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(54) **Gold alloys and master alloys for obtaining them**

Goldlegierungen und Vorlegierungen zu deren Herstellung

Alliages d'or et alliages-mères pour leur obtention

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- **PATENT ABSTRACTS OF JAPAN vol. 012, no. 444 (C-545), 22 November 1988 (1988-11-22) -& JP 63 169347 A (TOKURIKI HONTEN CO LTD), 13 July 1988 (1988-07-13)**
- **PATENT ABSTRACTS OF JAPAN vol. 1997, no. 12, 25 December 1997 (1997-12-25) -& JP 09 209060 A (SUMITOMO METAL MINING CO LTD), 12 August 1997 (1997-08-12)**
- **PATENT ABSTRACTS OF JAPAN vol. 1999, no. 04, 30 April 1999 (1999-04-30) -& JP 11 000792 A (SUMITOMO METAL MINING CO LTD), 6 January 1999 (1999-01-06)**
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- **www.bucksci.com/PDF/aa3008.pdf (Analysis of Gold Purity...)**

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Description

[0001] The present invention relates to gold alloys and to master alloys for obtaining them, mainly for the manufacture of precious objects such as jewellery and gold works, coins and medals.

[0002] One of the fundamental problems is to obtain gold alloys exhibiting good fluidity (i.e. a good ability to fill the die) at the moment of casting.

[0003] According to the procedures commonly used today, this is obtained by adding to the alloy some silicon, which, in addition to having a fluidising effect on the alloys, also has a deoxidising effect.

[0004] During the process period in which the metal remains molten, the silicon tends to combine with the oxygen present both in the starting materials and in the surrounding atmosphere.

[0005] This gives rise to a protective ability of the silicon which is manifested both during the production of granules by casting, and during the process for producing the castings comprising the melting, superheating and filling of the cavity of the mould made of refractory material.

[0006] However, the use of silicon in gold alloys also gives rise to a considerable drawback constituted by the fact that these alloys exhibit, once solidified, a crystal grain of relatively large size, with a consequent degradation of the mechanical properties (especially in the case of 18 carat gold alloys), and a consequent undesired fragility of the pieces themselves.

[0007] Given this problem, one route followed by industry operators, to decrease grain size, has been to add to the alloys also a suitable quantity of elements such as iridium, ruthenium, cobalt, nickel and rhenium, which tend to refine crystal grain.

[0008] However, this solution too is not wholly free of drawbacks.

[0009] In the first place, silicon tends to combine with the refining elements commonly used giving rise to the formation of silicides which go to constitute spheroidal conglomerates of inter-metallic compounds with high hardness, originating flaws known as "hard spots".

[0010] Such inclusions can appear on the surface of the finished piece after the final work process, entailing either the rework of the piece, or its discarding.

[0011] It is also known, from EP 381 994 and JP 63169347 the addition of Germanium to Gold alloys in order to improve their castability and their fluidity by lowering the melting point.

[0012] In this situation the technical task constituting the basis of the present invention is to provide gold alloys and master alloys for obtaining them which overcome the aforementioned drawbacks.

[0013] In particular the technical task of the present invention is to provide gold alloys and master alloys for obtaining them which exhibit an excellent fluidity in the molten state even without silicon additions.

[0014] The specified technical task and the indicated aims are substantially achieved by gold alloys and master alloys for obtaining them, as described in the accompanying claims.

[0015] An alternative element to silicon is germanium which, in the percentage of employment described in the present invention, has very distinct fluidising properties, superior to those of silicon: as described below, this feature is readily apparent in comparative melting tests between silicon based alloys and germanium based alloys, the latter described in the present invention.

[0016] In addition, the bath of germanium based alloys exhibits an extremely clean, slag-free surface, characteristic that is due to the fact that the germanium oxides which may be present on the surface of the bath are removed by sublimation at temperatures f around 710°C. Relative to silicon based alloys, therefore, the possibility of inclusions of oxide particles in the castings, with the consequent risk of brittleness, is drastically reduced.

[0017] Moreover, it has also been verified that germanium concentrations varying between 0.05% and 2% by weight have led to an increase in fluidity deemed to be even greater than the one provided by silicon in normal usage concentrations, whilst exhibiting an increase in grain size, following such addition, that is decidedly smaller than that observed in silicon alloys. Hence, in the case of germanium alloys, with low or nil silicon content, in addition to the fluidising effect obtained, exceeding that of silicon, the mechanical characteristics of the alloy are improved as well, as can be observed from the data illustrated below.

[0018] Moreover, a noticeable ameliorating effect of germanium has been observed on the ductility of the alloy obtained, superior to the effect of silicon.

[0019] Of interest is also the combined use of germanium and small quantities of silicon: this combination allows to obtain "clean and shiny" castings, without causing the immediate degradation of the mechanical properties as can be observed with the use of silicon alone in greater quantities.

[0020] One thereby also avoids the problem of the formation of hard spots, harmful when polishing the finished pieces, avoiding the insertion in the alloy of refining elements (with the aim of bringing mechanical properties back to functional values) such as cobalt and nickel.

[0021] The ameliorative effect of germanium on mechanical properties can also be exhibited in nickel based white alloys, as is evident from the formulations described hereafter.

[0022] Further characteristics and the advantages of the present invention shall become more readily apparent from the detailed description of some preferred, but not exclusive, embodiments of gold alloys and master alloys for obtaining them, and from the accompanying figures, in which:

- Figure 1 shows in graph form the effect of different

elements and compounds on the grain size of a gold alloy;

- Figure 2 shows in graph form the effect of the quantity of silicon and germanium on the grain size of the gold alloy;
- Figure 3 shows in graph form the effect of the elements and compounds of Figure 1 on the maximum load bearable by the gold alloy obtained therewith;
- Figure 4 shows in graph form the effect of the elements and compounds of Figure 1 on the ductile properties (lengthening as a result of traction) of the alloy.

[0023] The gold alloy of the present invention is defined in claim 1.

[0024] As stated, the fundamental characteristic of said alloy is that of containing germanium as a fluidising element, while being able to be free of silicon.

[0025] The better to meet particular productive requirements, to complete the alloy several other chemical elements can also be used.

[0026] Secondarily, the alloy can also contain, in a proportion not exceeding 4% by weight, at least one of the elements of the group constituted by cobalt, manganese, tin and indium.

[0027] To improve the qualities of the alloy, one ore more deoxidising elements such as magnesium, silicon, boron and lithium can also be added, each in a proportion not exceeding 0.15% by weight.

[0028] Note that, even when silicon is added to the alloy, it is added only in small quantities (in particular not exceeding 0.05% by weight in 18 carat alloys, and not exceeding 0.15% by weight in 14 carat alloys) solely in order to guarantee the protection of the alloy against the formation of oxides, and not to improve its fluidity.

[0029] Due to particular productive requirements in which a particularly reduced grain size is required, the alloy can also comprise refining elements such as ruthenium, rhenium and platinum in a suitable quantity and preferably not exceeding 0.4% by weight.

[0030] For the production of precious objects, moreover, there are two preferential ranges for the quantity of gold present in the alloy.

[0031] A first preferred range is the one associated with obtaining 18 carat gold, in which the quantity of gold present in the alloy is between 74% and 77% by weight.

[0032] A second preferred range is the one associated with obtaining 14 carat gold, in which the quantity of gold present in the alloy is between 57% and 60% by weight.

[0033] In regard to master alloys for obtaining the above gold alloys, they are defined in claim 2.

[0034] Some examples of gold alloys which can be obtained with a composition in accordance with the present invention are set out below.

Example A.

[0035] 14 carat yellow gold alloy whose composition in terms of weight percentage is as follows:

Gold	58.5

with master alloy comprising (as a percentage on the weight of the gold alloy):

Silver	8.0
Zinc	6.0
Iridium	0.01
Germanium	0.4

[0036] Copper, sufficient to reach 100 (in this specific case, 27.09%).

Example B

[0037] 18 carat yellow gold alloy whose composition in terms of weight percentage is as follows:

Gold	75.0

with master alloy comprising (as a percentage on the weight of the gold alloy):

Silver	15.0
Iridium	0.01
Germanium	0.2.

[0038] Copper sufficient to reach 100 (in this specific case 9.79%)

Example C

[0039] 18 carat yellow gold alloy whose composition in terms of weight percentage is as follows:

Gold	75.0

with master alloy comprising (as a percentage on the weight of the gold alloy):

Silver	12.5
Zinc	0.5
Germanium	0.25
Silicon	0.04.

[0040] Copper sufficient to reach 100 (in this specific case 11.71 %).

[0041] To obtain the three yellow gold alloys described in examples A, B and C set out above, a preferential process comprises the following phases:

- melting in controlled atmosphere or in an inert gas such as argon, of the elements in the respective doses, inside graphite or ceramic crucibles at a temperature ranging between 880 and 940°C;
- subsequent heating to a temperature ranging between 970 and 1030 °C before proceeding with casting;
- casting the material in appropriate dies;
- cooling the die in air;
- subsequent cooling of the die in water.

[0042] The present invention achieves important advantages.

[0043] In the first place, laboratory tests conducted by the Applicant have shown that use of Germanium in weight concentrations ranging between 0.05% and 2% leads to an increase in the fluidity of the alloy in the molten state that is even greater than the one brought about by the use of silicon in normal usage concentrations.

[0044] Moreover, the increase in grain size consequent to the use of germanium was lesser than the one that takes place in traditional alloys containing silicon, as shown in Figures 1 and 2.

[0045] Figure 1 shows the variation in the dimensions of the crystal grain of the alloy as a result of the addition, thereto, of the elements and compounds indicated in the x-coordinate. It is evident that the influence of Silicon (CuSi) on the increase in grain size is considerably lesser than the influence of Germanium (Ge).

[0046] Figure 2 shows the effect of the concentration of Silicon and germanium on the grain dimension of the gold alloy. In this case, too, it is evident that a low concentration of silicon, in the graph from 0 to 300 ppm, entails a considerable increase in crystal grain size, even exceeding the size increase caused by additions of germanium in concentrations that are 10 times greater.

[0047] This has positive repercussions on the mechanical behaviour of the alloy, as can be seen in Figure 3, which shows the (positive or negative) variation of the maximum load (measured with a traction test) bearable by the alloy, following the addition to the alloy of equal quantities of the different elements or compounds indicated in the x-coordinate.

[0048] Figure 4 shows the percent variation of the lengthening of the gold alloy subjected to traction test, as a function of the addition to the alloy of the elements and compounds, indicated in the x-coordinate, in equal quantities.

[0049] The use of germanium instead of silicon also yielded positive effects on the percent of lengthening of the alloy following the traction test.

[0050] In regard to the combined use of germanium and silicon, respectively to improve the fluidity and decrease the oxidation of the alloy, very encouraging results were obtained.

[0051] The combined use of these two elements gave rise to deoxidised alloys which at the same time show a very good mechanical behaviour, generally better than the one exhibited by the alloys in which silicon is used both as a fluidising element, and as a deoxidising element.

[0052] Moreover, the alloys obtained according to the present invention (be they gold alloys or master alloys for obtaining gold alloys), thanks to the small size of the crystal grain, are normally able not require the use of other refining elements.

[0053] In any case, where the use of refining elements becomes necessary to obtain even smaller grain dimensions, the formation of silicides does not take place, thanks to the absence, or near absence, of silicon.

[0054] It should further be noted that the present invention is relatively easy to implement and that also the cost connected to the implementation of the invention remains within the standards of the industry.

Claims

1. Yellow gold alloy **characterised in that** it comprises, in terms of weight, at least:

   Gold: WITHIN EITHER THE RANGE $74 \leq AU \leq 77$ % OR THE
   RANGE $57 \leq AU \leq 60$ %;
   Iridium: $0 < Ir \leq 0.2$ %;
   Germanium: $0 < Ge \leq 2$ %;
   Silver: $0 < Ag \leq 34$ %
   Zinc: $0 < Zn \leq 12$ %
   Copper: Cu sufficient to reach 100;

   and optionally one or more of the following elements:

   Silicon: $0 < Si \leq 0.15$ %;
   Lithium: $0 < Li \leq 0.15$ %;
   no more than 4 % by weight of at least one of the elements of the group constituted by Cobalt, Tin and Indium;
   no more than 0.15 % by weight of at least one of the elements of the group constituted by Magnesium and Boron; and
   no more than 0.4 % by weight of at least one of the elements of the group constituted by Ruthenium, Rhenium and Platinum.

2. Master alloy for obtaining yellow gold alloys as claimed in claim 1 **characterised in that** it comprises, by weight, at least:

   Iridium:$0< Ir \leq 0.4$ %;
   Germanium: $0 < Ge \leq 4$ %;
   Silver: $0 < Ag \leq 72$ %;
   Zinc: $0 < Zn \leq 25$ %;
   Copper: Cu sufficient to reach 100;

and optionally one or more of the following elements:

Silicon: 0 < Si ≤ 0.36 %;
Lithium: 0 < Li ≤ 0.36 %;
no more than 8 % of at least one of the elements of the group constituted by Cobalt, Tin and Indium;
no more than 0.36 % of at least one of the elements of the group constituted by Magnesium and Boron; and
no more than 0.96 % by weight of at least one of the elements of the group constituted by Ruthenium, Rhenium and Platinum.

Patentansprüche

1. Goldlegierung, **dadurch gekennzeichnet, dass** sie in Gewichtsanteilen wenigstens wie folgt enthält:

Gold: innerhalb des Bereiches 74 AU 77% oder des
Bereiches 57 AU 60%;
Iridium: 0 < Ir 0.2%;
Germanium: 0 < Ge 2%;
Silber: 0 < Ag 34%;
Zink: 0 < Zn 12%;
Kupfer: ausreichend Cu zum Erreichen von 100;

und optional eins oder mehrere der folgenden Elemente:

Silikon: 0 < Si 0.15%;
Lithium: 0 < Li 0.15%;

nicht mehr als 4% Gewichtsanteil von wenigstens einem der Elemente der Gruppe bestehend aus Kobalt, Zinn und Indium;
nicht mehr als 0.15% Gewichtsanteil von wenigstens einem der Elemente der Gruppe bestehend aus Magnesium und Boron; und
nicht mehr als 0.4% Gewichtsanteil von wenigstens einem der Elemente der Gruppe bestehend aus Ruthenium, Rhenium, und Platin.

2. Vorlegierung zum Erhalten von Goldlegierungen nach Patentanspruch 1, **dadurch gekennzeichnet, dass** sie in Gewichtsanteilen wenigstens wie folgt enthält:

Iridium: 0 < Ir 0.4%;
Germanium: 0 < Ge 4%;
Silber: 0 < Ag 72%;
Zink: 0 < Zn 25%; Kupfer: ausreichend Cu zum Erreichen von 100;

und optional eins oder mehrere der folgenden Elemente:

Silikon: 0 < Si 0.36%;
Lithium: 0 < Li 0.36%;

nicht mehr als 8% Gewichtsanteil von wenigstens einem der Elemente der Gruppe bestehend aus Kobalt, Zinn und Indium;
nicht mehr als 0.36% Gewichtsanteil von wenigstens einem der Elemente der Gruppe bestehend aus Magnesium und Boron; und
nicht mehr als 0.96% Gewichtsanteil von wenigstens einem der Elemente der Gruppe bestehend aus Ruthenium, Rhenium, und Platin.

Revendications

1. Alliage d'or jaune **caractérisé en ce qu'**il contient, en poids, au moins :

Or : soit dans une dans une proportion de 74 Au 77 % soit proportion de 57 Au 60 %
Iridium : 0 < Ir 0,2 %
Germanium : 0 < Ge 2 %
Argent : 0 < Ag 34 %
Zinc : 0 < Zn 12 %
Cuivre : dans une proportion suffisante pour atteindre 100 ;

et, en option, un ou plusieurs des éléments suivants :

Silicium : 0 < Si 0,15 % ;
Lithium : 0 < Li 0,15 % ;

pas plus de 4 % en poids d'au moins l'un des éléments du groupe constitué par le cobalt, l'étain et l'indium ;
pas plus de 0,15 % en poids d'au moins l'un des éléments du groupe constitué par le magnésium et le bore ; et
pas plus de 0,4 % en poids d'au moins l'un des éléments du groupe constitué par le ruthénium, le rhénium et le platine.

2. Alliage-mère pour obtenir les alliages d'or jaune tels que décrits dans la revendication 1, **caractérisé en ce qu'**il contient, en poids, au moins :

Iridium : 0 < Ir 0,4 %
Germanium : 0 < Ge 4 %
Argent : 0 < Ag 72 %
Zinc : 0 < Zn 25 %
Cuivre :dans une proportion suffisante pour atteindre 100 ;

et, en option, un ou plusieurs des éléments suivants :

Silicium : 0 < Si 0,36 % ;
Lithium : 0 < Li 0,36 % ;

pas plus de 8 % en poids d'au moins l'un des éléments du groupe constitué par le cobalt, l'étain et l'indium ;
pas plus de 0,36 % en poids d'au moins l'un des éléments du groupe constitué par le magnésium et le bore ; et
pas plus de 0,96 % en poids d'au moins l'un des éléments du groupe constitué par le ruthénium, le rhénium et le platine.

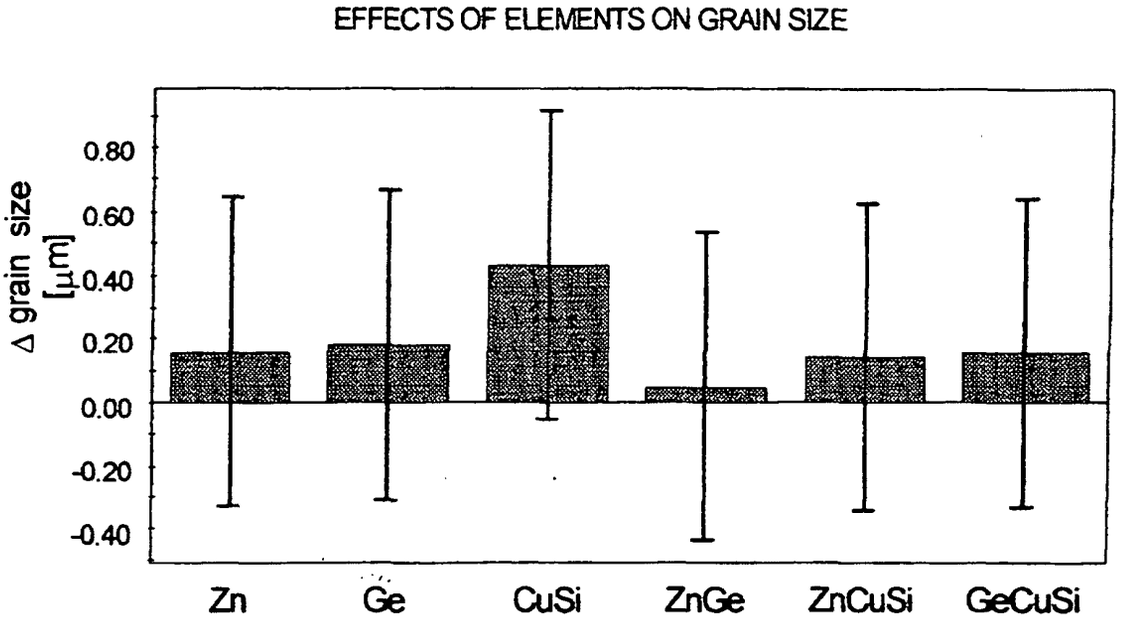

EFFECTS OF ELEMENTS ON GRAIN SIZE
Δ grain size [μm]
0.80
0.60
0.40
0.20
0.00
-0.20
-0.40
Zn
Ge
CuSi
ZnGe
ZnCuSi
GeCuSi

FIG. 1

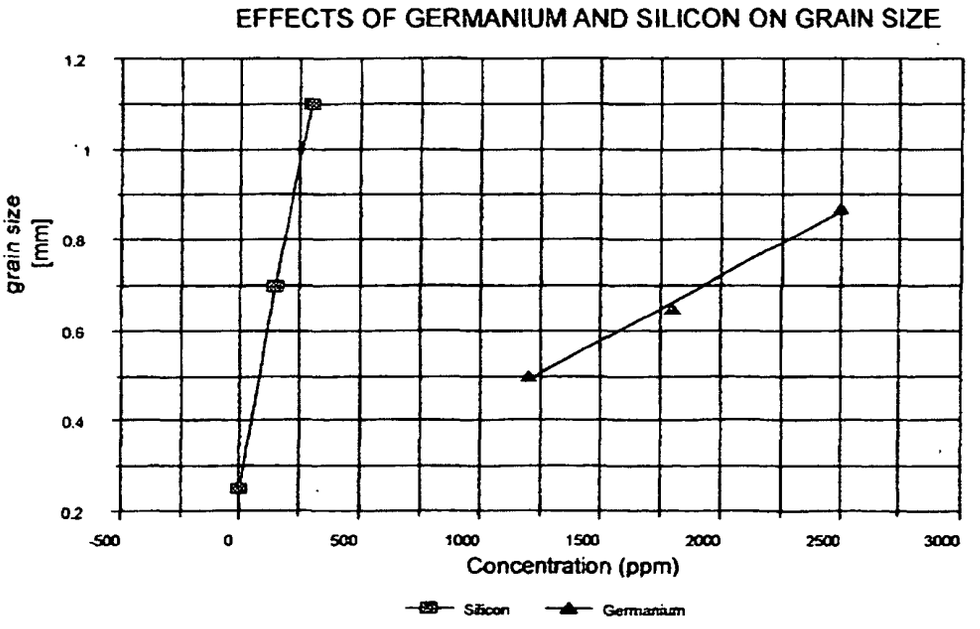

EFFECTS OF GERMANIUM AND SILICON ON GRAIN SIZE
grain size [mm]
1.2
1
0.8
0.6
0.4
0.2
-500
0
500
1000
1500
2000
2500
3000
Concentration (ppm)
Silicon
Germanium

FIG. 2

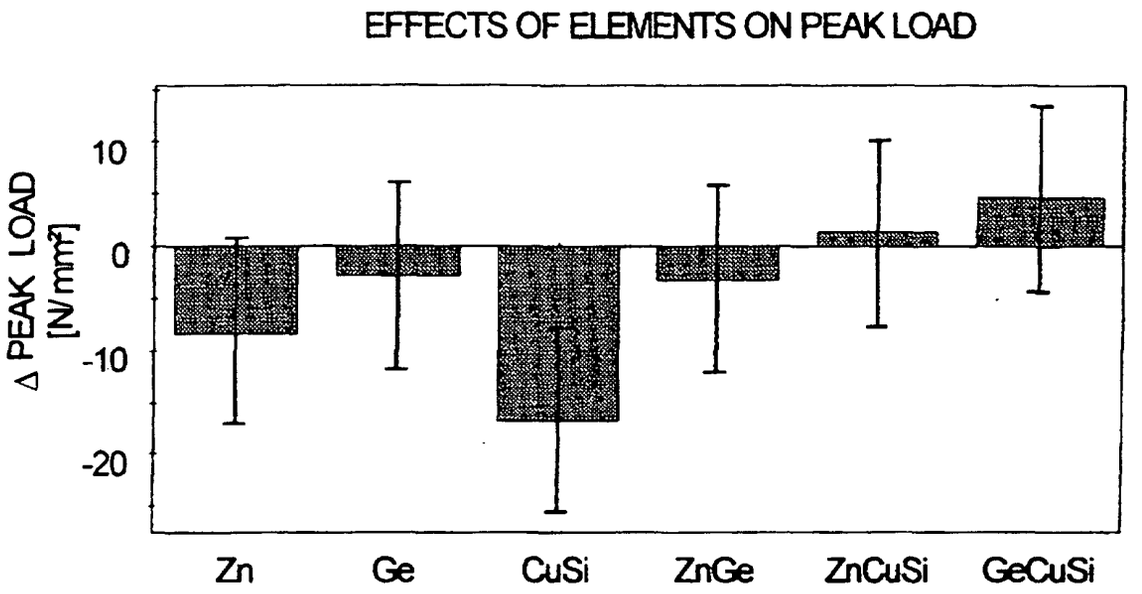

EFFECTS OF ELEMENTS ON PEAK LOAD
Δ PEAK LOAD [N/mm²]
10
0
-10
-20
Zn
Ge
CuSi
ZnGe
ZnCuSi
GeCuSi

FIG. 3

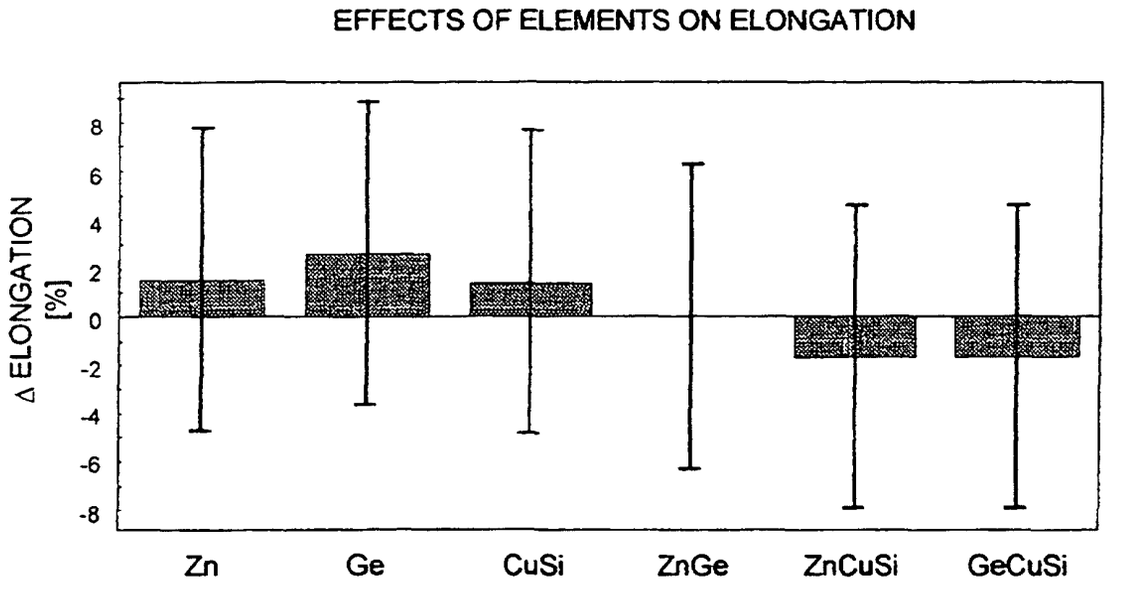

EFFECTS OF ELEMENTS ON ELONGATION
Δ ELONGATION [%]
8
6
4
2
0
-2
-4
-6
-8
Zn
Ge
CuSi
ZnGe
ZnCuSi
GeCuSi

FIG. 4