



Tripling hardness of gold by micro alloying coupled with cold processing



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ABSTRACT

Gold has broad applications in jewelry, but suffers from low hardness. In the present work, we show that simultaneous addition of 0.1 wt.% Ce and Si can nearly double the hardness of fine gold. We further show that hardness can be tripled by subsequent cold processing. By systematic structural characterizations and thermal analysis, we find that Ce and Si tend to segregate to grain boundaries and impede grain growth. Our work is helpful for development of new gold micro alloys and for design of jewelry that is more wear and scratch resistant.

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1. Introduction

Gold has been utilized since ancient times in a wide variety of applications ranging from culture, decoration to finance, and remains one of the most important materials because of its excellent thermal conductivity, high electrical conductivity, and high corrosion resistance. The arsenic value of gold makes it one of the essential materials for jewelry making [1]. In modern jewelry industry, gold jewelry is fabricated by various techniques, such as press-forming, casting, and electro-forming, etc. [2–6]. Despite the fabrication routes, the value of gold jewelry is largely associated with the purity of gold [1,4].

Gold is one of the most ductile metals and exhibit low hardness, which are beneficial for jewelry fabrication [7]. However, for the same reason, fine gold jewelry can be easily deformed in use [7]. A common approach to circumvent this problem is to increase jewelry thickness to avoid deformation. Nonetheless, the usage of more gold adds more costs on the gold products and thus less profitability. Therefore, enhancing the hardness of fine gold is of

great interest [7] and metallurgists have tried many methods [7–12], among which alloying with trace elements is a basic option. For example, addition of Ti can harden fine gold [9]. The underlying mechanism is attributed to precipitation strengthening [9]. Among the available additions, rare earth elements are of particular interest because not only can they increase the strength through solid solution strengthening, precipitation strengthening, grain refinement and dispersion strengthening, but also retard recovery and recrystallization induced softening [10,11]. It should be pointed out that the amount of addition cannot exceed 1 wt.% (wt.% weight percent hereafter), because the purity has to be maintained to be better than 99% to satisfy the customers' traditional needs [1,7]. According to the customs in gold jewelry industry, such alloys are called gold-based micro-alloys [1,7,8,10,11,13]. Gold-based micro-alloys with addition less than 0.1 wt. % are special types of micro-alloys.

It has been found that rare earth elements and Si are effective in strengthening fine gold [11,14,15]. In the present work, we investigate the effect of simultaneous addition of Ce and Si on mechanical property of gold. We show that hardness of gold can be nearly doubled by simultaneous addition of small amount (less than 0.1% by weight) of rare earth element Ce and Si, and tripled by subsequent cold rolling. We further investigate the microstructure origin leading to the greatly enhanced hardness.

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2. Experimental

The micro alloy was melted in Al₂O₃ crucible by using medium frequency melter (MFM). The amount of addition of Ce and Si is 0.05% by weight, respectively. Ingots of diameter of ~13 mm and thickness of 6 mm were obtained by casting the melt in an argon atmosphere. Chemical analysis was conducted by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Auger Electron Spectrum (AES), and energy dispersive x-ray spectroscopy (EDS) attached to a Nova 400 Nano scanning electron microscope (SEM). Vickers hardness was measured under the condition of 100 g load and 10 s holding. Calibration conducted using standard sample indicated a standard deviation better than ±5% in the measured hardness. Cold rolling was conducted using a rolling mill, and the sample of dimension of 25 × 10 × 2 mm³ was rolled to thickness reduction of 40%, 60%, and 70%, respectively.

To observe the microstructures, the ingots were polished to mirror finish better than 0.05 μm using traditional metallographic techniques followed by etching in hot aqua regia to reveal grain boundary. The microstructures were examined under optical microscope (OM) and SEM. X-ray diffraction characterizations were performed using Co radiation (1.78890Å).

Differential thermal analysis (DTA) was performed using TG-MG Joint Analyzer, STA449C-QMS403C, at heating/cooling rate of 10 °C/min. In situ observations of microstructure change during heating/cooling were conducted with a confocal laser scanning (CLS) heating microscope at heating and cooling of 1 °C/s. A cube sample of polished surface was used. The dimension of the sample was 5 mm × 4 mm × 2 mm.

3. Results

3.1. Chemical analysis

Even though fine gold has high purity, chemical analysis indicates that there are many elements detectable by ICP-MS, as shown in Table 1. However, these impurity elements seem not to be effective strengthening agents due to their extremely low concentration. As shown in Table 1, addition of Ce and Si leads to a few more impurity elements, but their concentration remains on the same level of the initial impurity. It is worth noting that the purity

Table 1
Chemical composition (wt. %) of fine gold before and after micro alloying by Ce and Si, analyzed by ICP-MS.

Element	wt.% Before micro alloying	wt.% After micro alloying
Au	99.98	99.9419
Ce	–	0.048
Si	<0.002	0.0066
Ag	0.0087	0.0027
Cu	0.0008	<0.0003
Fe	0.0012	0.0008
Pb	<0.0003	<0.0003
Bi	<0.0005	<0.0003
Sb	<0.0003	<0.0003
Pd	<0.0003	<0.0005
Mg	<0.0003	<0.0003
As	<0.0003	<0.0003
Sn	<0.0005	<0.0003
Cr	<0.0003	<0.0003
Ni	<0.0003	<0.0003
Mn	<0.0003	<0.0003
Ge	–	<0.0003
Be	–	<0.0003
Y	–	<0.0003
Zr	–	<0.0003
Ti	–	<0.0003

of gold remains to be better than 99.9% after addition of Ce and Si.

While the concentration of Ce measured by ICP-MS (0.048%) is comparable to the nominal addition amount (0.05%), which indicates the success of Ce micro alloying, the concentration of Si seems to deviate from the expected value. To confirm the addition of Si is successful, we further measure the chemical composition of our micro alloy by using AES. Table 2 summarizes the AES measured concentration of Si and Ce together with some of the impurity elements which have been detected by ICP-MS. As can be seen in Table 1, the concentration of Si is 0.045%, nearly the same as the nominal addition amount (0.05%). In addition, the concentration of Ce and the impurity elements measured by AES is almost identical to that by ICP-MS, indicating that the low concentration of Si measured ICP-MS is due to the instrument detecting limitation. The chemical analysis by AES confirmed that the micro addition of Si is as successful as that of Ce.

3.2. Hardness enhancement

Mechanical property of the Au–Ce–Si micro alloy is evaluated by hardness, an important property closely associated with wear and scratch resistance of jewelry. In comparison with the hardness of ~30 HV of pure gold, our Au–Ce–Si micro alloy exhibits a hardness value of 56 HV, nearly double that of pure gold as shown in Fig. 1(a). The enhanced hardness clearly demonstrates that micro alloying by simultaneous addition of Ce and Si is an effective way to strengthen gold. Joining is an important jewelry making technique. During this process, gold is subjected to higher temperature which can cause grain coarsening and thus lower hardness. However, the Au–Ce–Si micro alloy seems to be able to maintain high hardness even after heat treatment. The hardness of the alloy after heat treatment at 345 °C for 30 min is 48HV, which is comparable to that of as-cast alloy.

In the course of gold jewelry making, plastic deformation, such as drawing, forging, and rolling, is almost always involved to process gold into required shape. It is well known that deformation can change microstructures and then affect mechanical properties. To evaluate the effect of plastic deformation on our Au–Ce–Si micro alloy, we use cold rolling to deform the sample. Fig. 1(b) shows the change of hardness as functional of thickness reduction. As can be seen, hardness dramatically increases after cold rolling. The highest hardness achieved is 94 HV, which is more than three times higher than that of pure gold. With such a high hardness, one would naturally raise the question about ductility of the Au–Ce–Si micro alloy, because the common wisdom is that a material of higher hardness tends to be more brittle. However, no cracks can be observed in the sample after thickness reduction up to 70%, indicating that our micro gold maintain good ductility.

The combination of high hardness, good ductility, and thermal stability of the Au–Ce–Si micro alloy is of significant importance. On the one hand, since jewelry making often involves plastic deformation, good ductility indicates the possibility to form the alloy into desired shapes without fracture. On the other hand, the high hardness of our micro alloy after deformation suggests that

Table 2
Comparison of elements and concentrations detected by AES and ICP-MS, respectively.

Element	wt. % By AES	wt. % By ICP-MS
Si	0.045	0.0066
Ce	0.040	0.048
Ge	<0.0003	<0.0003
Be	<0.0003	<0.0003
Y	<0.0003	<0.0003

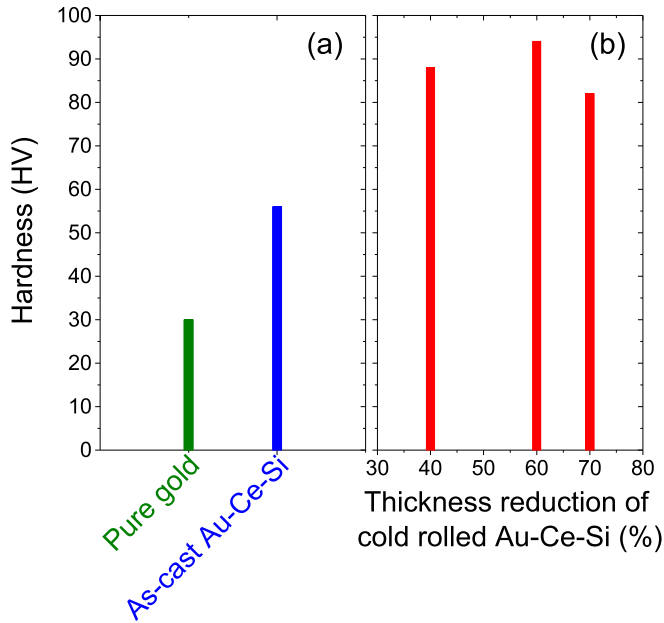


Fig. 1. (a) Hardness of pure gold and as-cast Au–Ce–Si micro alloy. (b) Hardness of Au–Ce–Si as function of thickness reduction during cold rolling.

the jewelry can be much more wear and scratch resistant in use.

4. Discussion

To understand the origins leading to the high hardness of Au–Ce–Si micro alloy, we study the microstructures and phase formation using XRD and microcopy combined with thermal analysis and in situ observation of dynamic microstructure evolution.

XRD pattern of Au–Ce–Si micro alloy is shown in the inset of Fig. 2(a). As can be seen, the Au–Ce–Si micro alloy consists of FCC phase, essentially the same as that of pure gold. Despite the slight increase of lattice parameter, addition of Ce and Si does not substantially alter the crystal structure. However, grain sizes of the micro alloy are greatly reduced. As shown in Fig. 2(a), the Au–Ce–Si alloy mainly consists of equiaxed grains with an average grain size approximately 150 μm , which is much smaller than that of pure gold [12]. According to Hall–Petch relation, smaller grains lead to higher strength, and thus higher hardness [16–18]. However, our estimation following the Hall–Petch equation ($\sigma_0 = 314.28 \text{ MPa}$, $K = 0.25 \text{ MPa m}^{1/2}$) indicates that the increase in yield strength is only ~10%, suggesting that grain refinement is not the main strengthening mechanism with Ce and Si addition.

To reveal the strengthening mechanism by Ce and Si addition, we examined the microstructures using backscattering electron (BSE) imaging, which is sensitive to the distribution of chemical compositions and phases. As shown in Fig. 2(b), the BSE image display dark regions embedded in bright matrix, suggesting the formation of secondary phase after Ce and Si addition. Chemical analysis by EDS indicates that the dark regions are rich in both Ce and Si (Table 3). According to Au–Ce [19] and Au–Si [20] phase diagrams (Fig. 3(a) and (b)), solubility of Ce and Si in Au is nearly zero. Therefore, Ce and Si should have been completely depleted to form secondary phases and segregated to grain boundaries, leading to barrier layer that not only impeded the growth of gold crystal and, but also precipitation strengthening.

The formation of secondary phase after Ce and Si addition is further confirmed by thermal analysis. Fig. 4(a) shows the DTA trace

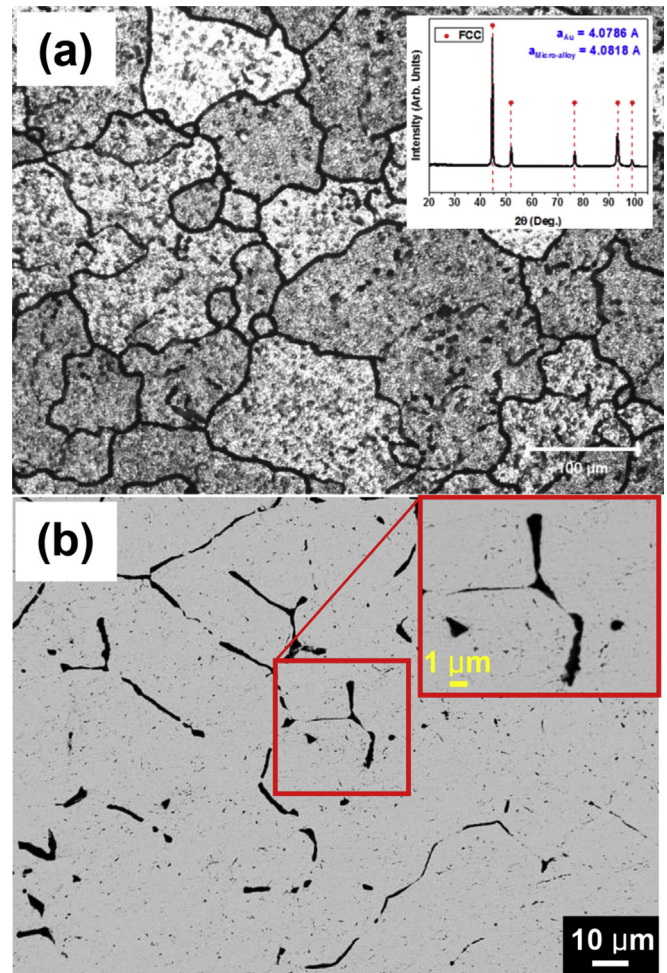


Fig. 2. OM morphology (a) and BSE image (b) of Au–Ce–Si micro alloy. XRD pattern of Au–Ce–Si micro alloy is shown as inset in (a).

Table 3

EDS chemical analysis on the bright and dark phases show in Fig. 2(b).

Elements	Bright region (at. %)					Dark region (at. %)				
	Au	Ce	Si	Fe	Cr	Au	Ce	Si	Fe	Cr
Au	98.28	98.48	98.11	98.75	95.13	98.59	86.29	81.45	93.86	
Si	1.64	1.35	1.89	1.25	4.87	1.34	13.71	17.44	5.85	
Ce	0.05	0.17	0	0	0	0.07	0	1.11	0.56	

during heating and subsequent cooling. Based on the measurement, melting and solidification temperatures are 1072.2 $^{\circ}\text{C}$ and 1043 $^{\circ}\text{C}$, respectively, which are comparable to the melting point of pure gold (1064 $^{\circ}\text{C}$). However, an additional phase transition occurs upon heating at temperature as low as 366.7 $^{\circ}\text{C}$. On the bases of Ref. [14] and Au–Ce, Au–Si, and Ce–Si phase diagrams, it is highly possible that CeAu_2Si_2 phase forms at boundaries, consistent with the EDS measurement. This silicide phase has low melting temperature and higher hardness [14,21].

The conclusion drawn above can be proofed by in situ heat microscopy which is capable of revealing dynamic changes in the structure, kinetics of phase transformation, and thermal stability [12]. Representative images collected at different temperatures during heating and cooling are shown in Fig. 4. When the alloy is heated to 388.9 $^{\circ}\text{C}$, small dots can be observed to emerge (Fig. 4(b)), which is an indication of phase transition. The temperature is well

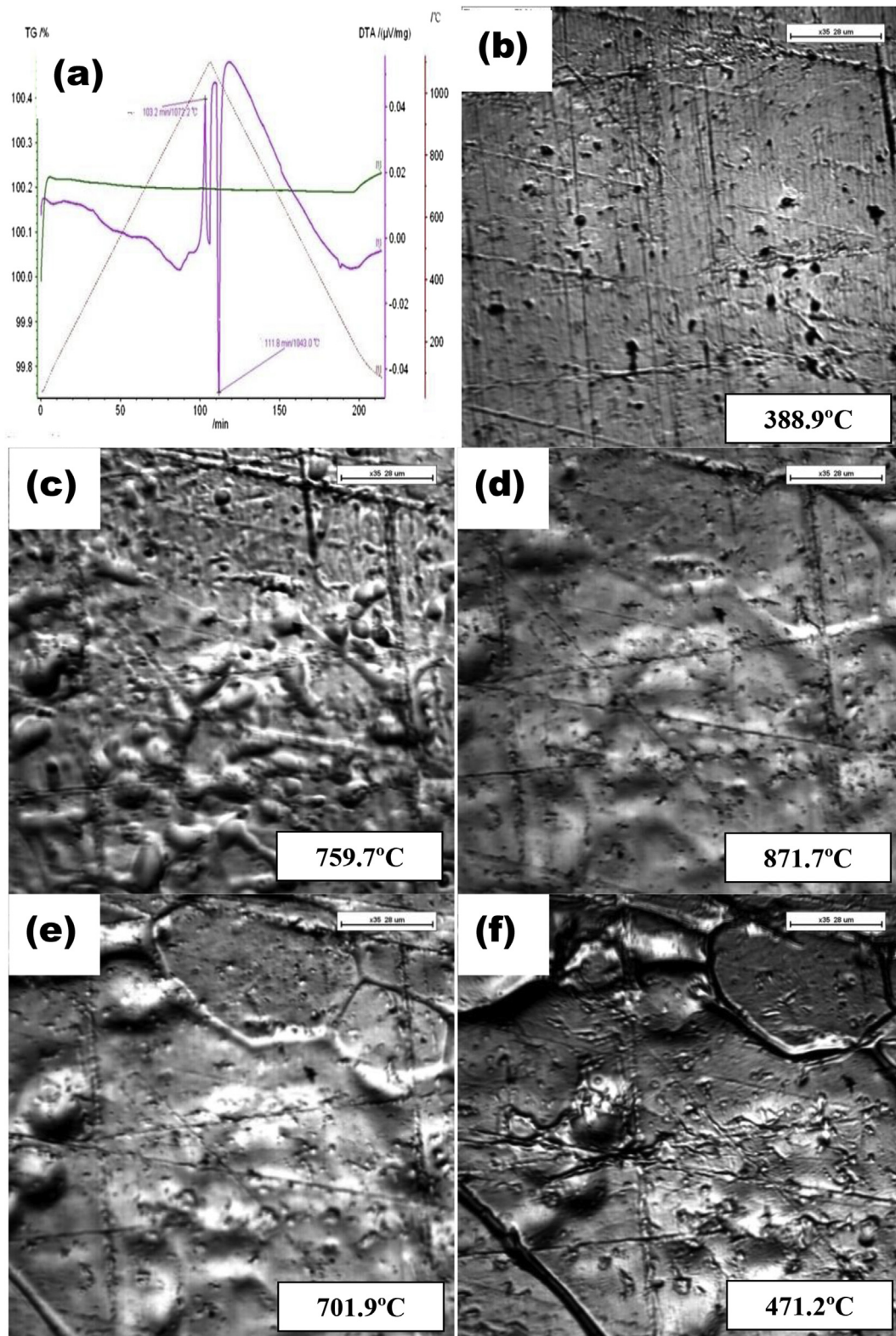


Fig. 3. DTA curve of Au–Ce–Si microalloy(a), and the microstructure change upon heating to (b) 388.9 °C, (c) 759.7 °C, and (d) 871.7 °C. (e) and (f) shows microstructures upon cooling to 701.9 °C and 471.2 °C, respectively.

consistent with the DTA measurement. With increasing temperature, bulge forms (Fig. 4(c)) and grain boundaries can be seen when the surface melt completely (Fig. 4(d)). The shape of grain boundaries is retained upon cooling (Fig. 4(e–f)). Although the alloy is

subjected to a heating–cooling cycle, the grain sizes seem to remain unchanged. This suggests that the Au–Ce–Si micro alloy has excellent thermal stability and explains the high hardness even after heat treatment.

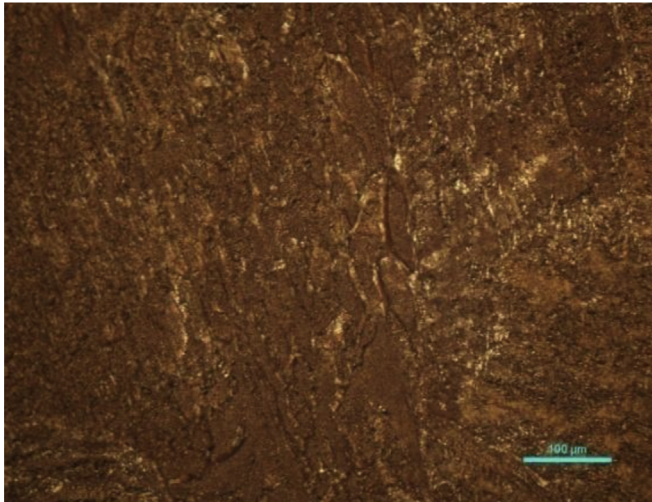


Fig. 4. Microstructure of Au–Ce–Si micro alloy after cold rolling up to 60% thickness reduction.

Fig. 4 shows the microstructures of the Au–Ce–Si alloy after cold rolling up to 60% thickness reduction. Remarkable changes can be observed. The grain sizes decrease to the range of 15 μm –110 μm from the range of 120 μm –550 μm in the as cast sample. The grains are elongated after cold rolling. It is known that plastic deformation proceeds via the motion of dislocations [22]. The severe plastic deformation upon cold rolling can cause increase of dislocation density within grains [22], leading to the high hardness of 94 HV after cold rolling. The decrease of grain size suggest that strengthening by grain refinement may also play a role in enhancing the hardness.

5. Conclusions

In summary, we showed that simultaneous addition of Ce and Si less than 0.1 wt.% can increase gold hardness from \sim 30 HV to 56 HV. By subsequent cold rolling, hardness can be further increased to 94 HV, more than three times higher than that of pure gold. We investigated the underlying origins resulting in the hardness enhancement by systematic characterization using XRD, microscopy, thermal analysis, and in situ observation of microstructure evolution. The main conclusions are the following:

- (1) Ce and Si are effective agents to enhance the hardness of gold. They can result in the precipitation of secondary phase and grain refinement, and thus higher hardness;
- (2) Because of the nearly zero solubility of Ce and Si in Au, they are depleted and segregated to grain boundaries upon solidification. This leads to barrier layer impeding the growth of gold crystals;
- (3) Cold rolling can further introduce and introduce interacting dislocations and reduced grain size, which results in significantly enhanced hardness.

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