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**Description**

USE OF yellow GOLD ALLOYS or RED IN POWDER FOR PRODUCTION OF precious objects with Rapid Prototyping by addition of material

**DESCRIPTION****Field of application**

[0001] The present invention is applicable in the field of jewelry and particularly relates to the use of yellow gold alloys or red in powder for production of precious objects with rapid prototyping by addition of material.

**Definitions**

[0002] In the present text, by the term "rapid prototyping or derived by the addition of material" is meant a shaping process of various materials for making layer by layer objects to be drawings computerized 3D. Merely by way of example, rapid prototyping methods by the addition of material in accordance with the present text are rapid prototyping and/or the direct production by selective melting laser (SLM) , electron beam melting (EBM) or selective laser sintering (SLS) .

[0003] In the present text, by the term "title" or derivatives of an alloy or of an object in precious gold is meant, unless otherwise indicated, the lowest concentration of gold in the alloy or object precious. Typically the by way of gold and expressed in thousandths of mass on mass or carat gold.

[0004] For Europe, the reference standard for the titers of alloys of precious metal and the DIN EN 29202.

[0005] In the present text, by the term "carato" or derived referred to by way of an alloy or of an object is meant precious, unless there are indications to the contrary the twenty part of the total mass of an alloy or of an object precious of gold. Thus, for instance, an alloy or an object precious 18 carat gold contains a minimum 75% of gold and carato. The symbol of a K which is arranged downstream of the number indicating the by way of the alloy (18K for 18 carat gold, 14K for 14 carat gold, 10K for 10 carat gold, 9K for 9 carat).

[0006] In the present text, by the term "consists essentially" or derived associated with a composition or product of interest consisting of two or more components is meant, unless there are indications to the contrary that that

product or composition consists of components listed (that is that the total of the components listed are 100% of the composition or product), minus the impurities.

[0007] In the present text, by the term "object precious" or derived means, unless otherwise indicated, a finished product of any shape and size, deriving from the treatment of an alloy.

[0008] In the present text, by the term "percentage by weight" or "% by weight" or derived means, unless otherwise indicated, the percentage by weight of a component of interest with respect to the total weight of the composition in which the component of interest is included.

### **State of the art**

[0009] some rapid prototyping processes by the addition of material the selective melting of metal powder by laser to construct layer by layer the desired object.

[0010] Each section of the object is constructed by the consecutive scanning of the laser beam, which determines the linear melting of the metal powder, with the consequent progressive formation of a compact layer of alloy.

[0011] One of the main problems of this method of machining and the reflection of the electromagnetic radiation which causes poor absorption of energy and a reduced capacity of melting of the metal particles.

[0012] This drawback is particularly felt in the field of jewelry, due to the high reflectivity of precious alloys, particularly those with matrix of gold, material that has an electrical resistivity significantly greater than the silver.

[0013] In order to obviate this drawback, additional surface treatments are carried out (oxidation, painting, etc. ) , which lead to the formation of thin layers having a highest adsorption of the substrate which is then heated in an indirect manner.

[0014] Moreover, the high reflectivity of precious alloys involves the formation of high surface roughness, consisting of the projection of particles of metal powder above the bed of construction which are also responsible for the formation of harmful blistering in the surface and porosity.

[0015] By W02013128413 silver alloys are known for rapid prototyping processes for addition of material.

**Presentation of the invention**

[0016] object of the present invention is to obviate the above mentioned drawbacks by providing yellow gold alloys or red powder for the production of precious objects with rapid prototyping by addition of material.

[0017] Another aim of the present invention is to provide gold alloys yellow or red powder for the production of precious objects with low surface roughness.

[0018] This and other objects are achieved by the use of a gold alloy powder of red or yellow by way 18, 14, 10 or 9 carat gold comprising:

(A) from 37.5 to 38.5 % or from 41.7 to 42.5 or from 58.5 % to 59.5 % by weight or from 75% to 76% by weight of gold

(D) from 0.05 % to 5% by weight, preferably from 0.05 % to 3 % by weight of at least a metalloid selected from the group consisting of germanium, silicon, boron

**, phosphorus, Tellurium and selenium;**

[0019] wherein the percentages by weight are percentages by weight with respect to the total weight of the alloy, for the manufacture of precious objects with rapid prototyping by addition of material, in such a way that the same precious objects have low surface roughness.

[0020] Conveniently, the precious objects may be made by selective laser (SLM) , electron beam melting (EBM) or selective laser sintering (SLS) .

[0021] The classical gold alloys in fact, while allowing to obtain precious objects with good mechanical characteristics do not allow to have a good surface roughness.

[0022] Therefore, to the classic gold alloys are added chemical elements metalloids, such as germanium, silicon, boron, tellurium, phosphorus and/or selenium, in percentages reported above.

[0023] The addition of these elements in the powder plays a fundamental role in the improvement of selective laser fusion and their effect can be appreciated both in terms of reduced surface roughness and porosity and in terms of reduced projection of metal particles during the laser action.

[0024] For the purpose, since the gallium creates potential problems linked to the formation of blisters, the alloys in powder form of the present invention may be free of gallium.

- [0025] Moreover, since the platinum and palladium present a reduced thermal conductivity, the alloys in powder form of the present invention may be free of these elements.
- [0026] Preferably the at least a metalloid is selected from the group comprising germanium, silicon and boron.
- [0027] In a preferred but not exclusive embodiment of the invention the powdery alloy may essentially consist of:
- (A) from 37.5 to 38.5 % or from 41.7 to 42.5 or 58.5 % to 59.5 % by weight or from 75% to 76% by weight of gold
  - (B) from 10% to 55% by weight of copper;
  - (C) from 2 % to 15 % by weight of silver;
  - (D) from 0.05 % to 5% by weight, preferably from 0.05 % to 3 % by weight of at least a metalloid selected from the group consisting of germanium, silicon, boron,
- [0028] Tellurium, phosphorous and selenium.
- [0029] Advantageously, a gold alloy powder by way 18 carat gold may consist essentially of
- (A) gold from 75% to 76% by weight;
  - (B) copper from 10% to 23% by weight;
  - (C) silver from 2 % to 15 % by weight;
  - (D) at least a metalloid from 0.05 % to 3% by weight.
- [0030] More in particular, a yellow gold alloy powder by way 18 carat gold may consist essentially of
- (A) gold from 75% to 76% by weight;
  - (B) copper from 10% to 14% by weight;
  - (C) silver from 10% to 14% by weight;
  - (D) at least a metalloid from 0.05 % to 3% by weight.
- [0031] On the other hand, a gold alloy powder of red by way 18 carat gold may consist essentially of
- (A) gold from 75% to 76% by weight;
  - (B) copper from 18% to 23% by weight;
  - (C) silver from 2% to 5% by weight;
  - (D) at least a metalloid from 0.05 % to 3% by weight.

[0032] Conveniently, a gold alloy red by way 14 carat gold may consist essentially of

- (A) gold from 58.5 % to 59.5 % by weight;
- (B) copper from 30% to 40% by weight;
- (C) silver from 5% to 10% by weight;
- (D) at least a metalloid from 0.05 % to 3% by weight.

[0033] In a preferred but not exclusive embodiment, a gold alloy red by way 10 carat gold may consist essentially of

- (A) gold from 41.7 % to 42.5 % by weight;
- (B) copper from 45% to 50% by weight;
- (C) silver from 8% to 13% by weight;
- (D) at least a metalloid from 0.05 % to 3% by weight.

[0034] Advantageously, a gold alloy red by 9 carat will consist essentially of

- (A) gold from 37.5 % to 38.5 % by weight;
- (B) copper from 47% to 55% by weight;
- (C) silver from 8% to 15% by weight;
- (D) at least a metalloid from 0.05 % to 3% by weight.

[0035] Advantageously, the alloy may have a particle size of between 1  $\mu\text{m}$  and 60  $\mu\text{m}$ .

[0036] The invention will be better understood thanks to the following examples which are provided for purely illustrative purposes and are not limitative of the invention.

### **Examples**

#### ***1 - of Preparation Example alloys***

[0037] were prepared various examples of alloys in powder that differ from each other in color and by way of the gold, in accordance with the table 1 below.

Tabella 1

	Es 1-18 Kt R	Es 2-18 Kt R	Es 3-18 Kt Y	Es 4-14 Kt R	Es 5-10 Kt R	Es 6-9 Kt R
(A) Au	75,2	75,2	75,2	58,7	41,9	37,7
(B) Cu	20,8	21,0	12,4	33,45	47,06	50,46
(C) Ag	3,6	3,6	12,0	7,45	10,64	11,44
(D) Ge	0,4	0,2	0,4	0,4	0,4	0,4

LEGENDA -> Es: Esempio;  
 18-14-10-9 Kt: Lega d'oro a titolo 18, 14, 10 o 9 carati;  
 R: Lega d'oro rosso;  
 Y: Lega d'oro giallo.

[0038] The alloys of examples 1-6 reported in Table 1 were prepared by a gas atomizer which operates in environment completely protected with argon and atmospheric pressure.

[0039] It is reported in FIG. 1 The scanning electron microscopy (SEM, EDS) of the powder of example 1, a red gold alloy 18 carat gold ( $d_{50}$  15,44  $\mu\text{m}$ ,  $d_{90}$  35,90  $\mu\text{m}$ ) it is evident that the atomization ensures the formation of powders consisting of particles having a prevalently spherical shape.

***Example 2 - embodiment of precious objects in red gold SLM***

[0040] was performed by a laminar block (parallelepiped having a length of 10.0 mm and a width of 5.0 mm and a thickness of 5.0 mm and a nominal distance uniform between the individual laminae of 500 pm) in red gold by the powder of example 1.

[0041] An apparatus was used SLM 50 (Realizer) provided with a fiber laser ( $W_{\text{max}} = 100$  Watt) having a spot from 10  $\mu\text{m}$  and a table of circular construction (70 mm), inserted in a protected atmosphere chamber with inert gas (Ar).

[0042] To evaluate the effect of the inclusion in the alloy of metalloids, in addition to above sample was made another sample without metalloids (same dimensions and the same apparatus) with a gold alloy red 18 carat gold to consisting of 75.2 % by weight copper with 20.8 % by weight and silver 4% by weight

[0043] For both of the samples, the laser power was set to 72,5 Watt.

[0044] As can be seen visually from the comparison between Fig . 2 and 3 the sample made with the gold alloy with germanium of example 1 has led to

the formation of surfaces parallel to the table of construction, with a total roughness of about  $R_t=55\mu\text{m}$ , that is to say about the 30% lower than the same free alloy of germanium.



