

Properties and Applications of Some Gold Alloys Modified by Rare Earth Additions

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Abstract

The influence of rare earth (RE) additions on the microstructure and some properties of gold and gold alloys have been studied. RE additions can refine the grain size of gold alloys, but show a tendency to segregation, both dendritic segregation in cast alloys and grain boundary segregation in annealed alloys. For gold alloys, RE additions are generally used in trace amounts or dilute concentrations in order to avoid a large segregation of RE and the potential embrittlement of gold alloys. The experimental results demonstrate that RE additions can inhibit recovery softening, increase the recrystallization temperature and enhance the strength of gold alloys. The strengthening mechanisms of RE additions in gold alloys are discussed. Some gold alloys with RE additions have been developed and their applications are illustrated briefly.

Introduction

As we know, gold is soft and can be strengthened through alloying. The conventional alloying elements typically used include silver (Ag), copper (Cu), nickel (Ni), platinum (Pt), palladium (Pd), manganese (Mn) and chromium (Cr). Of these, Ag, Cu and Ni are the main strengthening elements, and Mn and Cr are used mainly as resistance-sensitive elements. Gold can also be strengthened by microalloying (1). Of the possible microalloying elements, rare earth (RE) metals are very effective strengthening agents for both pure gold and gold alloys (2). In the present paper, the influence of RE additions on some properties of gold and gold alloys, such as Au-Ni, Au-Ni-Cr, Au-Ag-Cu and Au-Ag-Cu-Mn, have been studied and applications of such RE-modified gold alloys are reported.

1 Structure of gold alloys modified by RE additions

1.1 Distribution of RE in gold alloys

The dendritic segregation of RE in cast Au-RE alloys has been studied: Fig.1a shows the distribution of cerium (Ce) in cast Au-0.2Ce alloy. The concentration of Ce in the alloy was low in the dendrite crystals and high between the dendrites. It is related to the crystalline features of Au-RE alloys. The gold-rich end of any Au-RE phase diagram is a eutectic system. The RE additions lower the melting temperatures of Au-RE alloys. As a consequence, there is constitution undercooling of the alloy melt and the dendritic segregation in the cast structure. In annealed Au-RE alloys, the dendritic segregation disappears but segregation of RE along grain boundaries occurs, as shown in Fig.1b. The RE concentration at grain boundaries is much higher than that within the grains.

In Au-9Ni-Gd alloys, the microstructure is sensitive to the gadolinium (Gd) content. The solid solubility of Gd in Au-9Ni alloy at room temperature is very small. Except for the minor amount of Gd dissolved in the matrix of the Au-9Ni alloy, the majority of the Gd forms complex compounds, Au(Ni)₃Gd, with the Au and Ni (3). These Gd-containing compounds form a eutectic with the alloy matrix. The eutectic mixture has a low melting point and is distributed at grain boundaries. At annealing temperatures above 800°C, the eutectic mixture melts. The distribution of the eutectic mixture along grain boundaries can be seen in Fig.2a and its melting behaviour in the Au-9Ni-1Gd alloy annealed at 850°C

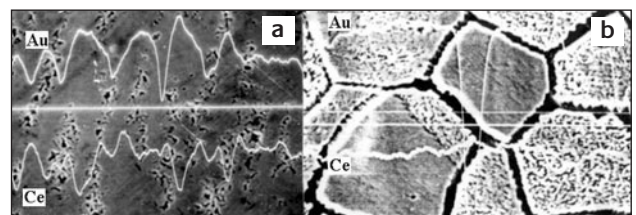


Figure 1

Distribution of cerium in (a) cast and (b) annealed Au-0.2Ce alloy

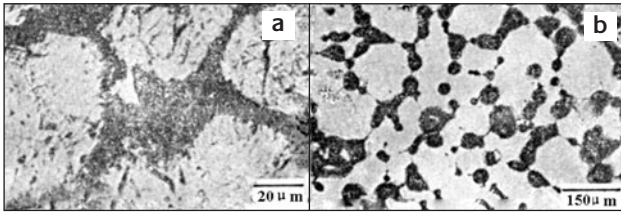


Figure 2
Distribution of the eutectic mixture containing the Gd intermetallic compound (a) along the grain boundary and (b) its melting behavior in Au-9Ni-1Gd alloy annealed at 850°C

is evident in Fig.2b. Noting that the melting temperature of Au₆Gd+(Au) eutectic mixture in the gold-rich Au-Gd system is 804°C, it is possible that the compound Au(Ni)₆Gd is Au(Ni)₆Gd.

The distribution tendency of a solute in an alloy is related to its concentration in the solidification front in the liquid alloy and can be expressed by a parameter $\omega = \alpha / \beta(A)$, where α is the maximum solid solubility of the solute in the solvent and β is the solute concentration in the liquid alloy at the same temperature. A small ω value means a large constitutional undercooling. So, the smaller the ω value, the larger the tendency to dendritic segregation. For Au-RE alloys, the ω values are quite small and lie in the range of 0.01-0.03 for the light RE metals (from La to Eu) and 0.07-0.63 for the heavy RE metals (from Gd to Lu) as well as for scandium (Sc) and yttrium (Y) (2). This indicates that the segregation tendency of the light RE metals is larger than that of the heavy RE metals. So, RE additions in gold alloys are generally present as a trace amount or a dilute concentration in order to avoid a large segregation of RE and a tendency to embrittlement.

1.2 Lattice expansion of Au-RE alloys

RE metals have much larger atomic radii than gold with the difference in values of atomic size between the RE metals and gold in the range of 13.9% (for Sc) – 41.8% (for Eu). Hence, RE additions expand the lattice of Au and Au alloys. According to the lattice parameters determined for some Au-RE alloys with a dilute concentration of RE, the increments of lattice parameters of Au-RE alloys normalized on 0.1at% RE are listed in Table 1 and are essentially in agreement with the experimental results reported by Rider et al (5). The light RE metals show a larger effect than heavy RE metals for lattice expansion of gold. In other words, the lattice expansion of gold produced by RE additions decreases with the lanthanide

Table 1

The increments (Δa , 10^{-4} nm) of lattice parameter expansion of Au-RE alloys normalized on 0.1at% RE addition and the solid solution strengthening parameters (H_s) of RE addition in gold

RE	Δa	H_s	RE	Δa	H_s	RE	Δa	H_s
La	1.6	0.43	Nd	1.0	0.36	Dy	0.7	0.28
Ce	1.4	0.38	Gd	0.9	0.31	Yb	0.5	0.24
Pr	1.2	0.37	Tb	0.8	0.29	Lu	0.5	0.23

contraction. RE additions in Au-based alloys also expand the lattice. For example, Gd additions in Au-9Ni alloy increase the lattice spacing of the alloy from 0.4009nm for Au-9Ni alloy to 0.4018nm and 0.4027nm for 0.3Gd and 0.5Gd additions, respectively.

1.3 Grain refining of gold and gold alloys by RE addition

The grain size of gold and gold alloys can be refined by RE additions. Grain refining involves two mechanisms: dendritic segregation promotes fine dendrite growth for cast Au-RE alloys and the grain-boundary segregation produces fine grains in annealed Au-RE alloy. The grain size of pure gold can be reduced one or two order of magnitude by RE additions, depending on the difference in atomic radii between gold and RE metals. For example, the grain size of gold annealed at 600°C for 1h was about 150 μ m, whereas 0.5wt% RE additions reduced the grain size to several or tens of micrometers by light or heavy RE respectively. The light RE metals, with larger atomic radius and lower solid solubility in gold, have a stronger effect in grain refining than heavy RE metals. RE additions in Au-based alloys also hinder the growth of grains. Fig.3 shows the growth of grains in Au-9Ni and Au-9Ni-0.3Gd alloys annealed at 760°C, the large grains were formed in Au-9Ni alloy, but the finer grains were still kept for Au-9Ni-0.3Gd alloy. The grain refining effect in the gold alloy containing Gd addition is evident. The distribution of RE metals along grain boundaries in gold or gold alloys modified by RE additions hinders the growth of grains and promotes grain refining.

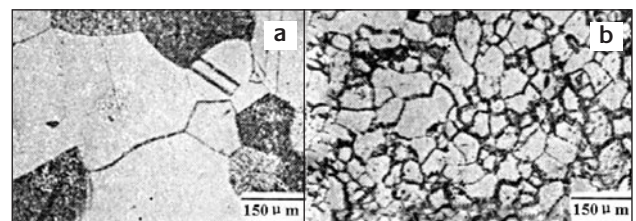


Figure 3
Grain growth in (a) Au-9Ni and (b) Au-9Ni-0.3Gd alloys annealed at 760°C

2 Some properties of gold alloys modified by RE addition

2.1 Retardation of recovery softening

High purity gold, heavily deformed, has a low recrystallization temperature. For 99.999%Au with a true strain $\eta > 4.6$, it is less than 120°C. This can cause the mechanical properties of foil or superfine wire of gold that has undergone heavy deformation to be unstable. In fact, such material could experience a recovery softening to a limited extent, even at ambient temperature, as shown in Fig.4. It exerts an unfavorable influence on the potential application of pure gold.

Fig. 4 also shows the change in tensile strength and elongation of a Au-0.005Ce alloy with time at room temperature. It indicates that a trace Ce addition in high purity gold clearly retards recovery softening. A XRD study indicates that the relaxation of the distorted lattice of high purity gold foil with $\eta = 5$ is quite large at room temperature, whereas the Au-0.005Ce alloy showed hardly any lattice relaxation, even at 50°C. At 120°C, the gold foil has fully recrystallized, in contrast to the Au-0.005Ce alloy. The 50ppm Ce addition raises the recrystallization temperature to about 250°C. The apparent recrystallization activation energy of high purity gold determined by the DSC method is about 75kJ/mol, which corresponds to the vacancy migration activation energy (79kJ/mol). It is increased to 92kJ/mol by a 50ppm Ce addition to high purity gold (6). It indicates that the resistance to recovery softening and recrystallization of high purity gold by trace RE additions is possibly related to the effect of RE atoms in hindering the migration of vacancies and grain boundaries in the alloy.

2.2 Retardation of recrystallization

The recrystallization temperature of commercial pure gold, 99.95%Au purity, that has undergone 75% cold deformation was determined to be 280°C. A RE addition at a dilute concentration should raise the crystallization temperature.

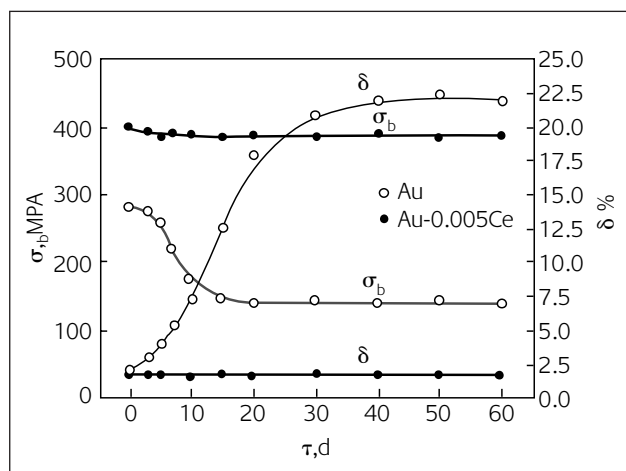


Figure 4
Time-dependent changes in tensile strength and elongation of high purity gold and Au-0.005Ce alloy, deformed to a true strain $\eta = 5$, at room temperature

For about 0.1%RE addition, the recrystallization temperature of the commercial gold is raised by about 150-200°C by light RE additions and by about 100-120°C by heavy RE additions on the base of 280°C. The light RE additions, with large atomic radii and small solid solubility, showed again a stronger effect on the properties of gold than heavy RE additions.

RE additions can also retard the recrystallization of gold alloys. For example, adding about 0.1% Gd to a Au-5Ni-1Cr alloy raises the recrystallization temperatures of the alloy by about 100°C from the 500°C of Au-5Ni-1Cr. A similar influence of Gd on the recrystallization temperature of a Au-9Ni alloy is also observed: The recrystallization temperature of Au-9Ni alloy, which is about 560°C, was raised to 650°C by a 0.1wt%Gd addition. The influence of Gd additions on the recrystallization temperatures of Au-5Ni-1Cr and Au-9Ni alloys is shown in Fig.5.

2.3 Strengthening effect of RE additions in gold alloys

RE metals as trace or dilute concentration additions are very effective strengthening elements in gold and its alloys. The tensile strength of annealed high purity gold is only about 130MPa, but that of the gold micro-alloyed with about 50ppm Ce rises to 220MPa. The tensile strength of commercial purity 99.95% gold is about 180MPa and this increases to 280-300MPa through the addition of about 0.1%RE. The changes of tensile strengths of some gold alloys without and with RE addition are listed in Table 2. The work hardening curves of Au-5Ni-1Cr and Au-5Ni-1Cr-0.5Gd alloys are shown in Fig 6 as a function of cold deformation. The strength of the latter alloy is obviously higher than the former. A similar effect on tensile strength was also observed for Au-Ni and Au-Ag-Cu-Mn alloys without and with RE additions. The experimental results confirmed that the light RE and Y additions in gold alloys have larger strengthening effect than heavy RE additions.

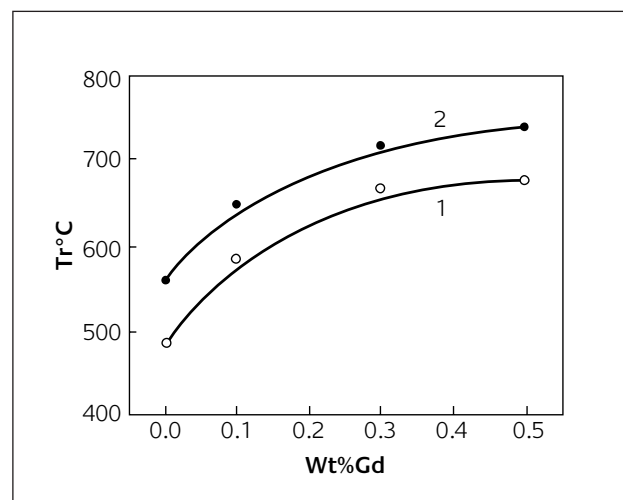


Figure 5
Dependence of the recrystallization temperature (T_r) of gold alloys on the gadolinium content. 1 - Au-5Ni-1Cr-Gd alloys; 2 - Au-9Ni-Gd alloys

Table 2

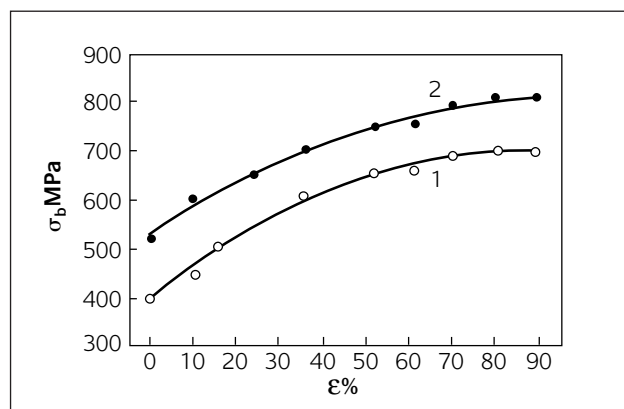
Tensile strength of gold and some gold alloys with or without RE additions in the fully annealed state

Alloy systems	Without RE	With RE	
	σ_b , Mpa	Wt% RE	σ_b , MPa
99.999 Au	130	0.005Ce	220
99.95 Au	180	0.1 RE	280-300
Au-9Ni	550	0.5Gd	700
		0.5Y	750
Au-5Ni-1Cr	400	0.5Gd	520
Au-33Ag-3Cu-2.5Mn	420	0.5Gd	550

The strengthening effect of RE additions in gold or gold alloys includes following mechanisms.

(1) *Solid Solution Strengthening*: The solid solution strengthening effect of the alloying element can be expressed roughly by a parameter $H_s = AB$ (2). Here A is the atomic weight ratio of gold to that of alloying element, which is approximately direct proportional to the ratio of the atom numbers of gold to solute at a particular weight percent; B is the relative difference in atom size between alloying element and gold where $B = (r_{M} - r_{Au}) / r_{Au}$. The H_s parameters of some lanthanide elements are listed in Table 1 and are directly proportional to the lattice expansion, Δa , parameters. This indicates that the solid solution strengthening of RE in gold is attributable to the lattice expansion caused by RE solutes. The order of H_s values for the rare earth metals in gold is $H_s(\text{Sc, Y, Eu}) > H_s(\text{light RE from La to Sm}) > H_s(\text{heavy RE from Gd to Lu})$. When compared with other elements in the Periodic Table, the solid solution strengthening effect of rare earths in gold alloys is less than that of the alkali-earth metals such as Be, Ca, Li, Mg etc, but much greater than that of the transition and other metals (2). So, rare earths are among the best solid solution strengthening elements for gold and gold alloys.

(2) *Precipitation Strengthening*: The limit of the solid solubility of rare earths in gold reduces with a decrease in temperature. Therefore, Au-RE alloy systems are amenable to precipitation strengthening. The precipitation phases in the

**Figure 6**

Work hardening curves of gold alloys: 1 - Au-5Ni-1Cr; 2 - Au-5Ni-1Cr-0.5Gd

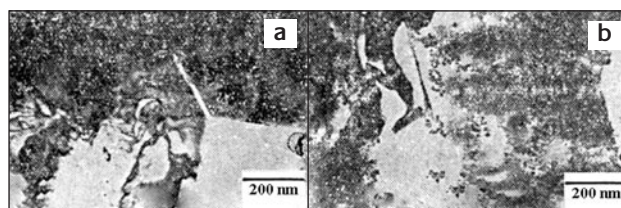
gold-rich Au-RE systems are the gold-rich compounds such as Au_6RE (for La, Ce, Pr, Nd, Pm, Sm, Gd, Tb, Dy, Ho), Au_5RE (for Eu) and Au_4RE (for Er, Tm, Yb, Lu, Sc) (2). The light REs show a higher precipitation strengthening effect than the heavy REs, even in alloy systems containing dilute RE concentrations, because of their lower solid solubility and because gold-richer precipitate phases exist in Au-light RE systems. On the other hand, the precipitation strengthening effect of RE metals is much higher than that of most transition and other metals, although it is inferior to that of Ti and Zr (1,2).

The precipitation strengthening effect is also apparent for gold-based alloys. In Au-9Ni-0.5Gd alloy, a large amount of fine precipitate particles of Au(Ni)₂Gd compound is observed, Fig.7. The particles can hinder dislocation motion and grain growth, which promotes an increase in strength of the alloy.

(3) *Dispersion strengthening by oxides of rare earths*: Oxides of rare earths have large and negative free energies of formation (ΔG_f^0). For example, Y_2O_3 has larger negative ΔG_f^0 value than that of Al_2O_3 in the range of 0~1400°C. So the oxides of rare earths are stable in gold alloys and can lead to strengthening when they are distributed as a dispersed phase (1,8). Dispersion strengthened gold alloys can be prepared by powder metallurgy for bulk material and by internal oxidation for foil and superfine wire of gold alloys.

(4) *Grain size strengthening*: According to the Hall-Petch relationship, the strengthening effect of RE metals in gold or gold alloys is partially attributable to the finer grain sizes that result.

Thus, gold alloys containing rare earths should be strengthened through single or multiple strengthening mechanisms, depending on the concentration of rare earths and the preparation technique of the gold alloys.

**Figure 7**

TEM photos of (a) Au-9Ni and (b) Au-9Ni-0.5Gd alloys, showing fine precipitate particles in the latter

3 Some Applications of gold alloys modified by RE addition

3.1 Gold bonding wire microalloyed by RE and other elements

Gold bonding wire for use in electronics demands high purity, above 99.99%Au, to guarantee the high bonding property and high mechanical properties, which can be achieved by microalloying. The microalloying elements in gold bonding wire cited in patents and references involve most metals in the Periodic Table. As mentioned above, trace RE additions (which can refine the grain size, retard recovery softening, raise the recrystallization temperature, increase the tensile strength and improve the comprehensive properties of high purity gold) are used the most as microalloying elements in gold bonding wire (6,7). As microalloying elements in gold bonding wire, RE metals are often combined with other elements such as Cu, Ag, Be, Ge, Ga, Pt and so on or other RE metals. Of possible RE additions, the light RE elements like Ce, La and Nd are the main microalloying metals. Cerium is often used, together with some heavy RE metals (from Gd to Lu), with a total concentration of 0.0001-0.01% RE. Yttrium can increase the thermal strength and stability of high purity gold, so it is also used as a microalloying element in gold bonding wire. As a trace element, the strengthening effect of RE additions in gold bonding wire is mainly attributable to solid solution and grain size strengthening.

3.2 Precision electrical resistance materials for use in potentiometer windings

The precision potentiometer winding alloys demand, generally, a stable electrical resistance and high durability. A series of Au-based alloys have been used as the precision potentiometer winding materials: Au-Ag-Cu-Mn and Au-Ni-Cr alloys are in common use and substituted successfully for some Pt- and Pd-based alloys. The Au-based alloys show poor wear resistance and low durability in some applications with a higher contact pressure. So, Au-Ag-Cu-Mn and Au-Ni-Cr alloys modified by RE additions (such as Gd and Y) have been developed. Except for high tensile strength and hardness, the RE-modified alloys retained the good conductivity and stability of electrical resistance, due to the dilute concentration of RE. Table 3 listed the specific resistivity of some gold alloys, with and without RE additions, used for potentiometer winding. It can be seen that the increment of resistivity change in the gold alloy caused by

a 0.5%Gd addition is less than 4%, and that the change rate of resistivity after aging 200h at 100°C is less 2%.

Simulated tests to assess the wear resistance of potentiometer windings, made with the gold alloys listed in Table 3 and contacted by a Au-9Ni alloy brush under 5g pressure, were performed (9). The experimental results indicate that the windings made in the Gd-modified gold alloys have a more stable resistance and longer life (wear resistance) than those made of gold alloys without Gd. In these tests, the wear life of gold alloys containing Gd attained 10^5 operations, which is one order of magnitude higher than that of gold alloys without Gd, Table 3. Of the alloys containing Gd, the wear life of the Au-Ni-Cr-Gd alloy is more than three times higher than that of Au-Ag-Cu-Mn-Gd alloy.

3.3 Electrical contacts in RE-modified gold alloys

Gold alloys can be used as breaking or sliding contacts. In such Au-based alloy contacts, the RE additions exist generally as solute, oxide or intermetallics and improve the electrical contact properties. Contacts of RE-modified Au-based alloys have at least the following advantages (10): (i) Retention of good electrical and heat conductivity as well as low contact resistance, due to the dilute concentration of the RE addition; (ii) Control of a fine grain size; (iii) Increase in the recrystallization temperature, thus conferring high structural stability; (iv) Enhanced strength and hardness, thereby conferring a high wear resistance; (v) Reduced arc erosion and anode weight loss; (vi) Resistance to adhesion and without environmental pollution.

In order to verify the wear resistance of some RE-modified gold alloys, simulated tests on frictional couples comprising a Cu-Ni alloy slip ring contacted by gold alloy brushes were carried out (11). Table 4 listed the hardness and the depth of the wear trace of the gold alloy brushes. It can be seen that the brushes of gold alloys with RE additions work hardened during testing. When the hardness difference, ΔH_V , of a brush before and after the wear test is about 1/3 of the original hardness of the brush, the brush had a smallest wear depth. The gold alloys containing Sm just showed this feature and had a higher life of wear resistance than the gold alloys containing Gd which hardened more. The result is essentially agreement with that of Shinohara et al (12).

In gold alloys, dispersion-strengthened by oxides such as Al_2O_3 , ThO_2 , TiO_2 , Y_2O_3 and CeO_2 , used as electric contact

Table 3

Specific resistivity (ρ) and wear life of some gold alloys with and without Gd additions

Alloy	$\rho_{20^\circ C}$, $\mu \Omega \cdot cm$	$\rho_{20^\circ C}$ $\mu \Omega \cdot cm$	$(\rho_{20^\circ C} - \rho_{20^\circ C}) / \rho_{20^\circ C}$ %	Wear Life** (operations)
Au-7Ni-1Cr	22.6	22.9	1.9	3×10^4
Au-7Ni-1Cr-0.5Gd	23.5	23.95	2.0	$> 9 \times 10^5$
Au-33Ag-3Cu-2.5Mn	21.8	22.2	1.85	2×10^4
Au-33Ag-3Cu-2.5Mn-0.5Gd	22.5	22.9	1.8	3×10^5

* $\rho_{20^\circ C}$ is the specific resistivity measured at 20°C for samples aged 200h at 100°C.

** The wear life is that of potentiometer winding made of the alloys listed contacted by a Au-9Ni alloy brush under 5 g contact pressure.

Table 4

The wear depth(ξ) and work hardening of several gold alloy brushes after wear tests on frictional couples with Cu-Ni alloy slip ring (brush pressure 50g, running times 10^6 revolutions)

Brush alloys	Hardness, Hv		Δ ,Hv	ξ , mm
	Before test	After test		
Au-Ni-Gd	187	304	117	0.183
Au-Cu-Ni-Ce	314	330	16	0.238
Au-Ag-Cu-Sm	216	287	71	0.113
Au-Cu-Ni-Sm	220	290	70	0.018

materials, a Au-0.38wt% CeO₂ alloy showed the best comprehensive properties with the smallest anode weight loss and metal migration and the highest resistance to arc erosion and adhesion. Gold alloys, dispersion-strengthened by RE oxides like CeO₂ are excellent electric contact materials (13).

4 Conclusions

Rare Earth (RE) metals are effective strengthening elements in both pure gold and gold alloys. In high purity gold, trace RE additions retard recovery softening and recrystallization and increase the strength. In commercial purity gold and gold alloys, RE additions in dilute concentration reduce the grain size, raise the recrystallization temperatures and enhance the strength. The strengthening effect of RE additions in gold and gold alloys is attributed to solid solution strengthening, precipitation strengthening, grain size strengthening and dispersion strengthening of RE oxides. On the other hand, RE additions show a tendency for dendritic segregation in cast alloys and grain boundary segregation in annealed alloys. Consequently, RE metal additions in gold and gold alloys are generally used in trace amounts or at dilute concentration.

Some RE-modified gold alloys have been developed and their advantageous use for some applications has been illustrated. High purity gold containing trace amounts of RE has been used as a gold bonding wire with high strength. Some gold alloys,

such as Au-Ni-RE, Au-Ni-Cr-RE, Au-Ni-Cu-RE, Au-Ag-Cu-RE, Au-Ag-Cu-Mn-RE and Au-RE-O₂ alloys, have been used as potentiometer winding and electric contact materials. These new RE-modified gold alloys have high resistance stability and wear resistance, long service life and good comprehensive properties. They are being used in industry.

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