

明 細 書

高純度硬質金合金及びその製造方法

技術分野

- 5 本発明は、電子部材、歯科部材及び装飾部材に関するものである。

電子部材は、半導体素子上の電極と外部リードを接続する耐熱性に優れた高純度金合金部材。より詳しくは金合金の細線化にも係わらず従来と同等以上の電気的特性と接合特性を維持する。本発明高純度金合金は電気特性がよく、特に機械的強度、熱間での破断強度に強い。

- 10 歯科部材として金合金は殆どの用途に使われている。金純度は、Au 42～95 mass %であり低い。本発明は、高純度金合金の成分組成で機械的特性を上げて、金特有の耐食性、色調等の特性を残し、歯科用高純度金合金を供給する。

金合金は純金色の山吹色で、鮮明色が求められる。本発明の硬質化方法で

- 15 純金色高純度金合金が得られる。

背景技術

半導体素子上の電極と外部リードとの間の接続に、主にボンディング線として金合金細線が使用されている。ボンディング技術として熱圧着法が採用

- 20 されている。合金細線の先端部分を電気トーチで加熱溶融し、ボールを形成させて、150～300℃で加熱した半導体素子の電極に、このボール部を圧着接合させる。更に外部リード側との接合を超音波圧着接合で行う。

半導体素子の高集積化に伴って、電極間距離の短ピッチ化、ボール径の小型化、ロングバス化等が図られているので、ワイヤーの細線化の期待が大きい。従来の高純度金合金では細線化によって、機械的強度の破断特性が低下

- 25 い。従来の高純度金合金では細線化によって、機械的強度の破断特性が低下するので、細線化の対応が難しい。機械的強度の強い、かつ耐熱性の有る金合金細線が要求されている。
- 従来の高純度金合金では、細線化のための過度の合金元素の添加によって、ボール形成時の添加元素の酸化によって、ボール表面に酸化物層を生じ、電
- 30 極との熱圧着時に十分な結合が出来なくなり結合強度が低下する。更に、ボ

ール部の硬度が増し、圧着時に変形率が低下しシエア強度が低下し、激しい時は半導体素子を破壊させる。ボールの先端に収縮孔が生じ易くなり接合面積の減少により、熱圧着後の接合強度が低下する。

5 歯科用金合金は、鑄造用と加工用に分けて使われてきた。用途によって適当な条件があり、硬度、引張強度も低いものから高いものまで用意されている。金合金は都市ガスでも溶解できるなど鑄造し易く、適合性もよいことから理想的な材料とされてきた。高価な金合金を使いながら、高純度で十分な強度が得られなかったので、金の持つ耐食性、色調等の特性を十分に生かすことが出来なかった。

10 機械的性質の硬度は80～280Hv、引張強度は350～1100MPaの範囲で、各々使い分けられている。合金の添加材は、体積%が大きく、色調を変えるものが主に使われている。体積%の小さい、鮮明な純金色を示す添加材が求められている。

従来の金合金は規則格子の時効硬化で硬度を上げるためにCuを、結晶粒15 微細化のためにインジウムやレニウムを、耐食性を上げるためにパラジウムを加えて、各々バランスの取れ特性を得ている。

発明の開示

ボンディング用高純度金にガドリウムGd添加、又は極微量のボロンBを20 複合添加することによって、機械的性質、硬度、破断強度が著しく向上し、ボール形成時の再結晶領域を拡大させる。微量のボロンBにガドリウムGd、更に第2群、第3群の元素と共存することによって、十分に効果があることを見出した(表1参照)。

細線化に適合したボールネック部、結粒の小さなボンディング高純度金25 合金細線が得られる。

高純度金線の欠点を解決するために、Ca、Be、B等を微量添加する金合金線が提案されている(特開昭53-105968、特開昭53-112059、特開昭59-65440)。今後、極細線を製造していく為には、まだまだ解決しなければならない問題が多い。

30 本発明ボンディング高純度金合金(Au99.985%以上)は、ガド

ニウムを重量%で、1 ppm～49.9 ppm、または1 ppm～99.9 ppmの範囲内に含有し、累計添加量は前者300 ppm範囲内、後者が199 ppm範囲内である。いずれも国際出願PCT/JP96/00510の請求範囲を拡大したものである。

- 5 ボロンBは金中の固溶度が小さく、機械強度が向上する。ボロンの微量添加によって加工硬度、引張強度は上がるが、耐熱性が向上しない。ガドリニウムGdを添加することによって、耐熱性が改善され、時効硬化、加工硬化、破断強度が顕著に向上し、相乗効果が見られた(表1参照)。

- 10 ボロンBを多量に添加すると硬くなりボールの組成変形量が少なくなり、十分な結合強度を得にくくなるか、半導体に微細な割れを生ずる。更に新球になりにくい欠点を有する。少量添加では、金中のボロン分布が不均一になり、機械的強度がバラツクので接合強度が不安定になり、製品としての欠陥を生じる。

- 15 ガドリニウムGdの添加量が少ないと熱処理効果が少ない。ガドリニウムを多量に添加しても、他の元素を組み合わせないと十分なバランスの取れた強度は顕著に現れない。

- 20 カルシウムCaを多量に添加すると、ボールの先端部収縮孔が生じ、ボール球が真球にならない。ボンディングの接合力が低下する。少ないと共同効果、複合効果が十分に現れない。ベリリウムBe、アルミニウムAl、アンチモンSb、シリコンSi、さまりうむSmもカルシウム添加と同様の傾向を示した。

ベリリウム添加はカルシウム添加と、イットリウム添加はサマリウム添加とは良く似た現象を示した。

- 25 ガドリウムGdは希土類、アルカリ土類金属と複合添加すると添加効果が顕著に現れた。

歯科用金合金としてガドリニウムGdを添加して、熱処理による時効処理を行うことによって、機械強度、硬度、引張強度、耐熱性が著しく向上した。ガドリニウム添加品は占有体積が小さく、純金色に近い

- 30 ガドリウムGdを添加して、時効処理すると、硬度、引張強度及び耐性が上がる。上記添加元素を複合添加するとガドリニウムGdと他の元素

添加の相乗効果が現れる

ボロン B は微量添加で加工硬化が顕著に向上するが、固溶度が低い。

カルシウム Ca、ベリリウム Be、イットリウム Y、サマリウム Sm を添加すると加工硬化による硬度と耐熱性が向上する。

5 シリコン Si を添加すると鑄造インゴット硬度と加工硬度が上がる。

アルミニウム Al を添加すると引張強度が顕著に上がり、加工硬度も上がる。アンチモン Sb は加工硬度が上がる。アルカリ土類金属や希土類の元素と添加すると上記特性が向上した。

1 0 図面の簡単な説明

第 1 図は本発明高純度金合金のガドリニウム Gd、ボロン B 及びアルミニウム Al 添加による軟化曲線の改善効果を示す。

第 2 図は試作高純度金合金ワイヤーの引張強度、ビッカス硬度及びボール形状を示す。

1 5 第 3 図は試作歯科用金合金の機械的特性（引張強度、ビッカス硬度）を示す。

発明を実施するための最良の形態

2 0 ボンディングワイヤーの高純度金合金は金純度 99.995 重量%の電解金を用いて、上記の元素を添加した母合金を溶製した。各々個別に高周波真空溶解装置で 20 mm × 20 mm × 150 mm インゴットに溶解鑄造した。

2 5 表 1 に示す化学成分の鑄塊高純度金合金を先ず圧延し、次に溝ロール加工を行い、最後に常温で直径 20 ミクロンまで伸線加工した。熱処理は最初に 800℃溶体化処理を行い、次に 250℃で 3 時間時効硬化処理を行った。

評価は常温引張試験の破断強度、ビッカス硬度及びボンディング時のボール形状を観測し、表 1 に示した。

3 0 ガドリニウム Gd、ボロン B、アルミニウム Al 添加金合金細線（直径

0. 8 mm) 軟化曲線を図 1 に示す。

ボール形状は、高速自動ボンダーを使って、電気トーチのアーク放電によって作成した金合金ボールを、走査型顕微鏡で観察して、良好な形状で接合しているものを○印で、良好で無いものを×印で表示した。

- 5 接合強度は、高速ボンディング後、リードフレームと測定する半導体素子を治具で固定した後に、ボンディング後の金合金細線の中央部を引っ張り、その細線破断時の引張強度を測定した。

- 本発明の高純度金合金細線は極細線化の進む中で、従来の高純度金合金細線より破断強度、硬度、耐熱性を一段と向上させたもので、バラツキや断線が少なく、極細線の安定したボンディングが可能である。電気特性も良い。特に常温の機械強度、硬度、耐熱性が向上しているので、高温引張強度も強く、接合ループ高さも低くでき、高速自動ボンディングも十分に対応できた。ボール形状も真球で小さくでき、歩留まり向上とコスト低減が図られた。
- 1 0

- 1 5 歯科用金合金は、金純度 99.99 重量%の 4 N 純金を用いて、上記元素を添加して母合金を溶製した。各々個別に高周波真空溶解で、インゴット (20 mm × 20 mm × 150 mm) を鑄造した。先ず 800℃ で 1 時間行い水で急冷した。次に加工硬化処理と時効硬化処理を行った。加工率は、99.5% まで行い、時効処理は 250℃ で 3 時間行った。

- 2 0 機械的特性をビッカス硬度と引張強度で評価し、表 2 に示した

本発明は金含有量 95.5 重量%以上の金合金で、機械的性質の硬度と引張強度を一段と向上させ、更に耐熱性と色調を改善したものである。歯科用部材としての強度を十分に示した

- 2 5 歯科用部材機械的性質以外に生物学的安全性が重要な問題である。高純度金合金は添加元素が少ないので、量的には安全性が高いと言える。添加元素を選択すれば機械的にも、生物学的にも満足する歯科用部材が得られると思われる。生物学的安全性に関しては、国によって種々の承認制度があり、日本国では薬事法によって厚生省の承認が必要である。

希土類元素とアルカリ土類金属の元素を 1000 ppm 添加し、金純度 99.9 重量%の高純度金合金を試作し、純金色について調査下ところ

Gd、La、Ce、Sm、Ybが良く、ガドリニウムGdは最も純金色を鮮明に表示することが分かった。

産業上の利用可能性

以上のように、本発明の高純度硬質金合金部材はネックレス、時計等の装飾部材、ボンディングワイヤー、リードフレーム、薄膜等の電子部材、及び歯科用部材として有用であり、適している。

請 求 の 範 囲

1. 高純度金 99.98 重量%以上の Au に Gd を 1 ppm ~ 49.9 ppm 含有させた高純度金合金を用い、先ず溶解度曲線より高い温度で元素を均一に分散させて急冷する溶体化処理を行うこと。更に所望の線形又は形状まで加工処理を行う工程の前後で時効硬化処理を行う。加工処理しない場合も時効硬化処理を行うことを特徴とする高純度金合金硬質化方法。
2. 金 Au 98.50 ~ 99.96 重量%で、ガドリニウム Gd 50 ~ 149.9 ppm 含有する金合金を用い、先ず溶解度曲線より高い温度で元素を均一に分散させて急冷する溶体か処理を行い、次に所望の形状まで加工処理を行う工程の前後で、又は加工処理しない場合でも熱処理による時効硬化処理を行うことを特徴とする金合金部材硬質化方法。
3. 請求項 1、2 及び 11 の成分組成にボロン B を 0.1 ~ 150 ppm 複合添加した請求項 1、2 及び 11 の高純度金合金硬質化方法。
4. 上記製造高純度金合金を溶体化処理として 600℃ ~ 2800℃ で加熱処理後急冷し、150℃ ~ 350℃ の温度で時効処理することを特徴とする高純度金合金硬質化方法。
5. 溶解化処理後、加工硬化処理と時効処理を交互に繰り返す請求項 1、2、3 及び 4 の高純度金合金硬質化方法。
6. 高純度金 Au 99.98 重量%以上で請求項 1 のガドリニウム Gd を添加した成分組成、又は請求項 2 のガドリニウム Gd とボロン B を添加した成分組成にベリリウム Be、アルミニウム Al、シリコン Si、カルシウム Ca、サマリウム Sm、イットリウム Y 及びアンチモン Sb のうち一種以上を添加し、累計添加量で 1 ~ 199 ppm の範囲内で含有する高純度金合金を用いて、請求項 1、3、4、5 の溶体化処理と時効処理を行うことを特徴とする高純度金合金硬質化方法。
7. 高純度金 Au 99.98 重量%以上で請求項 1 のガドリニウム Gd とボロン B を添加した組成に希土類、及びアルカリ土類金属うち一種以上を添加し、累計添加量で 1 ~ 199 ppm の範囲内で含有する高純度金合金を用い、請求項 1、3、4、5、6 の溶体化処理と時効処理を行うことを特徴とする高純度金合金硬質化方法。



8. 上記請求項 1、3、4、5、6、7 でガドリウム Gd 添加量 5 ～ 99 ppm とし、累計添加量を 1 ～ 99 ppm とすることを特徴とする高純度金合金硬質化方法。
9. 金 Au 98.5 ～ 99.6 重量% の範囲内で請求項 2 のガドリウム Gd を添加した成分組成又は請求項 3 のガドリウム Gd とボロン B を添加した成分組成にアルミニウム Al、シリコン Si、カルシウム Ca、ベリリウム Be、イットリウム Y、サマリウム Sm 及びアンチモン Sb のうち一種以上を添加し、累計添加量で 3001 ppm ～ 14999 ppm 含有する金合金を用いて、請求項 2、4、5、6 の溶体化処理と時効処理を行うことを特徴とする金合金硬質化方法。
10. 金 Au 98.5 ～ 99.6 重量% の範囲で請求項 2 でガドリウム Gd を添加した成分組成、又は請求項 3 のガドリウム Gd とボロン B を添加した成分組成に、希土類とアルカリ土類金属のうち一種以上を添加し、累計添加量で 3001 ～ 14999 の範囲で含有する金合金を用い、請求項 2 ～ 5 の溶体化処理と時効硬化処理を行うことを特徴とする金合金硬質化方法。
11. 純度 99.7 重量% 以上の Au に Gd、元素を 50 ppm 以上添加し、更に他の元素一種以上添加して、累計量 3000 ppm を含有することを特徴とする、高純度色高純度硬質金合金部材。
12. 純度 99.0 重量% 以上の Au に Gd、Lu、Ce、La、Yb を 100 ppm 以上添加し、更に他の元素一種以上添加して、累計量 10,000 ppm を含有することを特徴とする、高純度色高純度硬質金合金部材。
13. 請求項 11 と 12 の金合金鑄造後、600℃ ～ 2800℃ で溶体化処理し、後工程で 100℃ ～ 400℃ で時効処理すること、又はこの時効処理のみ行うことを特徴とする高純度色高純度硬質金合金の製造方法。



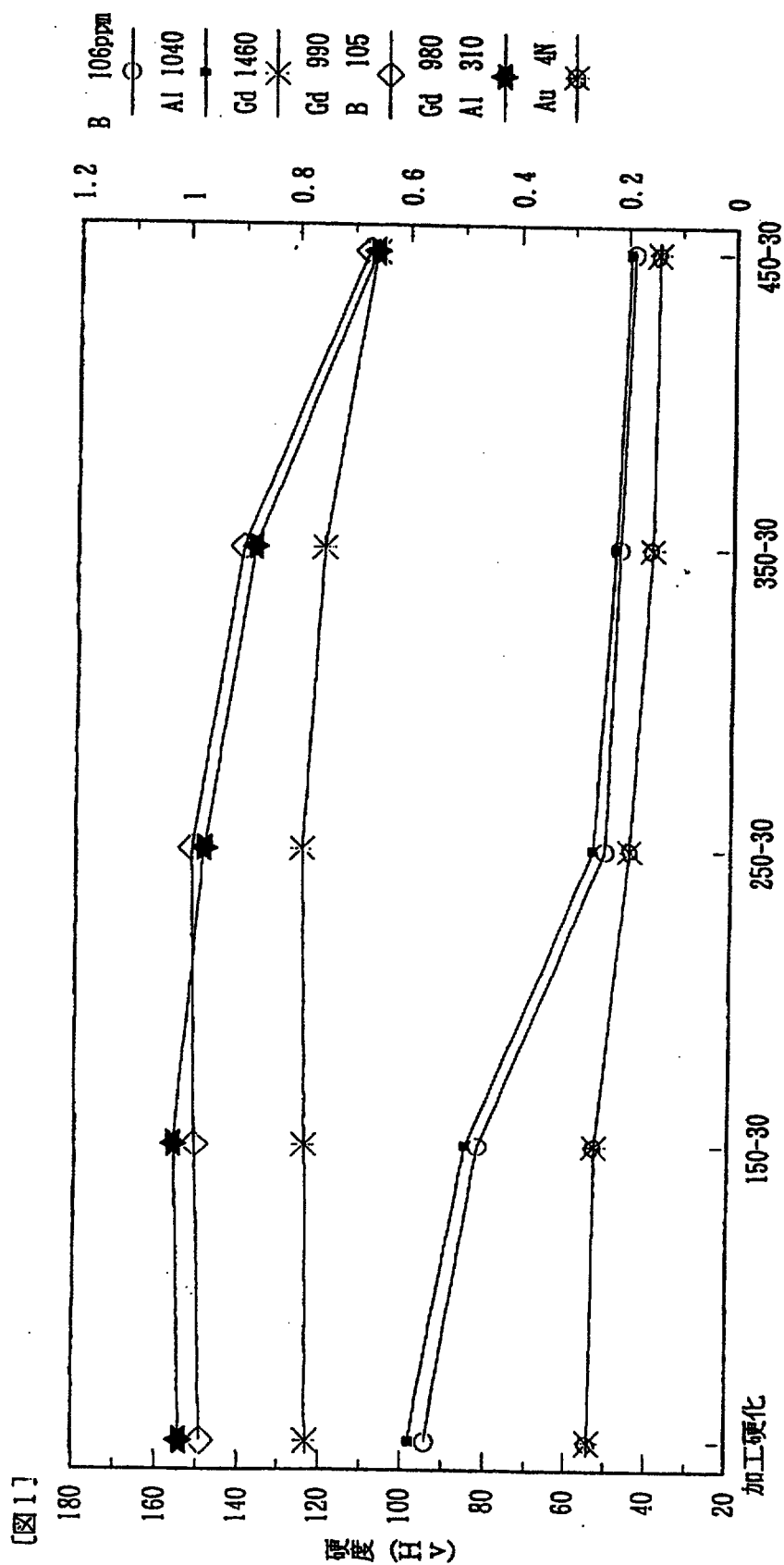


図1 ガドリニウムとボロンの添加効果
 — 軟化曲線の硬度改善 —

図 2 試作高純度金合金ワイヤーの特性

番号	添量元素(重量ppm)								引張強度		ビッカース 硬度 (Hv)	ボール 形状
	Gd	B	Ca	Be	Al	Si	Sb	Sm	破断加重 (gf)	伸び (%)		
1	30.2	107							23.5	4	112	○
2	31.5	57							19.8	4	95	○
3	30.4	1							9.8	4	83	○
4	0	104							18.9	4	89	○
5	0.9	101							19.8	4	90	○
6	31.5	109							23.5	4	111	○
7	108.5	105							27.8	4	132	○
8	30.2		52						16.8	4	81	○
9	31.2			58					16.6	4	80	○
10	30.5				53				14.2	4	74	○
11	30.4					56			16.8	4	81	○
12	31.1						57		14.8	4	75	○
13	30.9							52	13.9	4	70	○

注) 金原料としてAu (99.995%以上) を溶解した。

図 3 発明成分組合金成の機械的性質と色

No.	添加物組成 (重量%)								機械的性質	
	Gd	B	Ca	Al	Si	Sm	Sb	Auと 不純物	引張強度 (N)	硬度 (Hv)
1	0							残部	120	42
2	1,760								193	123
3		26							130	76
4		104							163	96
5			986						220	109
6				1,980					250	123
7					300					
8						1,520			230	126
9							185		214	118
10	720	98							163	98
11	940		490						290	176
12		28		3,580					320	136
13	1,480	30		3,480					396	162
14	1,530		880						270	194
15	1,480		1,510	3,650					470	273
16	1,980		1,960	9,890					720	295
17	1,970	102		9,920					672	271
18	1,950			9,890		1,980			668	282

DESCRIPTION

HIGH-PURITY HARD GOLD ALLOY AND METHOD OF MANUFACTURING SAME

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Technical Field

The present invention relates to an electronic member, a dental member and a decorative member.

10 A high-purity gold alloy member as an electronic member is used to connect an electrode on a semiconductor device and an external lead and has excellent heat resistance. More specifically, the gold alloy has electrical characteristics and bonding characteristics equivalent to or superior to those of conventional gold alloys despite its small wire diameter. The high-purity gold alloy according to the present invention has
15 good electrical characteristics and is especially excellent in mechanical strength and in breaking strength at hot working.

Gold alloy is used in most dental members and has a low purity of gold Au ranging from 42 to 95 mass %. The present invention provides a high-purity gold alloy for dental use which
20 has a composition of high-purity gold alloy and yet improved mechanical characteristics, and retains the characteristics specific to gold, such as corrosion resistance, color tone, etc.

Gold alloy is expected to be pure gold-like yellow in color and bright. A hardening method according to the present
25 invention provides a pure gold-colored, high-purity gold alloy.

Background Art

Fine wires of gold alloy are used chiefly as bonding wires for connecting electrodes on semiconductor devices and external
30 leads. Thermocompression bonding is adopted as a bonding technique. A distal end portion of a fine alloy wire is heated and melted with the use of an electric torch to form a ball, and the ball is compression-bonded to an electrode of a

semiconductor device heated at 150 to 300°C. Further, the alloy wire is bonded to an external lead by ultrasonic compression bonding.

5 A trend for higher integration of semiconductor devices has created needs for shorter pitch of interelectrode distances, smaller ball diameter, longer path, etc., and thus there is a great demand for finer wires. Conventional high-purity gold alloys have low breaking strength as a mechanical strength when reduced in wire diameter and thus difficulty arises in meeting
10 the requirements for further reduction in wire diameter. Fine wires of gold alloy with high mechanical strength and heat resistance are therefore demanded.

Conventional high-purity gold alloys are admixed with excessive alloying elements for reduction in wire diameter, and
15 due to oxidation of the additive elements during the formation of a ball, an oxide layer is formed on the surface of the ball, with the result that the bonding strength lowers because the ball fails to be satisfactorily bonded to an electrode at the time of thermocompression bonding. Further, since the ball has
20 increased hardness, its deformation factor and shear strength are low at the time of compression bonding, and in extreme cases, the ball breaks the semiconductor device. Also, a shrinkage hole is liable to be formed at the extremity of the ball, and because of consequent reduction in the bonding surface, the
25 bonding strength after the thermocompression bonding lowers.

Gold alloys for dental applications have been in use separately for casting and working. Suitable properties vary depending on uses, and therefore, gold alloys with low to high hardness and low to high tensile strength are available on the
30 market. Gold alloys have been considered an ideal material because they can be melted even with the use of town gas and thus are easy to cast and also they have good conformability. However, gold alloys, which are expensive, do not have high

purity and satisfactory strength, and the characteristics specific to gold, such as corrosion resistance, color tone, etc., could not be fully enjoyed.

5 Gold alloys having a hardness and a tensile strength as mechanical properties ranging from 80 to 280 Hv and from 350 to 1100 MPa, respectively, are used for different applications. As additives added to the alloys, those additives which have a large volume percentage and which change the color tone are mainly used. Therefore, there is a demand for additives that
10 are small in volume percentage and can retain bright pure gold color.

Conventional gold alloys are admixed with Cu to increase the hardness by age hardening of the ordered lattice, with indium or rhenium to reduce the size of crystal grains, and with
15 palladium to enhance the corrosion resistance, in such a manner that these characteristics are well-balanced.

Disclosure of the Invention

By admixing high-purity gold for bonding with gadolinium
20 Gd or further with a trace amount of boron B, mechanical properties, hardness and breaking strength are remarkably improved and also the recrystallization region for the formation of a ball is expanded. It was found that where a small amount of boron B coexisted with gadolinium Gd and further with
25 Group II and Group III elements, satisfactory additive effects could be achieved (see Table 1).

A fine bonding wire of high-purity gold alloy capable of forming a ball neck suited for reduction in wire diameter and having small bonding grains can be obtained.

30 There have been proposed gold alloy wires which are admixed with small amounts of Ca, Be, B, etc. to eliminate the drawbacks with high-purity gold wires (Unexamined Japanese Patent Publication (KOKAI) No. 53-105968, No. 53-112059 and No.

59-65440). Manufacture of very fine wires is, however, still associated with many problems to be solved.

A high-purity gold alloy (Au: 99.985% or more) for bonding according to the present invention has a gadolinium content ranging from 1 ppm to 49.9 ppm or from 1 ppm to 99.9 ppm in weight %, and the total amount of the additive is 300 ppm or less in the former case and 199 ppm or less in the latter case. These ranges are wider than that defined in the claims of International Application PCT/JP96/00510.

Boron B shows low solid solubility in gold and serves to enhance mechanical strength. Adding a small amount of boron increases work hardness and tensile strength, but heat resistance is not improved. By adding gadolinium Gd, heat resistance improved and age hardening effect, work hardening effect and breaking strength could be remarkably enhanced, and also a synergistic effect was observed (see Table 1).

If an excessive amount of boron B is added, hardness increases and the amount of plastic deformation of the ball decreases, with the result that a satisfactory bonding strength is not obtained or that a fine crack is formed in the semiconductor device. Further, difficulty arises in the formation of a perfectly spherical ball. If the amount of boron added is too small, then the distribution of boron within gold becomes uneven, and consequent variations in mechanical strength lead to unstable bonding strength, making products defective.

If the amount of gadolinium Gd added is too small, the effect of heat treatment is also small. Even if a large amount of gadolinium is added, well-balanced strength is not fully achieved unless gadolinium is used in combination with other elements.

If an excessive amount of calcium Ca is added, a shrinkage hole is formed at the extremity of a ball and the ball formed

is not perfectly spherical, lowering the bonding strength. If the Ca content is too small, on the other hand, cooperating effect and combined effect are not fully achieved. Beryllium Be, aluminum Al, antimony Sb, silicon Si and samarium Sm, when
5 added, showed a tendency similar to that observed in the case where calcium was added.

Adding beryllium showed an effect very similar to that achieved with calcium, and adding yttrium showed an effect closely similar to that obtained with samarium.

10 Gadolinium Gd, when added in combination with a rare-earth element or an alkaline earth metal, showed a marked additive effect.

For a gold alloy for dental use, its mechanical strength, hardness, tensile strength and heat resistance could be
15 remarkably enhanced by adding gadolinium Gd to the gold alloy and then subjecting the alloy to aging by heat treatment. Articles admixed with gadolinium are small in volume and the color thereof is close to pure gold.

If gadolinium Gd is added and then aging treatment is
20 performed, hardness, tensile strength and heat resistance are enhanced. Where gadolinium Gd is added in combination with the aforementioned additive elements, a synergistic effect can be achieved through the admixture of gadolinium with other elements.

25 Boron B can remarkably enhance the work hardness if added in a small quantity, but has low solid solubility.

Where calcium Ca, beryllium Be, yttrium Y or samarium Sm is added, hardness by means of work hardening and heat resistance are improved.

30 Silicon Si, when added, improves cast ingot hardness and work hardness.

Adding aluminum Al remarkably increases tensile strength and also enhances work hardness. Antimony Sb serves to increase

work hardness. Where these elements were added in combination with an alkaline earth metal or a rare-earth element, the above properties could be furthered.

5 Brief Description of the Drawings

FIG. 1 shows improvements in softening curve achieved by the addition of gadolinium Gd, boron B and aluminum Al in a high-purity gold alloy according to the present invention;

10 FIG. 2 shows tensile strength, Vickers hardness and ball shape of sample high-purity gold alloy wires; and

FIG. 3 shows mechanical characteristics (tensile strength, Vickers hardness) of sample gold alloys for dental use.

Best Mode of Carrying out the Invention

15 To obtain a high-purity gold alloy for bonding wire, mother alloys admixed with the aforementioned elements were prepared by using electrolytic gold having a gold purity of 99.995 weight %. Using a high-frequency vacuum melting furnace, the alloys were individually melted and cast into ingots of 20 mm
20 × 20 mm × 150 mm.

The cast ingots of high-purity gold alloys having the chemical compositions as shown in Table 1 were first rolled, then worked with the use of a grooved roll, and finally drawn at ordinary temperature to obtain a wire of 20 micrometers in
25 diameter. As heat treatment, solution heat treatment was performed first at 800°C, followed by three hours of age hardening at 250°C.

For the purpose of evaluation, breaking strength was measured by conducting a tensile test at ordinary temperature, and also Vickers hardness and the ball shape at bonding were
30 observed. The results are shown in Table 1.

FIG. 1 shows the softening curves of small-diameter gold alloy wires (diameter: 0.8 mm) admixed with gadolinium Gd, boron

B and aluminum Al.

For the evaluation of the ball shape, a high-speed automatic bonder was used to form a gold alloy ball by an arc discharge of an electric torch, and the ball shape was observed using a scanning electron microscope. A bond with a satisfactory shape is indicated by the mark "O" and a bond with a defective shape is indicated by the mark "X".

For the evaluation of the bonding strength, after the high-speed bonding, a lead frame and a semiconductor device to be measured were fixed by means of a jig, and a central portion of the small-diameter gold alloy wire was pulled apart to measure the tensile strength at breakage of the wire.

In view of a trend for finer wires, very fine wires produced using the high-purity gold alloys according to the present invention have higher breaking strength, hardness and heat resistance than conventional high-purity gold alloy wires, are less subject to variations or disconnection, and permit stable bonding. Excellent electrical characteristics can also be achieved. Since the gold alloy wires of the present invention are improved especially in mechanical strength, hardness and heat resistance at ordinary temperature, tensile strength at high temperature is also high, the junction loop height can be reduced, and the gold alloy wires could be used satisfactorily in high-speed automatic bonding. Also, the ball shape was perfectly spherical and thus small, making it possible to improve the yield and reduce the cost.

To obtain gold alloys for dental use, mother alloys admixed with the aforementioned elements were prepared by using 4N pure gold having a gold purity of 99.99 weight %. The alloys were individually melted by high-frequency vacuum melting and were cast into ingots (20 mm × 20 mm × 150 mm). Subsequently, the ingots were heated at 800°C for one hour and then rapidly cooled in water, followed by work hardening and age hardening. The

working ratio was 99.5% and the aging treatment was performed at 250°C for three hours.

Mechanical characteristics were evaluated as to Vickers hardness and tensile strength. The results are shown in Table 2.

The gold alloys according to the present invention have a gold content of 98.5 weight % or more, have increased hardness and tensile strength as mechanical properties, and are also improved in heat resistance and color tone. The gold alloys showed satisfactory strength for use in dental members.

Dental members are required to ensure biological safety, besides good mechanical properties. The above high-purity gold alloys have small amounts of additive elements contained therein, and thus it can be said that their degree of safety is high. By suitably selecting the additive elements, it is possible to obtain dental members satisfying both the mechanical and biological requirements. As for biological safety, different approval systems are adopted in different countries, and in Japan, approval by the Ministry of Welfare is required under the Pharmaceutical Affairs Law.

High-purity gold alloys admixed with 1000 ppm of rare-earth elements and alkaline earth metals and having a gold purity of 99.9 weight % were prepared by way of experiment and the colors thereof were examined; as a result, it was found that the gold alloys admixed with Gd, La, Ce, Sm or Yb had a pure gold-like color and that among them, the gold alloy admixed with gadolinium Gd had a color most close to pure gold.

Industrial Applicability

As described above, the high-purity hard gold alloy member according to the present invention is suitable for use as a decorative member such as a necklace, a watch, etc., an electronic member such as a bonding wire, a lead frame, a thin

film, etc., and a dental member.



CLAIMS

1. A method of hardening a high-purity gold alloy, characterized in that a high-purity gold alloy having a Gd content of 1 ppm to 49.9 ppm contained in high-purity gold Au of 99.98 weight % or more is subjected to solution heat treatment in which the elements of the high-purity gold alloy are uniformly dispersed at a temperature higher than a solubility curve and then rapidly cooled, and then to age hardening treatment before or after a working process for working the high-purity gold alloy into a desired line shape or other desired shape, the age hardening treatment is performed also when the working process is not executed.

2. A method of hardening a gold alloy member, characterized in that a gold alloy having a gadolinium Gd content of 50 to 14,999 ppm contained in gold Au of 98.50 to 99.96 weight % is subjected to solution heat treatment in which the elements of the gold alloy are uniformly dispersed at a temperature higher than a solubility curve and then rapidly cooled, and then to age hardening treatment by heat treatment before or after a working process for working the gold alloy into a desired shape, the age hardening treatment is performed also when the working process is not executed.

3. A method of hardening a high-purity gold alloy according to any one of claims 1, 2 and 11, wherein 0.1 to 150 ppm of boron B is additionally mixed in the composition as defined in claim 1, 2 or 11.

4. A method of hardening a high-purity gold alloy, characterized in that the cast high-purity gold alloy is subjected to solution heat treatment in which the high-purity gold alloy is heated at 600°C to 2800°C and then rapidly cooled, and then to aging treatment at a temperature of 150°C to 350°C.

5. A method of hardening a high-purity gold alloy according to any one of claims 1, 2, 3 and 4, wherein after the





solution heat treatment, work hardening and aging treatment are alternately repeated.

6. A method of hardening a high-purity gold alloy, characterized in that a high-purity gold alloy in which one or more additives selected from the group consisting of beryllium Be, aluminum Al, silicon Si, calcium Ca, samarium Sm, yttrium Y and antimony Sb are added to the composition of claim 1 in which gadolinium Gd is mixed in high-purity gold Au of 99.98 weight % or more, or to the composition of claim 2 having gadolinium Gd and boron B admixed therein, and which has a total additive amount of additives ranging from 1 to 199 ppm is subjected to the solution heat treatment and the aging treatment as defined in any one of claims 1, 3, 4 and 5.

7. A method of hardening a high-purity gold alloy, characterized in that a high-purity gold alloy in which one or more rare-earth elements and/or alkaline earth metals are added to the composition of claim 1 in which gadolinium Gd and boron B are mixed in high-purity gold Au of 99.98 weight % or more, and which has a total additive amount of additives ranging from 1 to 199 ppm is subjected to the solution heat treatment and the aging treatment as defined in any one of claims 1, 3, 4, 5 and 6.

8. A method of hardening a high-purity gold alloy according to any one of claims 1, 3, 4, 5, 6 and 7, characterized in that gadolinium Gd is added in a range of 5 to 99 ppm and the total additive amount ranges from 1 to 99 ppm.

9. A method of hardening a gold alloy, characterized in that a gold alloy in which one or more additives selected from the group consisting of aluminum Al, silicon Si, calcium Ca, beryllium Be, yttrium Y, samarium Sm and antimony Sb are added to the composition of claim 2 in which gadolinium Gd is mixed in gold Au of 98.5 to 99.69 weight %, or to the composition of claim 3 having gadolinium Gd and boron B admixed therein, and





which has a total additive amount of additives ranging from 3001 ppm to 14,999 ppm is subjected to the solution heat treatment and the aging treatment as defined in any one of claims 2, 4, 5 and 6.

- 5 10. A method of hardening a gold alloy, characterized in that a gold alloy in which one or more rare-earth elements and/or alkaline earth metals are added to the composition of claim 2 in which gadolinium Gd is mixed in gold Au of 98.5 to 99.69 weight %, or to the composition of claim 3 having gadolinium
10 Gd and boron B admixed therein, and which has a total additive amount of additives ranging from 3001 to 14,999 is subjected to the solution heat treatment and the aging treatment as defined in any one of claims 2 through 5.

- 15 11. A high-purity gold-colored, high-purity hard gold alloy member, characterized in that Au having a purity of 99.7 weight % or more is admixed with 50 ppm or more Gd element and further with one or more other elements such that a total additive amount of additives is 3000 ppm.

- 20 12. A high-purity gold-colored, high-purity hard gold alloy member, characterized in that Au having a purity of 99.0 weight % or more is admixed with 100 ppm or more of Gd, Lu, Ce, La or Yb and further with one or more other elements such that a total additive amount of additives is 10,000 ppm.

- 25 13. A method of manufacturing a high-purity gold-colored, high-purity hard gold alloy member, characterized in that after the gold alloy according to claim 11 or 12 is cast, solution heat treatment is performed at 600°C to 2800°C and then aging treatment is performed at 100°C to 400°C as post-treatment, or the aging treatment alone is performed.



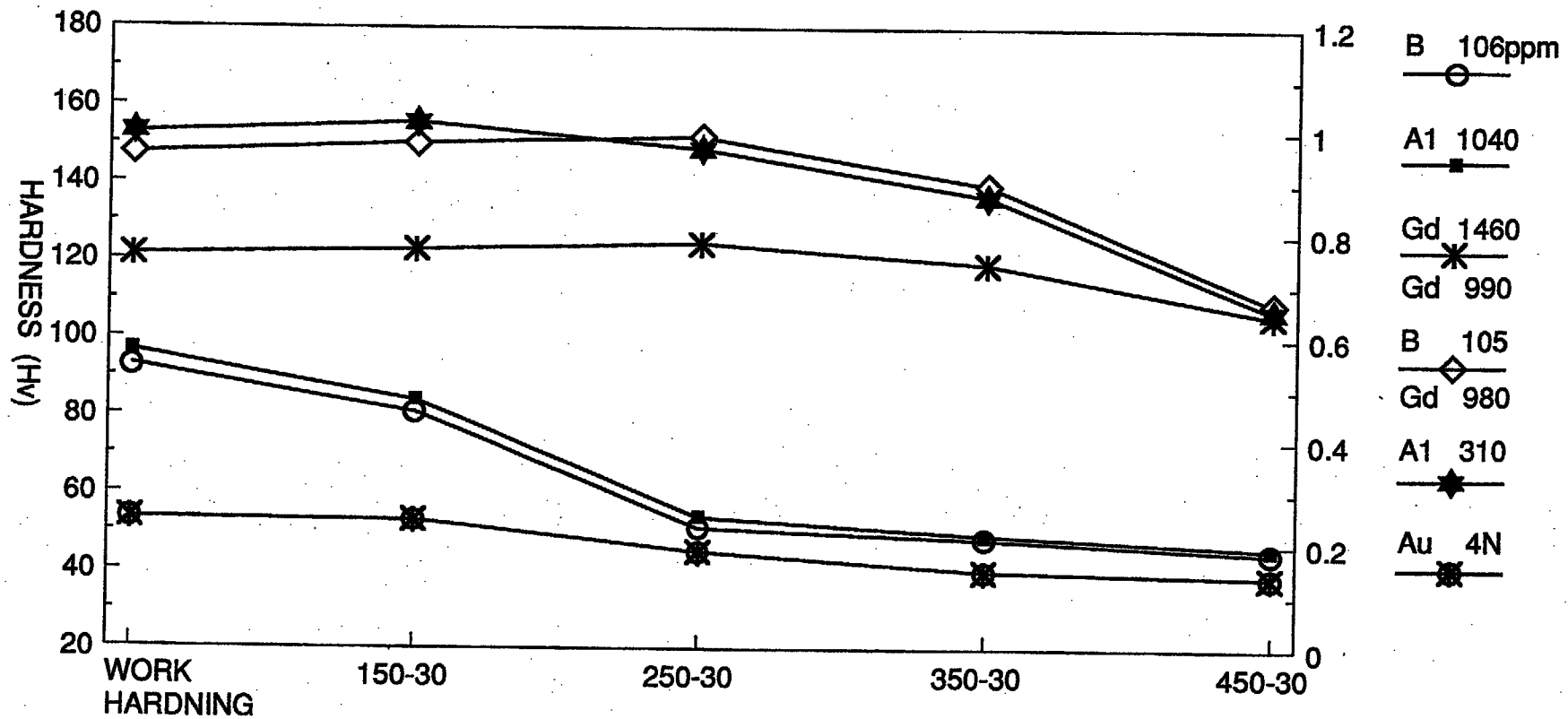
Abstract

Electronic member: in a trend for finer line using a high purity gold alloy wire, this gold alloy wire further improves breaking strength, hardness, heat resistance and the like as compared with a conventional gold alloy wire, and achieves stable bonding with less scatter and disconnection. Further, the gold alloy wire increases dispersion of fine additive agents, improves electric conductivity and thermal conductivity, and enables automatic, high speed bonding having a less junction loop height. Such high purity hard gold alloy is also suitable for electronic members such as lead frame and the like.

Dental member: a high purity gold alloy enhances hardness and tensile strength which are important mechanical properties, further improves heat resistance and tone, and provides dental, high purity hard gold alloy members which are well balanced.

High purity golden-colored alloy: a high purity gold alloy for high purity golden-colored, decorative members, electronic members, dental members and the like is available.

FIG.1



CONDITIONS OF HEAT TREATMENT

ADDITIVE EFFECT GADOLINIUM AND BORON

— IMPROVEMENT OF HARDNESS IN SOFTENING CURVE —

FIG.2

CHARACTERISTICS OF SAMPLE HIGH-PURITY GOLD ALLOY WIRES

NO.	ADDITIVE ELEMENT (IN WEIGHT ; ppm)								TENSILE STRENGTH		VICKERS HARDNESS (Hv)	BALL SHAPE
	Gd	B	Ca	Be	Al	Si	Sb	Sm	BREAKING LOAD (gf)	ELONGATION (%)		
1	30.2	107							23.5	4	112	○
2	31.5	57							19.8	4	95	○
3	30.4	1							9.8	4	83	○
4	0	104							18.9	4	89	○
5	0.9	101							19.8	4	90	○
6	31.5	109							23.5	4	111	○
7	108.5	105							27.8	4	132	○
8	30.2		52						16.8	4	81	○
9	31.2			58					16.6	4	80	○
10	30.5				53				14.2	4	74	○
11	30.4					56			16.8	4	81	○
12	31.1						57		14.8	4	75	○
13	30.9							52	13.9	4	70	○

2/3

NOTE : AS A GOLD MATERIAL , Au (99.995% or MORE) WAS MELTED.

MECHANICAL PROPERTIES AND COLORS OF GOLD ALLOYS HAVING
COMPOSITIONS ACCORDING TO THE PRESENT INVENTION

FIG.3

NO.	COMPOSITION OF ADDITIVES (WEIGHT%)								MECHANICAL PROPERTIES	
	Gd	B	Ca	Al	Si	Sm	Sb	Au + IMPURITY	TENSILE STRENGTH (N)	HARDNESS (Hv)
1	0							BALANCE	120	42
2	1,760								193	123
3		26							130	76
4		104							163	96
5			986						220	109
6				1,980					250	123
7					300					
8						1,520			230	126
9							185		214	118
10	720	98							163	98
11	940		490						290	176
12		28		3,580					320	136
13	1,480	30		3,480					396	162
14	1,530		880						270	194
15	1,480		1,510	3,650					470	273
16	1,980		1,960	9,890					720	295
17	1,970	102		9,920					672	271
18	1,950			9,890		1,980			668	282

CLAIMS

REPLACEMENT SHEETS SG

☐ Description : paged to paged
☒ Claim(s) : paged 10 to paged 126
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged

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1. A method of manufacturing a high-purity gold alloy, wherein a high-purity gold alloy having a Gd content of 1 to 49.9 ppm contained in Au having a purity of 99.98 weight % or more is subjected to solution heat treatment in which the elements of the high-purity gold alloy are uniformly dispersed at a temperature higher than a solubility curve and then rapidly cooled, and then to age hardening treatment before or after a working process for working the high-purity gold alloy into a desired line shape or other desired shape, the age hardening treatment is performed also when the working process is not executed.

2. A method of manufacturing a high-purity alloy according to claim 1, wherein B is additionally contained in a range of 0.1 to 150 ppm.

3. A method of manufacturing a high-purity gold alloy according to claim 1, wherein the high-purity gold alloy additionally contains one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

4. A method of manufacturing a high-purity gold alloy according to claim 1, wherein the high-purity gold alloy additionally contains one or more additives selected from rare-earth metals and alkaline earth metals, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

5. A method of manufacturing a high-purity gold alloy according to claim 2, wherein the high-purity gold alloy additionally contains one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

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6. A method of manufacturing a high-purity gold alloy according to claim 2, wherein the high-purity gold alloy additionally contains one or more additives selected from
5 rare-earth metals and alkaline earth metals, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

7. A method of manufacturing a high-purity gold alloy according to claim 3, wherein the high-purity gold alloy additionally contains one or more additives selected from
10 rare-earth metals and alkaline earth metals, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

8. A method of manufacturing a high-purity gold alloy, wherein a high-purity gold alloy having a Gd content of 5 to 99 ppm contained in Au having a purity of 99.98 weight % or more
15 is subjected to solution heat treatment in which the elements of the high-purity gold alloy are uniformly dispersed at a temperature higher than a solubility curve and then rapidly cooled, and then to age hardening treatment before or after a working process for working the high-purity gold alloy into a
20 desired line shape or other desired shape, the age hardening treatment is performed also when the working process is not executed.

9. A method of manufacturing a high-purity alloy according to claim 8, wherein B is additionally contained in a range of
25 0.1 to 150 ppm.

10. A method of manufacturing a high-purity gold alloy according to claim 8, wherein the high-purity gold alloy additionally contains one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and wherein
30 a total additive amount of additives ranges from 1 to 199 ppm.

11. A method of manufacturing a high-purity gold alloy according to claim 8, wherein the high-purity gold alloy additionally contains one or more additives selected from rare-earth metals and alkaline earth metals, and wherein a total

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additive amount of additives ranges from 1 to 199 ppm.

12. A method of manufacturing a high-purity gold alloy according to claim 9, wherein the high-purity gold alloy
5 additionally contains one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

13. A method of manufacturing a high-purity gold alloy according to claim 9, wherein the high-purity gold alloy
10 additionally contains one or more additives selected from rare-earth metals and alkaline earth metals, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

14. A method of manufacturing a high-purity gold alloy according to claim 10, wherein the high-purity gold alloy
15 additionally contains one or more additives selected from rare-earth metals and alkaline earth metals, and wherein a total additive amount of additives ranges from 1 to 199 ppm.

15. A method of manufacturing a high-purity gold alloy, wherein a high-purity gold alloy having a Gd content of 50 to
20 1499 ppm contained in Au of 98.50 to 99.69 weight % is subjected to solution heat treatment in which the elements of the high-purity gold alloy are uniformly dispersed at a temperature higher than a solubility curve and then rapidly cooled, and then to age hardening treatment before or after a working process
25 for working the high-purity gold alloy into a desired line shape or other desired shape, the age hardening treatment is performed also when the working process is not executed.

16. A method of manufacturing a high-purity alloy according to claim 15, wherein B is additionally contained in
30 a range of 0.1 to 150 ppm.

17. A method of manufacturing a high-purity gold alloy according to claim 15, wherein the high-purity gold alloy additionally contains one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and wherein



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a total additive amount of additives ranges from 3001 to 14999 ppm.

18. A method of manufacturing a high-purity gold alloy
5 according to claim 15, wherein the high-purity gold alloy additionally contains one or more additives selected from rare-earth metals and alkaline earth metals, and wherein a total additive amount of additives ranges from 3001 to 14999 ppm.

19. A method of manufacturing a high-purity gold alloy
10 according to claim 16, wherein the high-purity gold alloy additionally contains one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and wherein a total additive amount of additives ranges from 3001 to 14999 ppm.

15 20. A method of manufacturing a high-purity gold alloy according to claim 16, wherein the high-purity gold alloy additionally contains one or more additives selected from rare-earth metals and alkaline earth metals, and wherein a total additive amount of additives ranges from 3001 to 14999
20 ppm.

21. A method of manufacturing a high-purity gold alloy according to claim 17, wherein the high-purity gold alloy additionally contains one or more additives selected from rare-earth metals and alkaline earth metals, and wherein a
25 total additive amount of additives ranges from 3001 to 14999 ppm.

22. A method of manufacturing a high-purity gold alloy according to any one of claim 1 through 21, wherein the solution heat treatment is performed at a heating temperature of 600 to
30 2800°C, and the aging treatment is performed at a temperature of 150 to 350°C.

23. A method of manufacturing a high-purity gold alloy according to any one of claim 1 through 21, wherein after the solution heat treatment, the working process and the age



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12b

hardening treatment are alternately repeated.

24. A high-purity gold alloy having a Gd content of 1 to 49.9 ppm contained in Au of 99.98 weight % or more, the
5 high-purity gold alloy additionally containing one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and which a total additive amount of additives ranges from 1 to 199 ppm.

25. A high-purity gold alloy having a Gd content of 1 to
10 49.9 ppm contained in Au of 99.98 weight % or more, the high-purity gold alloy additionally containing one or more additives selected from rare-earth metals and alkaline earth metals, and which a total additive amount of additives ranges from 1 to 199 ppm.

15 26. A high-purity alloy according to claim 24 or 25, wherein the alloy additionally contains B in a range of 0.1 to 150 ppm.

27. A high-purity gold alloy having a Gd content of 50 to 1499 ppm contained in Au of 98.50 to 99.69 weight %, the
20 high-purity gold alloy additionally containing one or more additives selected from the group consisting of Be, Al, Si, Ca, Sm, Y and Sb, and which a total additive amount of additives ranges from 3001 to 14999 ppm.

28. A high-purity gold alloy having a Gd content of 50 to 1499 ppm contained in Au of 98.50 to 99.69 weight %, the
25 high-purity gold alloy additionally containing one or more additives selected from rare-earth metals and alkaline earth metals, and which a total additive amount of additives ranges from 3001 to 14999 ppm.

29. A high-purity alloy according to claim 27 or 28, wherein
30 the alloy additionally contains B in a range of 0.1 to 150 ppm.



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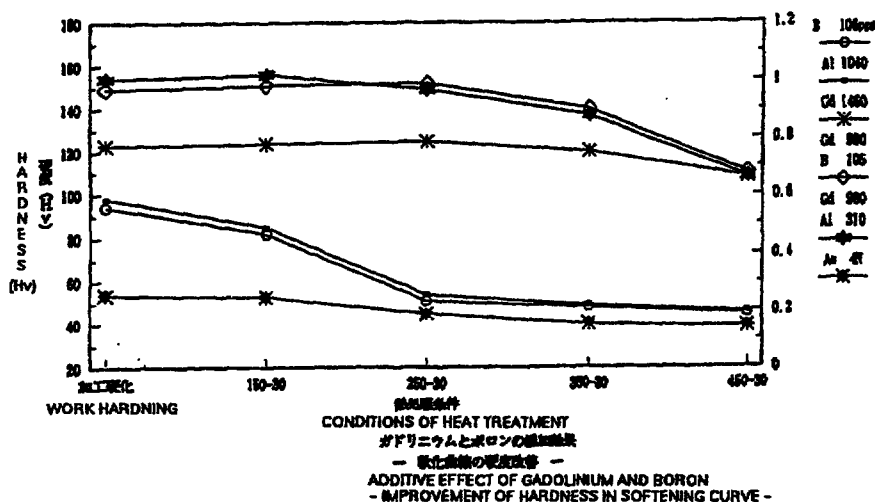
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(54)Title: HIGH PURITY HARD GOLD ALLOY AND METHOD OF MANUFACTURING SAME

(54)発明の名称 高純度硬質金合金及びその製造方法



(57) Abstract

Electronic member: in a trend for finer line using a high purity gold alloy wire, this gold alloy wire further improves breaking strength, hardness, heat resistance and the like as compared with a conventional gold alloy wire, and achieves stable bonding with less scatter and disconnection. Further, the gold alloy wire increases dispersion of fine additive agents, improves electric conductivity and thermal conductivity, and enables automatic, high speed bonding having a less junction loop height. Such high purity hard gold alloy is also suitable for electronic members such as lead frame and the like. Dental member: a high purity gold alloy enhances hardness and tensile strength which are important mechanical properties, further improves heat resistance and tone, and provides dental, high purity hard gold alloy members which are well balanced. High purity golden-colored alloy: a high purity gold alloy for high purity golden-colored, decorative members, electronic members, dental members and the like is available.

(57) 要約

電子用部材

高純度金合金線で細線化の進む中で、従来の金合金線よりも破断強度、硬度、耐熱性等を一段と向上させ、バラツキや断線が少なくした安定したボンディングを達成する。更に微小添加材の分散を上げ、電気伝導性、熱伝導性を向上させ、接合ループ高さの低い、高速自動ボンディングを可能にさせる。この様な高純度金合金はリードフレーム等の電子用部材にも好適である。

歯科用部材

高純度金合金で重要な機械的性質の硬度、引張強度を向上させ、更に耐熱性や色調を一段と改善し、バランスの取れた歯科用高純度金合金部材を提供する。

高純度金色部材

高純度金色をした装飾用部材、電子用部材、歯科用部材等の高純度金合金を得る

参考情報

PCTに基づいて公開される国際出願のパンフレット第一頁に記載されたPCT加盟国を特定するために使用されるコード

AL	アルバニア	ES	スペイン	LR	リベリア	SG	シンガポール
AM	アルメニア	FI	フィンランド	LS	レソト	SI	スロヴェニア
AT	オーストリア	FR	フランス	LT	リトアニア	SK	スロヴァキア共和国
AU	オーストラリア	GA	ガボン	LU	ルクセンブルグ	SL	シエラレオネ
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CG	コンゴ	IT	イタリア	NE	ニジェール	UZ	ウズベキスタン
CH	スイス	JP	日本	NL	オランダ	VN	ヴェトナム
CI	コート・ジボアール	KE	ケニア	NO	ノルウェー	YU	ユーゴスラビア
CM	カメルーン	KG	キルギスタン	NZ	ニュージーランド	ZW	ジンバブエ
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CU	キューバ	KR	大韓民国	PT	ポルトガル		
CZ	チェッコ共和国	KZ	カザフスタン	RO	ルーマニア		
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EE	エストニア	LK	スリランカ	SE	スウェーデン		