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(54) **A method for reducing the allergenicity of metal products made using alloys comprising allergenic elements**

(57) A method for reducing the allergenicity of products made using alloys comprising allergenic elements, in particular gold alloys comprising Ag, Ni, Cu and Zn, comprises the operating step of subjecting the product to a treatment for homogenising the internal structure, preferably done by subjecting the product to an annealing heat treatment. Annealing can take place in an at-

mosphere which is controlled or not controlled.

In some preferred forms of implementation of the method, the annealing step takes place at a temperature between 680°C and 850°C with a duration of between 10 and 90 minutes.

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Description

[0001] The present invention relates to a method for reducing the allergenicity of products made using alloys comprising allergenic elements.

[0002] Hereinafter the term products refers to both industrial semi-finished products and to finished products, such as decorative objects which can be worn.

[0003] In particular, the present invention is designed to be implemented relative to objects made of gold alloy which are worn for decorative and non-decorative purposes.

[0004] It is known that for sensitised persons many components of gold alloys can cause allergic reactions mainly in the form of allergic dermatitis, where there is prolonged contact with the skin from objects containing such components, for example pieces of jewellery, and stomatitis for example in the case of products used in the dental and dental technology fields.

[0005] Amongst the various elements of which gold alloys are composed, the one recognised as having the greatest allergenic capacity is definitely nickel.

[0006] Due to the recognised allergenicity of nickel, products known as nickel-free and nickel-tested have spread over the years.

[0007] Whilst the former are simply products without said element, the latter are products which although they contain nickel are considered substantially anallergic.

[0008] The concept of nickel-tested products is linked to the knowledge of the physical - chemical mechanism which forms the basis of the above-mentioned allergic phenomena.

[0009] Studies carried out have shown that the level of allergenicity of a certain element is linked to the capacity of the product which contains it to release it in contact with the substances produced by the human body, in particular sweat and saliva.

[0010] It was found that allergic reactions only occur when a relatively large amount of nickel is released.

[0011] With regard to this, European Standard EN1811:1998, which substantially established the category of nickel-tested products, indicated the nickel release threshold value below which a product may be considered anallergic as $0.5 \mu\text{g}/\text{cm}^2/\text{week}$.

[0012] According to that standard, the value indicated must be checked by immersing the product in a predetermined solution whose composition is a sort of artificial human sweat.

[0013] Despite the spread of nickel-tested products, procedures for the production of such products are not known.

[0014] Therefore, at present, first one obtains a predetermined alloy with which to make the relevant product, then one checks whether or not it may be considered a nickel-tested product.

[0015] Also, at present there are no known jewellery products made of low carat gold alloy which, although containing nickel, satisfy the requirements of the standard that would allow them to be called nickel-tested.

[0016] However, as already indicated, nickel is not the only element which can cause allergic reactions such as dermatitis and stomatitis.

[0017] In particular, the elements recognised as having more or less marked allergenicity include cobalt, gold, palladium, and rhodium.

[0018] In contrast, silver and zinc do not seem to cause allergic reactions.

[0019] Finally, the role of copper, zinc, tin, platinum and titanium is uncertain.

[0020] Two groups may be identified amongst the above-mentioned elements: on one hand cobalt, gold, palladium and rhodium, which have an allergenic capacity (with reference to their release) comparable with that of nickel; and on the other hand the other elements, whose allergenic capacity is significantly lower than that of nickel.

[0021] However, as yet for elements other than nickel there are no normative or other references to indicate the allergenicity thresholds.

[0022] In this situation the technical need which forms the basis of the present invention is to provide a method for reducing the allergenicity of products made using alloys comprising allergenic elements.

[0023] In particular, the technical need of the present invention is to provide a method for reducing the allergenicity of products made using alloys comprising allergenic elements, which allows a simultaneous reduction of the allergenicity linked to each of the individual allergenic elements.

[0024] A further technical need of the present invention is to provide a method for reducing the allergenicity of products made using alloys comprising allergenic elements, in particular for treating products made of gold alloy, therefore, linked to the goldsmiths' sector, whether they are semi-finished or finished products.

[0025] The technical need specified and the aims indicated are substantially achieved by a method for reducing the allergenicity of products made using alloys comprising allergenic elements as described in the claims herein.

[0026] Other features and advantages of the invention are more clearly indicated in the detailed description which follows, of several preferred non-restricting forms of implementation of a method for reducing the allergenicity of products made using alloys comprising allergenic elements.

[0027] As already indicated, the allergenicity of a product relative to one of its components depends on the product's capacity to release that component upon contact with secretions from the human body.

[0028] Therefore, the method for reducing allergenicity disclosed is substantially implemented in the form of a method for reducing the release of allergic elements from the products which contain them.

[0029] It is substantially a method of treating the product which allows the release of each individual element to be brought below a threshold value considered safe for that element.

[0030] This threshold value may be higher for those elements which have a lower level of allergenicity. As already said, the present invention is intended in particular for implementation in the sector of products made using gold alloy, such a semi-finished products from the goldsmiths' and jewellery sector (particularly those which are designed to make contact with the skin such as earrings, rings, necklaces, watches, etc.).

[0031] A fundamental aspect of the present invention is the fact that the main step of the method for reducing allergenicity consists of subjecting the product to be treated to a treatment which homogenises its internal structure.

[0032] According to the preferred forms of implementation of the present invention, this step of homogenising the internal structure involves subjecting the product to an annealing heat treatment, at a temperature and with a duration which vary according to the characteristics of the alloy with which the product is made.

[0033] In this case the main parameters are the composition of the alloy, in terms of both the elements of which it is composed and the percentage of the individual elements, and the method with which the product was obtained, as seen below.

[0034] The best results are achieved by carrying out the annealing step in a controlled atmosphere, especially a reducing environment, although the annealing can also be carried out in an unprotected atmosphere (therefore in oxidative conditions) or in an inert atmosphere.

[0035] Tests have shown that the annealing step should preferably take place at a temperature between 680°C and 850°C, and the duration should be between 10 and 90 minutes.

[0036] However, as already indicated, the precise temperature and optimum duration for each type of product must be established in each case based on experimental tests.

[0037] The results of some experimental tests carried out on products made using four different types of alloys are indicated below by way of example.

[0038] In particular, the first two examples refer to products obtained by investment casting alloys, whilst the other two refer to products obtained by mechanical working alloys, in the case in question rolling with a 70% reduction of the original thickness.

[0039] Table 1 shows the compositions of the four alloys.

Table 1

Example	Au	Zn	Cu	Ag	Ni	Pd	Grain Refinement	Other	As-cast Grain size (μm)
Investment casting alloys									
1C	37.5	10.2	36	4	12.1	-	Medium	Si	630
2C	37.5	12.1	36	1.5	12.5	-	No	Si	600
Mechanical working alloys									
1M	37.5	9.7	43	-	9.7	-	Medium	Si	370
2M	58.5	6	22.7	12.2	-	-	Medium	Si,Co	nd

[0040] Each alloy was subjected to at least one annealing treatment.

[0041] The release of the individual elements of each alloy before and after annealing was measured.

[0042] To measure the release of each element, the standard proposed by European directive EN1811:1988 relative to nickel was used.

[0043] The following safety threshold values were identified for the individual elements (based on the differing dangerousness of the different elements):

for cobalt, nickel and silver: release 0.5 μg/cm²/week;

for gold and palladium: release 0.2 μg/cm²/week;

for the other elements: release 2.0 μg/cm²/week.

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Example 1C - Investment casting alloy

[0044]

Table 2

	Zn	Cu	Ag	Ni	Au
Composition (%) Release ($\mu\text{g}/\text{cm}^2/\text{week}$)	10.2	36	4	12.1	37.5
1.1 as-cast	0.81	2.80	0.00	1.62	0.00
1.2 820°C x 40' H ₂ O	0.41	0.41	0.00	0.33	0.00

[0045] As can be seen, the annealing treatment at 820° with a duration of 40 minutes allowed all of the release values to be brought under the safety threshold.

Example 2C - Investment casting alloy

[0046]

Table 3

	Zn	Cu	Ag	Ni	Au
Composition (%)	12.1	36	1.5	12.5	37.5
Release ($\mu\text{g}/\text{cm}^2/\text{week}$)					
1.1 as-cast	0.99	1.36	0.00	1.66	0.00
1.2 820°C x 40' H ₂ O	1.26	0.34	0.00	0.44	0.00

[0047] As can be seen, the annealing treatment at 820° with a duration of 40 minutes allowed all of the release values to be brought under the safety threshold, although it caused a slight increase in the release of zinc.

Example 1M - Mechanical working alloy

[0048]

Table 4

	Zn	Cu	Ag	Ni	Au
Composition (%)	9.7	43	-	9.7	37.5
Release ($\mu\text{g}/\text{cm}^2/\text{week}$)					
1.1 After 70% reduction	4.77	4.14	-	7.89	0.00
1.2 550°C x 40'	7.03	3.80	-	11.28	0.00
1.3 600°C x 40'	3.46	4.29	-	8.17	0.00
1.4 680°C x 40'	1.50	3.88	-	1.83	0.00
1.5 760°C x 40'	0.17	0.67	-	0.20	0.00
1.6 820°C x 40'	0.22	0.39	-	0.14	0.00

[0049] As can be seen, in this case the annealing treatments at 760° and at 820° with a duration of 40 minutes both allowed all of the release values to be brought under the safety threshold.

Example 2M - Mechanical working alloy

[0050]

Table 5

	Zn	Cu	Ag	Co	Au
Composition (%)	6	22.7	12.2	0.4	58.5

Table 5 (continued)

	Zn	Cu	Ag	Co	Au
Release ($\mu\text{g}/\text{cm}^2/\text{week}$)					
1.1 After 70% reduction	0.03	0.06	0.10	0.55	0.00
1.2 550°C x 40'	0.03	0.07	0.30	0.69	0.00
1.3 600°C x 40'	0.02	0.09	0.60	3.11	0.00
1.4 680°C x 40'	0.04	0.06	0.47	2.21	0.00
1.5 760°C x 40'	0.09	0.14	0.68	0.21	0.00
1.6 820°C x 40'	0.24	0.14	1.40	0.42	0.00

[0051] As can be seen, in this case the annealing treatment at 760° with a duration of 40 minutes allowed the best results to be achieved. It should be noticed how treatment at 820°C, although satisfactory, is not optimum in this case.

[0052] It may be imagined how further tests at temperatures between 680°C and 820°C could allow the ideal temperature for implementing the present invention for the product 2M to be found.

[0053] The present invention brings important advantages.

[0054] Firstly, the method disclosed allows a reduction of the release of elements in the products treated using it. Consequently, it allows a reduction of the allergenicity of products made using alloys comprising potentially allergenic elements.

[0055] Once perfected for the specific alloy used to make the product to be treated, the method described above allows the release of all of the allergenic elements to be simultaneously kept at a safe level. Secondly, the method disclosed allows a reduction of the allergenicity of products made using gold alloys comprising allergenic elements.

[0056] This advantage is particularly important for the goldsmiths' sector, for both semi-finished and finished products.

[0057] Relative to this, it should be emphasised how products made using low carat gold alloys (for example, 9 carat) comprising nickel cannot normally pass the test established in order to define them as nickel-tested.

[0058] By applying the method disclosed, nickel-tested products can be made of 9 carat gold alloy

(Examples 1C) .

[0059] It should also be noticed that the present invention is relatively easy to produce and the cost linked to its implementation is not very high. The invention described may be subject to modifications and variations without thereby departing from the scope of the inventive concept.

[0060] All details of the invention may be substituted with other technically equivalent elements according to requirements.

Claims

1. A method for reducing the allergenicity of products made using alloys comprising allergenic elements, **characterised in that** its comprises the operating step of subjecting the product to a treatment which homogenises its internal structure.

2. The method for reducing the allergenicity of products made using alloys comprising allergenic elements according to claim 1, **characterised in that** the step of homogenising the internal structure involves subjecting the product to an annealing heat treatment.

3. The method for reducing the allergenicity of products made using alloys comprising allergenic elements according to claim 2, **characterised in that** the annealing step takes place in a controlled atmosphere.

4. The method for reducing the allergenicity of products made using alloys comprising allergenic elements according to claim 3, **characterised in that** the controlled atmosphere is a reducing environment.

5. The method for reducing the allergenicity of products made using alloys comprising allergenic elements according to claim 3, **characterised in that** the controlled atmosphere is an inert environment.

6. The method for reducing the allergenicity of products made using alloys comprising allergenic elements according to claim 2, **characterised in that** the annealing step takes place in an unprotected atmosphere.

7. The method for reducing the allergenicity of products made using alloys comprising allergenic elements according to any of the foregoing claims from 2 to 6, **characterised in that** the annealing step takes place at a temperature between 680°C and 850°C.

5 **9.** The method for reducing the allergenicity of products made using alloys comprising allergenic elements according to any of the foregoing claims from 2 to 7, **characterised in that** the duration of the annealing step is between 10 and 90 minutes.

10 **10.** The method for reducing the allergenicity of products made using alloys comprising allergenic elements, the products consisting of objects which can be worn and the alloys comprising precious or semi-precious metals, **characterised in that** it comprises at least the following operating steps:

- 15 - a first step of producing the object using the alloys comprising precious or semi-precious metals;
- a second step of heating the object to a temperature suitable for relaxing mechanical tensions inside the structure of the object.

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Application Number
EP 04 42 5372

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Place of search The Hague		Date of completion of the search 26 October 2004	Examiner Bombeke, M
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