percentage of aluminium is greater than or equal to 8,0%, preferably greater than or equal to 8,8%, and/or less than or equal to 9,8%, preferably less than or equal to 9,2%.
- 10 4. Metal alloy according to anyone of the previous claims, wherein said weight percentage of manganese is greater than or equal to 13,0%, preferably greater than or equal to 14,4%, and/or less than or equal to 17,0%, preferably less than or equal to 15,0%.
- 15 5. Metal alloy according to anyone of the previous claims, wherein said weight percentage of iron is greater than or equal to 3,0%, preferably greater than or equal to 3,8%, and/or less than or equal to 5,0%, preferably less than or equal to 4,2%.
- 20 6. Metal alloy according to anyone of the previous claims, wherein said weight percentage of silver is greater than or equal to 0,6%, preferably greater than or equal to 0,8%, and/or less than or equal to 1,7%, preferably less than or equal to 1,3%.
- 25 7. Metal alloy according to anyone of the previous claims, wherein said overall weight percentage of zinc and tin is less than or equal to 1,0%, wherein said overall weight percentage of further impurity elements is less than or equal to 0,2%, preferably less than or equal to 0,08%, wherein said metal alloy contains a weight percentage of nickel less than or equal to 0,05%, and wherein a weight percentage of cobalt and/or beryllium is less than 0,01%.
- 30 8. Lost-wax casting process for the production of objects in the metal alloy according to any of the previous claims.
9. Lost-wax casting process according to claim 8, comprising:
- making a wax model of said objects, making a mould around said model and removing said wax from said mould;
  - melting said metal alloy;
  - filling said mould with said melted metal alloy;
  - solidifying said metal alloy inside said mould;
  - removing said mould from said solidified metal alloy;
- 35 wherein said filling said mould is made with a pressure gradient and/or with a centrifugal force, and wherein said filling said mould is made at a casting temperature of said metal alloy, greater than a melting temperature of said metal alloy.
- 40 10. Production process of objects comprising the lost-wax casting process according to claim 8 or 9, wherein said objects are parts of wearable accessories, for example glasses parts or costume jewellery.
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EUROPEAN SEARCH REPORT

Application Number  
EP 21 15 2386

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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The present search report has been drawn up for all claims			
Place of search <b>Munich</b>		Date of completion of the search <b>7 May 2021</b>	Examiner <b>Lilimpakis, Emmanuel</b>
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