Effects of Heat Treatment on the Microstructures of AuCuPtPdNiRh Alloys

ZHANG Kunhua^{1, 2}, CHEN Yuzeng¹, GENG Yonghong², BI Jun², KONG Jianwen²

(1. State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi'an 710072, China;

2. State Key Laboratory of Advanced Technologies for Comprehensive Utilization of Platinum Metals,

Kunming Institute of Precious Metals, Kunming 650106, China)

Abstract: The microstructures of Au-based alloy were investigated for the as-casted state, solution heat treated at 750°C for 1 h, 850°C for 4 h, and 950°C for 1 h, and uniform heat treated at 950°C for 4 h by metallurgical structure examination, differential thermal analysis (DSC), X-ray diffraction (XRD), scanning electron micrograph (SEM) and energy spectrum analysis (EDS). This Au-based alloy is composed of Au(Cu, Pd), Pt(Rh, Ni), and the mixture of both. With the heat treated temperature elevated, Pd solute segregated from the mixtures. AuCu3 phase with L1₂ structure formed as heat treated at 700°C, 850°C, and 950°C.

Key words: metals materials; heat treatment; AuCuPtPdNiRh alloy; microstructure; solution; ordered-disordered

CIF number: TG146.3 Document Code: A Article ID: 1004-0676(2014)S1-0049-08

热处理对 AuCuPtPdNiRh 合金显微组织的影响

张昆华^{1,2},陈豫增¹,耿永红²,毕 珺²,孔建稳²
(1.西北工业大学 凝固技术国家重点实验室,西安 710072
2. 昆明贵金属研究所 稀贵金属综合利用新技术国家重点实验室,昆明 650106)

摘 要:运用金相组织分析、差热分析(DSC)、X 射线衍射(XRD)、扫描电镜(SEM)和能谱(EDS)对 铸态、固溶态(750℃、1h,850℃、4h,950℃、1h)和热处理950℃、4h后的金基合金的显微组织 进行了研究。该金基合金由 Au(Cu,Pd)固溶体和 Pt(Rh,Ni)固溶体以及它们的混合物构成。随着热 处理温度的提高,Pd 溶质由混合物中偏析出来。在700℃、850℃和950℃进行热处理时,形成了 L12结构的 AuCu3 相。

关键词:金属材料;热处理;AuCuPtPdNiRh合金;显微组织;固溶体;有序-无序化

The pure gold is extremely malleable, ductile and has good electrical conductivity and biocompatible properties^[1-4]. However, it is always soft and wears easily which limit its applications in the industrial fields. Therefore, alloying elements are usually used to tailor both mechanical and functional properties of Au-based alloys in order to meet the requirements of

practical applications^[1, 5-10]. Aiming to different purposes of applications, a number of elements, such as Cu, Ag, Pd, Pt, Ni, Co, Fe, Mn, Cr, V etc. are commonly adopted to improve the performances of the Au-based alloys^[1, 11-14]. Concerning the different effects of these alloying elements on the properties of Au-based alloys, these elements can normally be

Received: 2014-05-12

Foundation item: State Key Lab. of Solidification Processing Opening Foundation (SKLSP201212) and the Yunnan Foundation (2010ZZC258). First author: ZHANG Kunhua, male, PhD. Professor, Research direction: phase structure evolution in alloys. E-mail: zhangkh69@163.com

divided into two main groups, hardening elements (Cu, Ag, Pd, Pt, Ni, Co) owing to ordering hardening or solution strengthening, and electrical resistivity sensitive elements (Fe, Mn, Cr, V and so on). On the other hand, alkali metals, alkaline earth, rare metals and transition elements with high melting point (such as Zr, Rh, Ir and so on) are also used as micro-alloying elements in Au-based alloys^[5, 15], which may as well play a vital role in the properties of Au-based alloys, such as precipitation hardening and refining of grain sizes. In all, by alloying these different elements, a series of structural and functional Au-based alloys can be developed which have been widely used as dental alloys, ornamental materials and electrical materials^[1-6, 17-23].

As a material for electrical contacts operating with light pressures and controlling small currents, gold has the advantages that it is free from high-resistance oxide and sulphide films [5-6, 18, 24-25]. However, the disadvantages of gold are its tendency to weld on closure and its softness^[22-23]. Au-based alloys are commonly used as electric brush materials in precise potentiometer and as elastic contact material for microrelays to overcoming the disadvantages^{[21-22,} ^{28-30]}. Those Au-based alloys must possess elastomeric property, abradability, corrosion resistance and lower contact resistance. Moreover, with the further development of aerospace industry, the electric contact material presents high reliability requirements. Therefore, A lot of efforts have been made to increase the hardness of Au-based alloys. One of examples is that Prof. Ning Yuantao in Kunming Institute of Precious Metals has introduced a novel Au-based electrical contact material in order to reach the new requirements by micro-alloying method^[31]. This Au-based alloy contains Cu, Pt, Pd, Ni and Rh as micro-alloving elements and is comprised of two phases, a gold-rich solid solution as the matrix and a platinum-rich solid solution as a strengthening phase^[31]. In order to optimizing the combination properties of electrical resistivity, hardness, tensile strength and so on, this material was reinvestigated by microstructure controlling^[1, 5, 18]. In present paper, the microstructure evolutions during various heat

treatments were investigated by optical and SEM microstructures.

1 Experimental procedures

The nominal composition of the Au-based alloy studied in this work is shown in Tab.1. The alloy ingot was produced by melting the pieces of Cu (99.9%, mass fraction), Pt (99.95%), Pd (99.95%), Ni (99.95%), Rh (99.95%), and Au (99.95%) in a high vacuum induction furnace. The ingot was re-melted for at least three times in order to avoid microsegregation. After melting, the alloy melt was casted into a water cooling copper mould under Ar atmosphere. In the end, a cylinder ingot with a diameter of 15 mm was obtained.

Tab.1 Nominal composition of the Au-based alloy studied in this work

表1 金基合金的名义成分

Element	Cu	Pt	Pd	Ni	Rh	Au
Mass fraction/%	10~15	10~15	10~15	1~5	1~5	Balance

The experiment specimens were cut from the ingots, sealed in the quartz capsule filled with argon gas and then heat treated at 700°C for 1 h, 850°C for 4 h, 950°C for 1 h (quenched into ice water) and homogenous treated at 950°C for 4 h (cooling in the furnace) in a resistance furnace.

Thermogravimetric analysis of the casted Aubased sample was carried out in Netzsch STA 409 PG/PC under the flowing Ar atmosphere. The sample was heated from 25°C to 1300°C with a heating rate of 10°C/min.

The microstructures of the alloys were observed in optical microscopy (HXS-1000 A). In order to reveal the micrograph of the alloy, the sample was polished and etched in an etchant of 50 mL HCl+1.5 g Cr_2O_3 at room temperature.

SEM and EDS analyses were performed in Phlips XL30ESEM scanning electron microscopy equipped with EDAX-Phoenix energy dispersive analyzer. X-ray diffraction measurements were conducted in a Rigaku D/max-RC diffractometer operated at 40 kV and 100 mA with Cu-K_{α} radiation.

2 Results and discussion

2.1 Thermogravimetric analysis

A typical DTA curve of the as-casted alloy is shown in Fig.1, where an exothermic peak and three endothermic peaks can be observed at 581, 869.3, 1103.8 and 1143.6 °C, respectively. The exothermic peak might be ascribed to the ordering of the disordered intermetallic compounds, which normally occurs during heating and leads to the release of heat, while the endothermic peaks may be attributed to the dissolution of the precipitates. Accordingly, there are at least three different precipitates existing in the ascasted alloy. According to their binary phase diagram and ternary phase diagram^[32-34], the dissolution of AuCu-based phase is expected to take place at a lower temperature, while that of PtRh-based phase may happen at a higher temperature.



According to the elements properties, shown in Tab.2 and phase diagrams, it can be deduced that the exothermic peak is owing to phase transformation such as ordering to disordering and the endothermic peaks are resulting from the solutionizing of the second phase or solute. Accordingly, there are at least two kinds of second phases. The low solution temperature one is AuCu-based phase while the high temperature one is PtRh-based phase. Moreover, there is no solid solubility in Au-Rh system but others system. It is to be noted that Rh element is hard to solute in Au-based alloys at low temperature.

Tab.2 Properties of comprising elements of Au-based alloy 表 2 金基合金中各组成元素的物理性质

Elements	Melting	Cell Parameter	Atomic Radius
	Point/°C	/pm	/pm
Au	1046.18	407.82	144
Cu	1084.62	361.49	128
Pt	1768.3	392.42	138.5
Pd	1554.9	389.07	137
Ni	1455	352.4	124
Rh	1964	380.34	134

2.2 Microstructures

Fig.2 shows the microstructures of the as-casted Au-based alloy and the Au-based alloy heated treated under different conditions. In the as-casted state, the microstructure apparently consists of three different phases, i.e. the matrix phase, the dark phase, and the bright phase, see Fig.2 (a). After heat treatment at 700 $^{\circ}$ C for 1 h, the morphology of the bright phase does not change, while the border of the dark phase becomes obscure, see Fig.2 (b). As the samples heat treated at 700°C and 850°C, the luminance one keeps the same condition as in casted samples while the shade one has an obscure profile. Moreover, the volume fraction of the dark phase increases compared to the casted sample and keeps at the same levels as treated at 700℃ and 850℃. As treated at 950℃, the amount of the shade one severely decreases while the luminance one keeps no change. Moreover, the grains of matrix show growth up tendency. It can be confirm that the solution temperature of the shade second phase is near 850°C and that of the luminance phase is more than 950°C. As the samples homogenous heat treated at 950°C for 4 h and then cooling in the furnace, the luminance phase locate in the matrix grain boundaries and the shade phase almost dissolve into matrix.



Fig.2 Metallurgical structure of the Au matrix alloy

[(a). as cast; (b). solution treated at 700 $^{\circ}$ C for 1 h; (c). solution treated at 850 $^{\circ}$ C for 4 h; (d). solution treated at 950 $^{\circ}$ C for 1 h;

(e). uniform heat treated at 950° C for 4 h]

图 2 金基合金的金相图谱

2.3 Scanning electron microscopy

Fig.3 (a)~(e) shows the SEM images of the Aubased alloy samples. The results are as the same as the metallurgical structure. The microstructures of the Aubased alloy are consist of matrix phase, granule phase (shade phase as in Fig.2) and block phase (luminance phase as in Fig.2). As shown in Fig.3 (a)~(d), the block phase almost have no changes during those heat treatments. Fig.3 (e) shows both the granule and block second phases display composition re-distribution owing to the limit solid solubility near the equilibrium conditions.



Fig.3 ESM images of the Au based alloy

[(a). as cast; (b). solution treated at 700 $^{\circ}$ C for 1 h; (c). solution treated at 850 $^{\circ}$ C for 4 h; (d). solution treated at 950 $^{\circ}$ C for 1 h;

(e). uniform heat treated at 950 $^\circ\!\mathrm{C}$ for 4 h]

图 3 金基合金的扫描电镜图谱

2.4 Composition distribution

Fig.4 shows the composition regions of tested Au-based alloy samples. The EDS results are shown in Tab.2 to Tab.7. As casted state, the main composition of the matrix is Au and Cu, and that of the block phase is Pt, Rh, Ni. The granule second phase consists of Au, Cu, Pt, Ni, Rh, Pd. As solution treated at 700°C for 1 h, the main composition of the matrix is Au, Cu, Pd. Both the granule and block phases show no change. However, the Pd content in the granule second phase decreases. This indicated that the Pd element redistribute between matrix and granule phase. As heat treated at 850°C for 4 h, the Pd element has almost resolved into matrix. As treated at 950°C for 1 h, the main composition of the block phase is Pt, Ph, Ni, Cu, and that of the granule phase is also Pt, Rh, Ni, Cu. This demonstrates that the Cu element redistribution between granule and block phase. In summary, as heat treated at low temperature, the Pd element migrates from granule phase to matrix while at high temperature, the Cu element resolves in block phase.



Fig.4 EDS analysis regions of Au based alloy with different heat treatment

[(a). as cast; (b). solution treated at 700 $^{\circ}$ C for 1 h; (c.) solution treated at 850 $^{\circ}$ C for 4 h; (d). solution treated at 950 $^{\circ}$ C for 1 h;

(e). uniform heat treated at 950°C for 4 h]

图 4 不同热处理状态的金基合金的能谱分析

Tab.3 EDS analysis data of Au-based alloy as-casted /% 表 3 铸态金基合金的能谱分析

Element	Rh	Pd	Ni	Cu	Pt	Au
1	25.08	7.05	20.2	12.04	28.69	6.95
2	0.25	7.75	6.75	29.16	6.35	49.75
3	7.9	7.29	13.01	24.51	15.62	31.68
4	13.14	9.14	14.13	20.86	18.22	24.51

Tab.4	EDS	analysis	data	of	Au-based	alloy	solution	treated
	at 70(0°C						/%

表 4 700℃固溶处理后的金基合金的能谱分析								
Element	Rh	Pd	Ni	Cu	Pt	Au		
1	27.69	4.68	24.06	8.67	32.42	2.48		
2	1.98	10.03	8.02	29.15	7.39	43.43		
3	17.44	4.31	22.4	16.72	20.8	18.32		
4	25.37	1.95	30.52	9.37	29.65	3.13		
5	17.91	4.23	25.56	13.8	25.43	13.07		

Tab.5 EDS analysis data of Au-based alloy solution treated at 850°C /%

表5 85	0℃固溶	处理后的	日金基合金	金的能谱	分析	
Element	Rh	Pd	Ni	Cu	Pt	Au
1	27.98	4.76	22.98	8.12	32	4.16
2	0.68	10.14	5.83	30.39	7.44	45.52
3	15.91	4.21	22.91	15.41	24.03	17.53

Tab.6 EDS analysis data of Au-based alloy solution treated at 950°C /%

表 6 950℃固溶处理后的金基合金的能谱分析							
Element	Rh	Pd	Ni	Cu	Pt	Au	
1	2.52	9.76	8.06	29.47	7.34	42.85	
2	27.14	4.82	22.38	10.98	30.17	4.52	
3	26.52	3.68	26.45	10.8	26.83	5.73	
4	24.73	3.18	26.53	10.94	28.32	6.3	

Tab.7 EDS analysis data of Au-based alloy uniform treated at 950°C /%

从田丘的人甘人人的能涉八七

及 / 950 C 单 处理归的 亚 圣 古 亚 的 能 信 力 机							
Element	Rh	Pd	Ni	Cu	Pt	Au	
1	25.36	4.31	23.72	12.09	28.54	5.97	
2	23.99	3.89	25.19	10.57	27.6	8.75	
3	2.27	10.63	7.82	28.14	8.32	42.81	
4	0.25	10.13	7.07	29.77	7.93	44.85	
5	25.67	4.75	25.86	10.43	23.31	9.99	
6	20.53	4.09	24	13.49	23.43	14.46	

2.5 XRD results

05000 畄

The XRD results of the samples are shown in Fig.5. There are two phases in the XRD patterns, namely FCC phase (noted as 1) and the ordered phase with $L1_2$ structure (noted as 2). Based on the crystalline structure analysis, the main phase is corresponding to Pd element diffraction data. However, according to the above analysis, it can be concluded that this FCC diffraction peak patterns must be belong to both Au-based matrix and Pt-based second phase.

According to Bragg diffraction equation^[35]:

$$2d\sin\theta = \lambda$$
 (1)

Where *d* is spacing of the atomic layers of crystals, θ is diffraction angle and λ is wavelength. As λ is a constant, *d* value increases or decreases with θ decreasing or increasing. In cubic crystalline structure,

lattice parameter a is in direct proportion to d value. From Tab.1, it can be get as follows:

$$a_{Au} > a_{Pt} > a_{Pd} > a_{Rh} > a_{Cu} > a_{Ni} >$$
 (2)
According to the binary diagrams^[32-33, 36], every
element can be solute with each other except Au and
Rh system. Moreover, their atomic radius ratio is less
than 16%. In another word, as Au or Pt element
formed substitution solid solution with other elements
(their lattice parameter is less than Pd's), the new
crystalline structure lattice parameter is less than pure
Au or Pt. Accordingly, the 1 diffraction pattern is
corresponding to Au-based alloy, Pt-based alloy, or
complex solute consisted of both Au-based and
Pt-based solute.



Fig.5 XRD patterns of Au-based alloys (1. undetermined main phase; 2. AuCu3 second-phase)

图 5 金基合金的 XRD 图谱

3 Conclusions

(1) The new Au-based alloy is consist of matrix Au (Cu, Pd), block phase Pt (Rh, Ni) and granule phase.

(2) As 700 °C, 850 °C solution treated and 950 °C homogenous treated, there is a AuCu3 type with $L1_2$ ordering structure in Au-based alloy.

(3) As heat treated at low temperature, the Pd element migrates from granule phase to matrix while at high temperature, the Cu element resolves in block phase.

References:

赵怀志, 宁远涛. 金[M]. 长沙: 中南大学出版社, 2003.
 Zhao Huaizhi, Ning Yuantao. Gold[M]. Changsha:

Central South University Press, 2003.

- [2] Strang R, Whitters C J, Brown D, et al. Dental materials: 1996 literature review[J]. Journal of Dentistry, 1998, 26: 191-207.
- [3] Strang R, Whitters C J, Brown D, et al. Dental materials: 1996 literature review: Part 2[J]. Journal of Dentistry, 1998, 26: 273-291.
- [4] Whitters C J, Strang R, Brown D, et al. Dental materials:
 1997 literature review[J]. Journal of Dentistry, 1999, 27:
 401-435.
- [5] Chaston J C. Industrial Uses of Au[J]. Int Met Rev, 1977, 22: 25-38.
- [6] Goodman P. Current and future uses of gold in electronics[J]. Gold Bulletin, 2002, 35(1): 21-26.
- [7] Xie Y Q. Relationship between partial and average atomic volumes of components in Au-Ni alloys[J]. Transactions of Nonferrous Metals Society of China, 2011, 21(8): 1801-1807.
- [8] Xu X N, Ren Y P, Li C F, et al. Thermodynamic assessment of Au-Pt system[J]. Transactions of Nonferrous Metals Society of China, 2012, 22(6): 1432-1436.
- [9] Xie Y Q, Li Y F, Liu X B, et al. Characteristic atom occupation patterns of Au₃Cu, AuCu₃, AuCuI and AuCuII based on experimental data of disordered alloys[J]. Transactions of Nonferrous Metals Society of China, 2011, 21(5): 1092-1104.
- [10] Xie Y Q, Liu X B, Li X B, et al. Potential energies of characteristic atoms on basis of experimental heats of formation of AuCu and AuCu₃ compounds(I)[J]. Transactions of Nonferrous Metals Society of China, 2009, 19(5): 1243-1256.
- [11] Ning Y. Influence of gd addition on the structure and properties of Au-Ni and Au-Ni-Cr alloys[J]. Gold Bulletin, 2006, 39(4): 220-225.
- [12] 宁远涛. Au 与 Au 合金材料近年的发展与进步[J]. 贵金属, 2007, 28(2), 57-64.
 Ning Y. Development and progress of gold and gold alloy materials[J]. Precious Metals, 2007, 28(2): 57-64.
- [13] Ning Yuantao. Microalloying of gold and gold alloys[J]. Precious Metals, 2008, 29(2):55-61.
- [14] 张康侯. 含金三元合金系的研究进展(1996~2007 年)[J]. 贵金属, 2008, 29(2): 47-54.
 Zhang K H. Recent Development in the investigation on ternary alloy systems containing gold (1996~2007)[J].

Precious Metals, 2008, 29(2): 47-54.

- [15] Antler M. The application of palladium in electronic connectors[J]. Platinum Met Rev, 1982, 26(3): 106-117.
- [16] 谷云彦,李宝绵,代恩泰.饰品用金合金及其新进展[J]. 云南冶金,1997,26(3):53-57.
- [17] Antler M. Electrical effects of fretting connector contact materials: a review[J]. Wear, 1985, 106(1): 5-33.
- [18] Antler M. Gold in electrical contacts[J]. Gold Bulletin, 1971, 4(3): 42-46.
- [19] 冯景苏. 牙科贵金属铸造合金[J]. 稀有金属, 2000, 24(6): 450-456.
 Feng J. Chinese Journal of Rare Metal[J]. 2000, 24(6): 450-456.
- [20] Li Y, Wang Y, Wu B. Non-Ferous Mining and Metallurgy[J]. 1999, 53.
- [21] Kim H I, Kim Y K, Jang M I, et al. Age-hardening reactions in a type III dental gold alloy[J]. Biomaterials, 2001, 22(11): 1433-1438.
- [22] Winn H, Tanaka Y, Shiraishi T, et al. Two types of checkerboard-like microstructures in Au-Cu-Pd ternary alloys[J]. Journal of Alloys and Compounds, 2000, 306(1/2): 262-269.
- [23] Kim Hyung-Il, Lee Doung-Hun, Sim Jae-Seong, et al. Age-hardening by miscibility limit of Au-Pt and Ag-Cu systems in an Au-Ag-Cu-Pt alloy[J]. Materials Characterization, 2009, 60: 357-362.
- [24] Krumbein S J, Antler M. Corrosion inhibition and wear protection of gold plated connector contacts[J]. Parts, Materials and Packaging, IEEE Transactions on, 1968, 4(1): 3-11.
- [25] Antler M. Gold connector contacts: developments in the search for alternate materials[J]. Parts, Hybrids, and Packaging, IEEE Transactions on, 1975, 11(3): 216-220.
- [26] Lafontan X, Pressecq F, Perez G, et al. Physical and reliability issues in MEMS microrelays with gold contacts[C] // Micromachining and Microfabrication. International Society for Optics and Photonics, 2001: 11-21.
- [27] Yang Z, Lichtenwalner D J, Morris A S, et al. Comparison of Au and Au – Ni alloys as contact materials for MEMS switches[J]. Microelectromechanical Systems, Journal of, 2009, 18(2): 287-295.
- [28] 曾婵, 刘丽, 孙平, 等. 贵金属齿科铸造合金时效后结构和性能研究[J]. 稀有金属材料与工程, 2005, 34(11): 1786-1789.

Zeng J, Liu L, Sun P, et al., Age-hardening behavior in the noble metal dental casting alloys[J]. Rear Metal Materials and Engineering, 2005, 34(11): 1786-1789.

- [29] Park J H, Cho M H, Park M G, et al. Gold Bull[J]. 2010, 43: 316-323.
- [30] 武海军,张国庆,宋泓清,等. Pd-Ag-Sn-In-Zn 合金时 效强化机制研究[J]. 稀有金属材料与工程, 2007, 36(8): 1487-1489.
 Wu H, Zhang G, Song H, et al. Age-hardening mechanism of Pd-Ag-Sn-In-Zn alloy[J]. Rear Metal Materials and Engineering, 2007, 36(8): 1487-1489.
- [31] Ning Y, Peng Y, Dai H. A new electrical contact alloy with high reliability based on gold[J]. Gold Bulletin, 2002, 35(3): 75-81.
- [32] Dai Y. Binary Alloy Phase Diagrams[M]. Beijing: Science

Press, 2009.

- [33] 长崎诚三,平林真.二元合金状态图集[M]. 刘安生, 译.北京: 冶金工业出版社, 2004.
 Seizo N, Makoto H. Binary Alloy Phase-diagrams[M]. Liu A, translate. Beijing: Metallurgical Industry Press, 2004.
- [34] 郭青蔚, 王桂生, 郭庚辰. 常用有色金属二元合金相图 集[M]. 北京: 化学工业出版社, 2010.
- [35] 周玉,武高辉. 材料分析测试技术[M]. 哈尔滨: 哈尔 滨工业大学出版社, 1998.
 Zhou Y, Wu G. Analysis and Test Technology in Materials Science[M]. Harbin: Harbin Institute of Technology Press, 1998.
- [36] 谢佑卿. Au-Cu 系中无序和有序相的晶格常数[J]. 金属 学报, 1998, 34(12): 1233-1242.