Influence of Gd Addition on the Structure and Properties of Au-Ni and Au-Ni-Cr Alloys

Yuantao Ning
Kunming Institute of Precious Metals, Kunming 650221, China PR
E-mail: ytning2002@yahoo.com.cn

Abstract

The influence of Gd additions on the microstructure and properties of Au-Ni and Au-Ni-Cr alloys are reported. The alloys remain single phase solid solution at Gd contents of ≤0.1wt%, but at contents > 0.1%, two phases structures are formed, consisting of (Au) and a low melting point intermetallic compound containing Gd. Trace additions of Gd refine the grain size, increase strength and the recrystallization temperature, but without detriment to the good electric conductivity of these alloys. The wear life of potentiometer windings made of gold alloys containing Gd are at least one order of magnitude higher than those made in the Gd-free gold alloys. The design of gold alloys for precise electrical contact and resistance materials by conventional and micro-alloying is discussed.

Introduction

In addition to high electrical and thermal conductivity, gold and gold alloys have high chemical stability and do not form surface films of oxide, sulfide and “brown powder” deposits in oxygen-, sulfur- and organic vapor-containing atmospheres, so maintain high reliability and good voltage-current characteristics in light duty circuit applications. Gold and its alloys are suitable for applications as light duty contacts and precision potentiometer winding materials [1,2]. Among the gold alloys, the Au-Ni and Au-Ni-Cr alloys have been used as the brush and winding materials in precision potentiometers and substituted successfully for some Pt- and Pd-based alloys. On the other hand, these gold alloys show poor wear resistance and low durability, due to their low yield strength, elasticity and hardness, in some applications with a higher contact pressure. So, it is desirable to increase the wear-resistance and operational life of these alloys.

Alloying is an effective measure to improve properties. It has been shown that microalloying via rare earth metal additions to gold increases not only the mechanical properties but also maintains good stability of electrical conductivity [3-6]. Based on this research, improved Au-Ni and Au-Ni-Cr alloys modified by RE additions have been developed. In present paper, the influence of Gd additions on the microstructure and some application-related performance of Au-Ni and Au-Ni-Cr alloys are reported.

Influence of Gd additions on the structure of Au-Ni and Au-Ni-Cr alloys

According to the Au-Ni and Au-Cr binary phase diagrams, the Au-Ni system is a continuous solid solution at elevated temperatures, with a large miscibility gap below 810°C, and Au-Cr is a peritectic system with the solid solubility of 47at% (19wt%) Cr at the peritectic temperature decreasing to a few percent of chromium at room temperature. So, Au-Ni-Cr alloys with Cr contents below about 3~4wt% are single phase solid solution. The influence of Gd on the phase compositions of Au-Ni-Cr alloys is not reported in the literature, but the binary phase diagrams of each metal with Gd is reported. In the binary phase diagrams of Ni or Cr with Gd, a series of eutectic systems and intermetallics are formed in the respective binary system with very small solid solubility of Gd in the metals. In the Au-Gd binary phase diagram, Figure1, at the gold-rich end of the Au-Gd system, (Au)+Au_6Gd eutectic forms with a eutectic temperature of 804°C. Gd has a maximum solid solubility of 0.7at% (0.6wt %) Gd in gold at the eutectic temperature, but a very low solubility as the temperature falls [7,8].

In present paper, Au-Ni-Gd and Au-Ni-Cr-Gd alloys, with contents of Ni, Cr and Gd below 9wt%Ni, 1wt%Cr and 1.0wt%Gd, were prepared. When the Gd content in the alloys is below 0.1wt%, the alloys remain single phase solid solution. Otherwise, the alloy is a two phase structure comprising (Au) solid solution and an intermetallic compound containing Gd. Figure 2 shows the microstructure

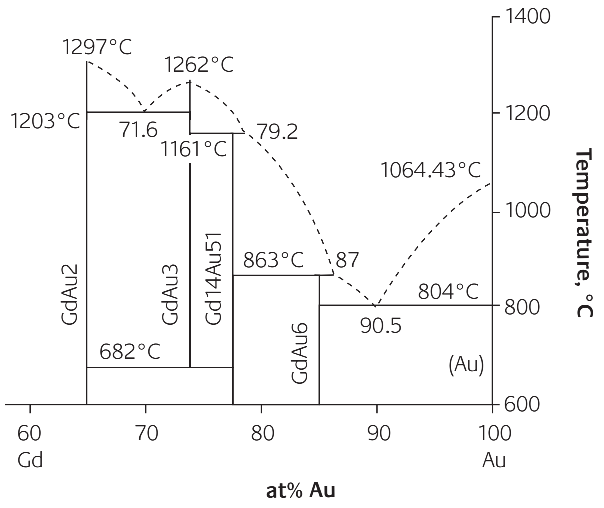

Figure 1
Phase diagram of gold-rich Au-Gd system [8]

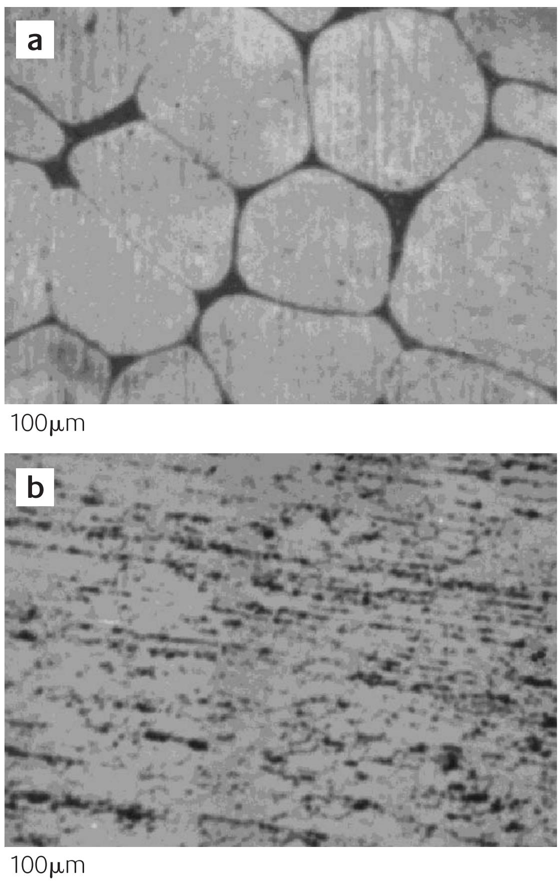

Figure 2
Microstructure of Au-5Ni-0.5Cr-0.5Gd alloy annealed at 800°C (a) and at 600°C (b)

of the Au-5Ni-0.5Cr-0.5Gd alloy. This alloy annealed at 800°C consists of a (Au) single solid Solution and a dark grain boundary phase made of a compound containing Gd, Figure 2(a). When this alloy is deformed by 60% reduction in thickness and annealed at 600°C, the compound containing

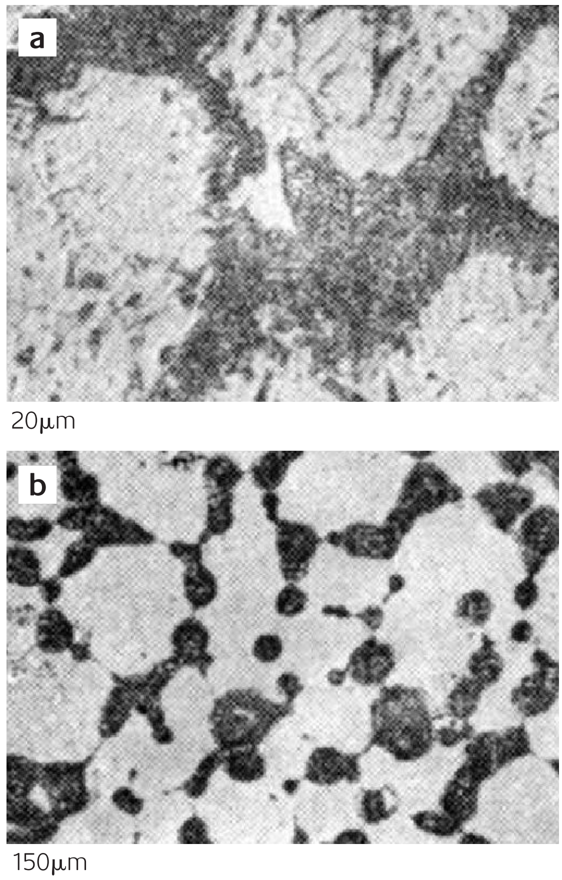

Figure 3
Distribution(a) and its melting behavior(b) of the eutectic mixture containing Gd intermetallic compound in Au-9Ni-1Gd alloy annealed at 850°C

Gd distributes along the deformed direction in fiber shape, Figure 2(b). In fact, the Gd-containing gold alloys form a eutectic mixture as the Gd content increases above 0.5%. The eutectic mixture has a low melting point and is distributed at grain boundaries. At annealing temperature above 800°C, the eutectic mixture melts. Figure 3 shows the eutectic mixture distributed along grain boundaries and its melting behaviour in a Au-9Ni-1Gd alloy annealed at 850°C.

Noting that the melting temperature of the (Au)+ Au_6Gd eutectic mixture in Figure1 is 804°C, it is possible that the Gd-containing compound in Au-Ni-Gd and Au-Ni-Cr-Gd alloys is $Au(Ni)_6Gd$ or $Au(Ni,Cr)_6Gd$. So, for this reason, the amount of Gd addition is restricted to below 0.5% in the Au-Ni and Au-Ni-Cr alloys. Otherwise, the workability of the gold alloys deteriorates.

It is also observed that Gd additions refine the grain size of Au-Ni and Au-Ni-Cr alloys. Figure 4 shows the growth of grains in Au-9Ni and Au-9Ni-0.3Gd alloys annealed at 760°C: large grains were formed in the Au-9Ni alloy, but finer grains were retained in the Au-9Ni-0.3Gd alloy. The grain refining effect is also evident in the Au-Ni-Cr-Gd alloys. The retardation of grain growth during annealing produced by the Gd addition is believed to be due to the formation of Gd-containing compound stimulated by grain boundary segregation of Gd additive. The remaining Gd solute with

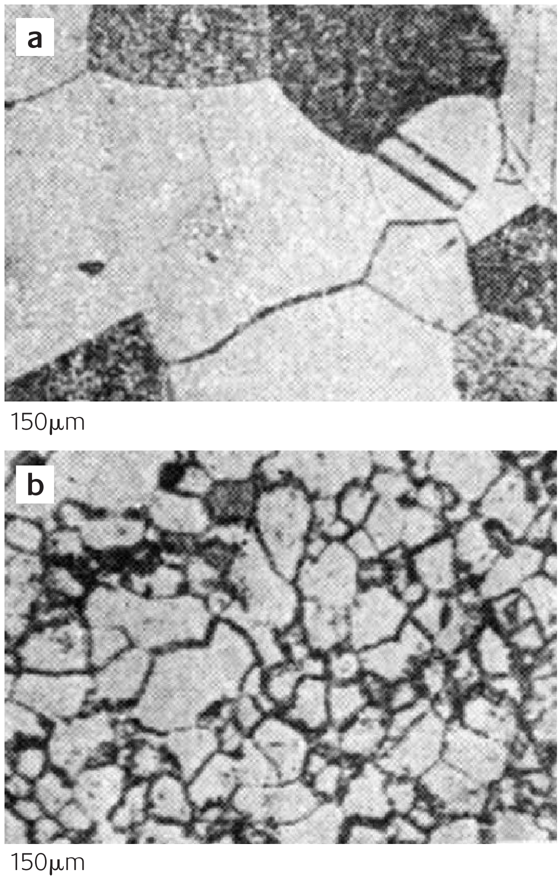

Figure 4

Grain growth in the Au-9Ni(a) and Au-9Ni-0.3Gd(b) alloys annealed at 760°C

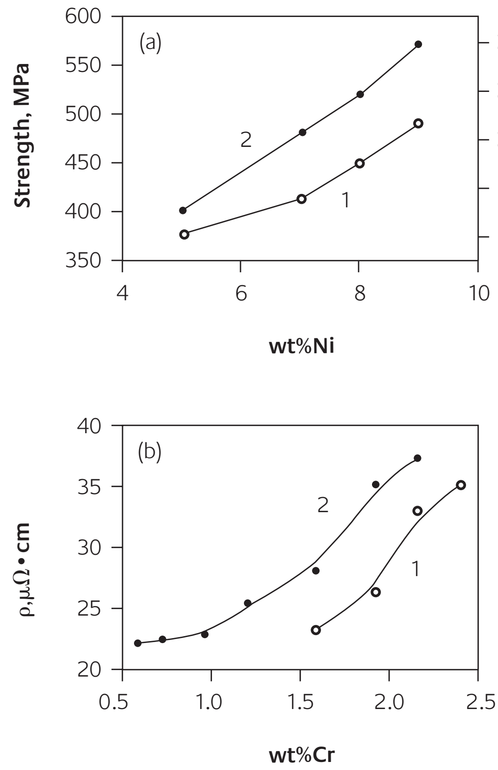

Figure 5

(a) Influence of Ni content on the hardness (curve 1) and strength (curve 2) of Au-1Cr-Ni alloy; (b) Influence of Cr content on the resistivity (ρ) of Au-Cr (curve 1) and Au-7Ni-Cr (curve 2) alloys

much larger atomic size could form a atmosphere of Gd atom around grain boundary, which hinders the growth of grains. The fine particles distributed along grain boundaries cause a local increase in grain-boundary length and thus create a drag of boundary motion. The upper limit for the grain size D_m in the present of particles is: D_m=4/3(r/f), here r is the fineness of the particles and the f is the volume fraction of the particles [9]. The particles may also accelerate recrystallisation and act as nucleation sites, hence finer grain size; this is well known, if the particles are larger than 0.5 microns approx.

Influence of Gd addition on properties of gold alloys

1 Influence of Ni and Cr content on the properties of Au-Ni-Cr alloys

In the Au-Ni-Cr ternary alloy system, Ni is mainly a strengthening element, although it also increases electrical resistance somewhat, and Cr is mainly a resistance-sensitive element. Figure 5 (a and b) shows the influence of the Ni content on the mechanical properties and of the Cr content on the specific resistance of Au-Ni-Cr alloys in the full-annealed state. For an Au-5Ni-1Cr alloy, the tensile strength and hardness are 400MPa and HV120, respectively. Increasing the Ni content up to 9%Ni, the mechanical properties of the alloy increase nearly linearly, Figure 5a. The specific resistance of both Au-Cr and Au-7Ni-Cr alloys increases markedly with increasing Cr content, Figure 5b. Generally speaking, the Au-Ni-Cr alloys used in industry have a Ni content of 5~9% Ni and a Cr content of 0.5~1.0%Cr. It can be seen from Figure 5b that the change of the specific resistance of the Au-7Ni – Cr alloy is relatively smooth in the range 0.5~1% Cr. It is undoubtedly favorable to maintain stability of the specific resistance of Au-Ni-Cr alloy even if the Cr content fluctuates a little.

2 Influence of Gd additions on the properties of Au-Ni and Au-Ni-Cr alloys

A trace addition of Gd is a very effective strengthening element in gold alloys. The Au-9Ni alloy, which was often used as a brush material in the precision potentiometer, has a tensile strength of about 550MPa in the full-annealed state and about 950MPa in the cold deformed state (80% deformation). These values can be increased to 750MPa and 1120MPa, respectively, with a 0.5wt% Gd addition as shown in Figure 6. The increase in the tensile strengths in the Au-9Ni alloy through microalloying with Gd is evident. Figure 7 shows the influence of Gd on the mechanical properties of a Au-5Ni-1Cr alloy. The strength and hardness of the alloy increases smoothly with increasing Gd content up to 0.5wt%Gd, and then decreases when the content of Gd

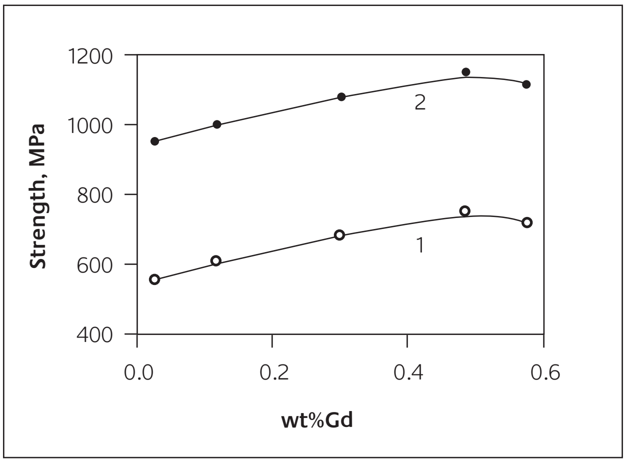

Figure 6

Influence of Gd content on the tensile strength of the annealed (1) and deformed (2) Au-9Ni alloy

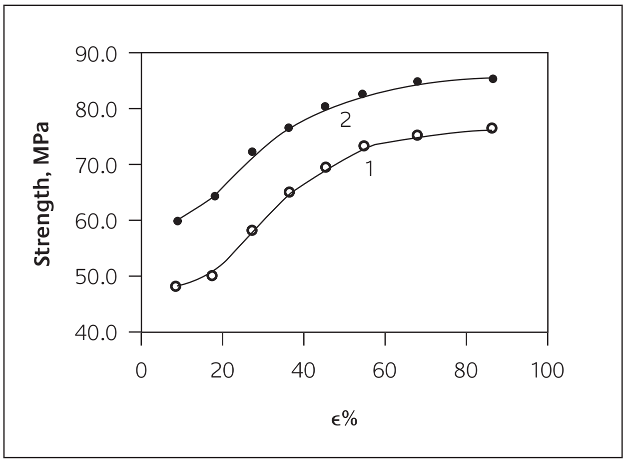

Figure 8

Work strengthening curves of Au-7Ni-1Cr (curve 1) and Au-7Ni-1Cr- 0.5Gd (curve2) alloys

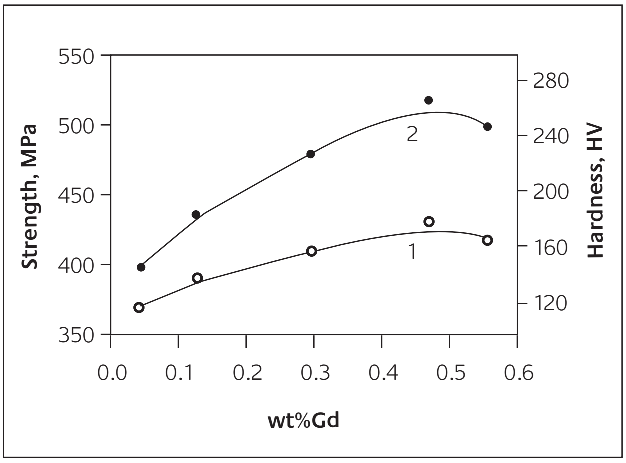

Figure 7

Influence of Gd content on the hardness (1) and strength (2) of Au-5N-1Cr alloy

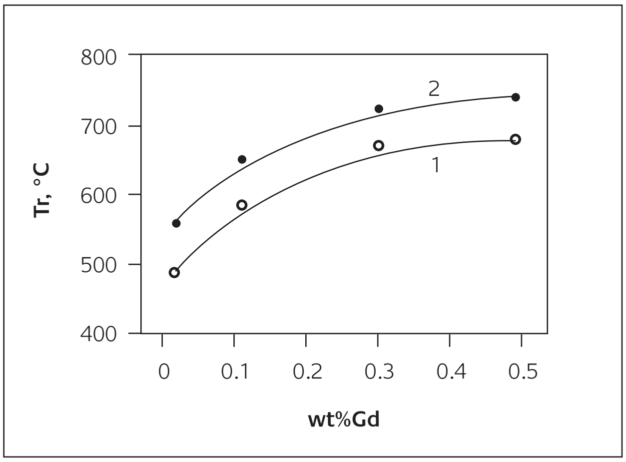

Figure 9

Recrystallization temperatures (Tr) of Au-5Ni-1Cr-Gd (curve 1) and Au-9Ni-Gd (curve 2) with different Gd content (for isothermally annealing 0.5h)

exceeds 0.5wt%. It is also observed that the Au-Ni-Cr-Gd alloy has a higher work hardening rate than the Gd-free alloy. The work hardening curves of Au-7Ni-1Cr and Au-7Ni-1Cr-0.5Gd alloys are shown in Figure 8 as a function of cold deformation. The strength of the latter alloy is considerably higher than the former. A similar effect on tensile strength was also observed for Au-Ni and other Au-Ni-Cr alloys with and without Gd additions [6]. The experimental results confirm that a Gd addition in Au-Ni and Au-Ni-Cr alloys has large strengthening effect.

As well as high tensile strength and hardness, Gd-containing Au-Ni and Au-Ni-Cr alloys can retain good conductivity and stability of electrical resistance. For example, the specific resistance values measured at 20°C are 22.6$\mu\Omega\bullet$cm and 23.5$\mu\Omega\bullet$cm for annealed Au-7Ni-1Cr and Au-7Ni-1Cr-0.5Gd alloys, respectively. After aging for 200h at 100°C, the specific resistances are 22.9$\mu\Omega\bullet$cm and 23.95$\mu\Omega\bullet$cm respectively. For the Au-7Ni-1Cr alloy, the change in the specific resistance after aging is about 1.9%. For the Au-7Ni-1Cr-0.5Gd alloy, the increment of the specific resistance caused by the Gd addition is less than 4%, and the change in the specific resistance after aging 200h at 100°C is about 2%. The stability of the resistance can be attributed to the low solid solution of Gd in the gold alloys. Gd additions can also retard the recrystallization of Au-Ni and Au-Ni-Cr alloys. It can be seen from Figure 9 that adding about 0.1 Gd to Au-9Ni and Au-5Ni-1Cr alloys raises the recrystallization temperatures of the gold alloys by about 100°C. For example, the recrystallization temperature of Au-9Ni alloy, which is about 560°C, was raised to 650°C and that of Au-5Ni-1Cr, which is about 480°C was raised to 570°C. Here, the recrystallisation temperature (Tr) is the temperature for 50% recrystallisation and determined on "half hardness method".

3 Influence of Gd additions on the wear resistance of gold alloys

It is generally recognized that the friction coefficient (f) and wear (W) of sliding contacts are related to the yield strength (σy) and hardness (H) of contact alloys by the equations: $f=S/\sigma_y$ and W= KPL/H. Here S is the shear strength of the joining points between sliding metals, P and L are the contact pressure and sliding distance; K is the coefficient related to the property and surface condition of contact materials. In view of this, the increase of yield strength and hardness of Au-Ni and Au-Ni-Cr alloys through microalloying additions of Gd should play an important role in improving the wear-resistance of sliding gold alloy contacts. The parallel simulated tests to assess the wear resistance of potentiometer windings made of Au-Ni-Cr and Au-Ni-Cr-Gd alloys, contacted by a Au-9Ni alloy brush under 5g contact pressure, were performed at a potentiometer manufacturer to an industrial criterion. The operation times, which are corresponding with 15% change rate of the resistance relative to the original resistance of the potentiometer windings, were taken as the criterion of the wear life. The wear life is $1.5x10^4$ and $3x10^4$ operations for the potentiometer winding made of Au-5Ni-1Cr and Au-7Ni-1Cr alloys, respectively, and it exceeds $7x10^5$ and $9x10^5$ operations, respectively, for potentiometer windings made of Au-5Ni-1Cr-0.5Gd and Au-7Ni-1Cr-0.5Gd alloys. For the Au-Ni-Cr alloy, the relative lower tensile strength and hardness resulted in a larger wear volume. During the running process of the brush on the surface of windings, wear debris of the alloys short circuit the coils of windings, causing the resistance of the windings to change. So, the windings made of Au-Ni-Cr alloys have a relatively larger reduction of the resistance at shorter operation times and lower wear life. On the other hand, the friction and wear of the windings made of the Gd-containing gold alloys are relatively lower due to the increased strength and hardness. When the operation times reached $7x10^5$ and $9x10^5$ for the windings made of Au-5Ni-1Cr-0.5Gd and Au-7Ni-1Cr- 0.5 Gd alloys, respectively, the reduction of the resistance of both windings is still less than the criterion of 15%. It indicates that the wear life of the gold alloys containing Gd is at least one order of magnitude higher than that of gold alloys without Gd.

Discussion

The design of compositions of new gold alloys as precision electrical contact and resistance materials adheres generally to two principles: multicomponent alloying and microalloying. The main alloying elements used for conventional gold alloys include Cu, Ag, Pd, Pt, Ni, Co, Fe, Mn, Cr and V [2]. The main function of the alloying elements vary: the first six metals are strengthening elements, and Fe, Mn, Cr, V are the main resistance-sensitive elements. Many gold alloys consist of both kinds of alloying elements. On the other hand, rare earth metals and some transition metals with high melting point, such as Zr, Rh, Ir, are often added to gold alloys as microalloying elements, in order to enhance the mechanical properties and to regulate electrical properties. Combining such elements has allowed many new multicomponent gold alloys to be developed. Table 1 lists some multicomponent gold alloy systems developed from binary gold alloys through a combination of conventional alloying and microalloying. Such multicomponent gold alloys can ensure good comprehensive properties and high reliability.

Experiments have testified that electrical contacts made of Au-based alloys modified by RE additions have following advantages: (a) maintain good electrical and heat conductivity as well as low contact resistance, due to the dilute concentration of the RE addition; (b) refine the grain size and increase the recrystallization temperature and the structural stability; (c) increase the strength and hardness as well as wear life; (d) reduce arc erosion and anode weight loss; (e) increase the resistance to adhesion and without environmental pollution [10,11]. It has been found that the brushes of gold alloys containing RE additions are work-hardened during operation. When the hardness difference of a brush before and after the wear test is about 1/3 of the original hardness of the brush, the brush had the smallest wearing depth [12].

Conclusions

Au-Ni-Gd and Au-Ni-Cr-Gd alloys with contents of Ni, Cr and Gd below 9wt%Ni, 1wt%Cr and 1.0wt%Gd were prepared. In the Au-Ni-Cr ternary alloy system, Ni is mainly a strengthening element and Cr is mainly a resistance-sensitive element. The alloys are single phase solid solution at a Gd content ≤0.1wt%, and become two phase structures (comprising (Au) solid solution and a intermetallic compound $Au(Ni)_6Gd$ or $Au(Ni,Cr)_6Gd$, with a low melting point) at a Gd content >0.1%. Additions of Gd refine the grain size and increase the recrystallization temperature of the gold alloys. Au-Ni and Au-Ni-Cr alloys modified by Gd addition possess the good conductivity and stability of electrical resistance. The resistance change caused by a 0.5Gd addition is less than 4%, and that the change of the resistivity after aging is about

Table 1

Some multicomponent gold alloy systems developed from binary gold alloys through multicomponent alloying and microalloying

Binary gold alloys	Alloying elements	Multicomponent gold alloy systems
Au-Ag	Cu, Mn, RE, Rh, etc	Au-Ag-Cu; Au-Ag-Cu-Mn; Au-Ag-Cu-Mn-RE; Au-Ag-Cu-Mn-Rh, etc
Au-Ni	Cr, Fe, Zr, RE, etc	Au-Ni-Cr; Au-Ni-Cr-RE; Au-Ni-Fe-Zr, etc
Au-Cu	Ag, Ni, Pd, Pt, Rh, Zn, Mn, RE, etc	Au-Cu-Ag-RE; Au-Cu-Ni-RE; Au-Cu-Ni-Zn-Mn; Au-Cu-Pt-Ag-Zn; Au-Cu-Pd-Pt-Ni-Rh, etc
Au-Pd	transition and simple metals	Au-Pd-Cr(V, Mo, Fe)-Al(Ga, In, Ce) systems

2%. Gd additions significantly increase the tensile strength, hardness, the work hardening and the wear resistance of Au-Ni and Au-Ni-Cr alloys. The wear life of gold alloys containing Gd are at least one order of magnitude higher than that of Gd-free gold alloys.

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