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Description

MADRELEGA FOR THE PRODUCTION OF A SILVER alloy for the manufacture of precious objects LOW SURFACE porosity

# DESCRIPTION

# Field of application

- [0001] The present invention is applicable in the field of jewelry and particularly relates to a madrelega and the use of the same for the production of a silver alloy by way 925 intended for manufacture of precious objects by investment casting.
- [0002] Further subject of the invention is a silver alloy by way 925 which includes that madrelega, as well as the use of the same for the manufacture of precious objects by investment casting.

# **Definitions**

- [0003] In the present text, by the term "title" or derivatives of an alloy or of an object in precious term silver, unless otherwise indicated, the minimum concentration of silver in the alloy or object precious. Typically, the title of the silver and expressed in thousandths of mass on mass.
- [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 "madrelega" or derivatives are intended, unless there are indications to the contrary, a blank intended to be bound with silver to the production of silver alloys.
- [0006] In the present text, by the term "alloy" or derived is meant, unless otherwise indicated, a product derived from a madrelega alloying and silver in the crude state, that is in output from the process of alloying between silver and madrelega.
- [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 in the crude state, that is in output from the process of alloying between silver and madrelega.
- [0008] 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. Without too tending to theory, it is possible to determine that a element is present as impurities if the same element does not materially affect the essential characteristics of composition in which is inserted and is less than 100 ppm by weight with respect to the total weight of the composition.

- [0009] 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.
- [0010] In the present text, by the term "grain refiner" or derived means, unless otherwise indicated, a compound or element or mixture of compounds and/or elements poorly soluble in the alloy is capable of promoting the formation of a large number of crystals minutes, rather than a few large grains dimensions. A fine grain alloy generally has better mechanical properties is often a high resistance to the corrosion.
- [0011] In the present text, by the term "deoxidizing agent" or derivatives are intended, unless there are indications to the contrary a compound or element able to capture the oxygen present in the alloy or madrelega in the molten state to prevent it combines with its functional elements, by modifying the composition, the purity and the properties optomeccaniche.

#### State of the art

- [0012] it is known that the investment casting and a production process used in the jeweller to make objects by very complex shapes and thin, therefore with a high volume area ratio.
- [0013] However, this process is traditionally accompanied by some disadvantages characteristic, such as porosity of gas and shrinkage, surface roughness oxidation and the inclusion of impurities of various nature.
- [0014] In particular, the surface porosity of precious objects made by such a production process is particularly high. Said porosity, can persist even

after the polishing step is often can be removed only with an intense grinding, risking to damage the geometry of the objects.

- [0015] Another disadvantage of the process investment casting is linked to the appearance of the hard spots in the object precious, that increase the surface roughness is negatively influence the metallic gloss.
- [0016] Another drawback of the investment casting and the excessive presence of residues in the crucible, which negatively affects the productivity of the industrial process.

#### Presentation of the invention

- [0017] object of the present invention is to overcome the disadvantages described above by providing a madrelega alligabile with silver to obtain a silver alloy by way 925 intended for manufacture of precious objects by investment casting which have reduced surface porosity.
- [0018] Another object of the invention is to provide an madrelega alligabile with silver to obtain a silver alloy intended for manufacture of precious objects by investment casting which have low surface roughness.
- [0019] Another object of the invention is to provide an madrelega alligabile with silver to obtain a silver alloy intended for manufacture of precious objects by investment casting which have high metallic gloss.
- [0020] Another object of the invention is to provide an madrelega alligabile with silver to obtain a silver alloy intended for manufacture of precious objects by investment casting which allows to obtain a high yield in the process of production of the same.
- [0021] This and other objects are achieved by a madrelega for the production of a silver alloy by 925 for the manufacture of precious objects by investment casting, consisting essentially of:

(A) from 0.15 % to 0.75 % by weight of germanium (Ge);

(B) from 0.035 % to 0.15 % by weight of silicon (Si);

(C) from 0.01 % to 0.1 % by weight of a grain refiner selected from the group consisting of: iridium (Ir), ruthenium (Ru), rhenium (Re), cobalt (Co)or rhodium (Rh), or a combination of two or more of these;

(D) the remaining part being constituted of copper (Cu);

wherein the percentages in weight are percentages by weight with respect

to the total weight of the madrelega.

- [0022] The copper (Cu)has the function of metal hardener for the silver alloy, whereas germanium (Ge)and the silicon (Si)are elements able to eliminate the oxygen from molten alloy and give a greater hardness. The content of the latter is calibrated to a minimum to avoid the formation of hard points, which are not tolerated in the jeweller because they create roughness and deterioration of the metallic gloss.
- [0023] Conveniently, the madrelega and free of zinc (Zn), gallium (Ga), tin (Sn), indium (In)and boron (B).
- [0024] As demonstrated below, in fact, the Applicant has surprisingly found that such metals negatively influence the madrelega.
- [0025] In particular, zinc (Zn), gallium (Ga)and tin (Sn)negatively influence the surface porosity while boron (B), although being a good deoxidizing agent gives rise to hard points.
- [0026] The indium (In)and boron (B), moreover, although positively affecting the surface porosity excessive leave residues in the crucible.
- [0027] Preferably, the germanium (Ge)can range from 0.25 % to 0.45 % by weight, and even more preferably from 0.3 % to 0.4 % by weight.
- [0028] it is also preferable that the silicon (Si)can range from 0.055 % to 0.085 % by weight, and even more preferably from 0.065 % to 0.075 % by weight.
- [0029] Preferably, moreover, the grain refiner may be from 0.02 % to 0.07 % by weight, and even more preferably from 0.03 % to 0.05 % by weight.
- [0030] Conveniently, the affnatore of grub screw can be iridium (Ir)or ruthenium (Ru). Advantageously, the madrelega can essentially be constituted by:(A) from 0.3 % to 0.4 % by weight of said germanium (Ge);
  - (B) from 0.065 % to 0.075 % by weight of said silicon (Si);
  - (C) from 0.03 % to 0.05 % by weight of grain refiner constituted by ruthenium (Ru);

the remaining part being constituted of copper (Cu).

- [0031] Preferably, the madrelega can be in the form of drops. For the purpose, may be prepared in a per se known manner for blasting.
- [0032] In a preferred but not exclusive embodiment to madrelega can be added, during the melting step, a small amount of lithium (about 0.01 %)with the

purpose of deoxidise the melting bath.

- [0033] It is understood that this element, while added with components (A) to (D) above will be part of the composition, not of functional madrelega but may be present only in line.
- [0034] In a further aspect of the invention, it is provided the use of madrelega having one or more of the characteristics mentioned above for the production of a silver alloy by 925 for the manufacture of precious objects by investment casting.
- [0035] In a further aspect of the invention can be provided with a silver alloy by way 925 mils for the manufacture of precious objects by investment casting, consisting essentially of:

- at least the 92.5 % of silver (Ag), preferably from 92.5 % to 93.5 % of silver (Ag);

- the remaining part of a madrelega having one or more of the characteristics mentioned above;

wherein the percentages by weight are percentages by weight with respect to the total weight of the alloy.

- [0036] The above alloys may be in the form of drops or bar respectively, and may be prepared in a per se known manner for blasting or for continuous casting.
- [0037] In a further aspect of the invention, it is provided the use of one of above silver alloys for the manufacture of precious objects by investment casting. This latter process is in itself known to the person skilled in the branch.
- [0038] By means of the alloys can be made of any type of object precious, for example earrings, bracelets, necklaces, rings or precious objects like.
- [0039] 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.

# Example 1 - of preparation examples madreleghe

[0040] were prepared various examples of madreleghe, which were subsequently used to prepare the alloys in accordance with the samples 1-38 of the following table 1.

- [0041] Such madreleghe were prepared by process of blasting.
- [0042] The various raw materials in suitable weight ratios, were inserted into a crucible protected by argon and then it has been reached a temperature of about 1200 °C for the homogenization. Before pouring it has inserted a small amount of lithium (0.01 % by weight with respect to the total weight of the sample)with the purpose of deoxidise the molten bath. Finally, the melt was passed through of the holes of about 1.2 mm placed in the die to cast so in a hydroalcoholic bath, in such a way as to form a grit with a distribution of diameters from about 1 mm to 5 mm

# Example 2 - Preparation of

- [0043] each of alloys madreleghe above was bound with silver to obtain a silver alloy 930 : madrelega 70, in accordance with the examples 1-38 described in Table 1. As a comparative example (standard sample), was also prepared a silver alloy standard 930 : copper 70.
- [0044] The above alloys were also prepared by blasting, by inserting the madrelega (or only for the standard sample) copper and silver in the appropriate weight ratios in a crucible and following the same above process.

# Example 3 - Measuring the depth of the pores of the samples prepared with the silver alloys of Example 2

- [0045] for each alloy was formed a series of massive pieces by investment casting. In order to each series of samples were introduced 400 grams of alloy in a crucible protected by argon gas or reducing gas and has been reached a temperature of 1000 °C.
- [0046] The melted alloy was then poured into molds refractory were then allowed to stand for 5 minutes and then immersed in water.
- [0047] Then it is performed the cleaning of the shaft by the refractory forming with a jet of water at high pressure was then left pickled in a solution of sulphamic acid to remove residues of surface oxides and mold.
- [0048] Once recovery has been performed by the shaft have been selected two pieces, one at the top and one at the rear end of the shaft, after which were sectioned at right angles to the axis of the hole in the crude state using a diamond circular saw. These pieces are in the form of square

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prisms pierced by a base to the other along the axis of the hole (FIG. 1) . The square base has the A and B sides of 14 mm and a depth C of 16 mm. The diameter D of the hole is 3 mm.

- [0049] The pieces were incorporated in an acrylic resin, so as to expose the face sectioned, which was subsequently ground and polished with abrasive paper with alumina powder.
- [0050] The mean depth P of the pores was calculated by measuring the maximum depth of the pores of three sides of section shown in FIG. 2 and then carrying out the arithmetic mean.
- [0051] For each piece was measured the mean depth of the pores by the use of a scanning electron microscope (SEM) starting from geometric profile of sectioned side up to the lower part of the pores deeper. The measurement of pore average depth of each sample is reported in the last column of Table 1.

	Profondità media dei pori (µm)	56	102	150	1	61	95	43	69	42	19	54	49	59	35	61	185	104	32	139	87	56	6†	52	109	138	82	61	79	113	93	108	144	100	64	69	97	103	69	75
Tabella 1	Ru [‰]		F	ı		1	0,030	0,030	0,030	0,030	0,030	I	ı	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.060	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	0.030	ı	,	0.030	0.030	0.030	0.030	0.030	•	0.060	0.030
	Ir [‰]		,	ı		0,050	1	,	1	1	1	1	0.050	ı	ı	1	ı	ı,	ı	,	•	1	•	1	I	I		•	ı		1	,	1	ı	ı	ı	ı	-	ı	1
	B [‰]		1	I	I	1	I	1	1	ł	0,028	0.028	0.028	0.300	0.028	0.028	0.028	0.028	0.060	060.0	0.028	0.028	t	0.028	1	ı			,		1	ı	•	ı	ı	ı	-	ı	I	1
	Si [‰]		0,050	I	I	1	ı	0,050	0,025	I	I	I	1	I	I	0.050	ı	0.050	1	•	1	0.050	0.050	,	1	1	0.025	0.025	0.025	0.025	0.050	0.025	0.050	0.050	0.050	1	,	•	I	0.050
	Ge [‰]	1	ı	0,500	1	1	0,500	0,250	0,250	ł	1	ı	1	1	ł	0.250	0.250	ŧ	1	1	1	1	1	ı	0.300	0.100	1	0.100	0.300	0.500	0.250	0.250	0.250	0.250	0.250	0.250	•	1	1	0.250
	In [‰]	,	1	ı	2,800	L	ı	ı	I	ı	1	I	1	1	ı	1	ı		١		t	0.250	0.250	0.250	1	-		•	1	8	ı		•		0.500	0.500	0.500	0.500	I	F
	Sn [‰]																																•	0.500	ı	ł		I	I	ł
	Ga [‰]	,	ı	ı	τ	1	ı		1	ı	1	ı	1	ı	ı	1	ı	t	1	•	•	ł	1	1	1	•	,	•	•	1	1		0.500	ı	ı	1	•	1	1	1
	Zn [‰]		0,232	0,900	1	1	1	,	1	1	1	1	1	1		ı	,		1	ı	E :	ſ	1	ı	•	ſ	*	1	ı	ı	,	,		,	1	1	1	•	ı	1
	Cu [‰]	70	Restante																																					
	Ag [‰]	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930	930
	Campione	Standard	-	2	ω	4	s	6	7	∞	6	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38

- [0052] The sample 3 has left too residue in the crucible, and therefore it has and then the measurement.
- [0053] By this measurement is result that the standard sample has an average depth of the pores of 56 μrn(FIGS. 3 4). Thus, a condition to which a sample must satisfy in order to fall within the scope of protection of the present invention is that the same must have an average depth of the

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pores measured as above described lower than 56 µm.

- [0054] It is evident that only samples 6, 8, 9, 10, 11, 13, , 17, 21 and 22 have an average depth of the pores less than 56 μrr.
- [0055] However, the samples 9, 10, 11, 13 and 17 have hard points and therefore do not fall within the scope of protection of the present invention.
- [0056] Further, the samples 8, 21 and 22 leave an excessive residue in the crucible, and therefore do not fall within the scope of protection of the present invention.
- [0057] From the above, the single sample falling within the scope of protection of the present invention and the sample 6 (FIGS. 5 6).
- [0058] In order to provide a term of comparison, FIGS. 7 8 are the electronic scanning SEM of the sample 31, whose average depth of pores is 144 μm.