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*Gold is an ancient metal, it can be widely used in the electronics, dentistry and jewelry industry. It is also well known that pure gold has good ductility and very lower vickers hardness. These mechanical properties of pure gold definitely lead to easy deformation, scratch, abrasion and so on when pure gold is put into application. Therefore, it is necessary to strengthen pure gold by micro-alloying to avoid its obvious deficiencies and maintain its excellent properties such as yellow color, good thermal conductivity, chemical stability.*

*Our group chose Zr, Ce and Si as the micro-alloying elements, which are no more than 1.0 wt.%, to strengthen pure gold. The investigations showed that Zr, Ce and Si can strengthen pure gold significantly at as-cast from 30HV to 69HV and wrought state to 121HV. In this presentation, we share the investigation to show how Zr, Ce and Si modify pure gold in structure, thermal characteristic, mechanical properties and what the distributions of different phases and elements are. We also present how the new gold materials can be used in jewelry industry.*

# “Strengthening pure gold significantly by no more than 1 wt.% Zr, Ce and Si”

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## 1. INTRODUCTION

Gold, as an ancient metal, has been utilized over 8000 years by mankind. To some degree, gold is a symbol of human civilization. Gold has beautiful yellow color which makes it full of charm and high aesthetic value. Gold also has good electrical conductivity, good thermal conductivity, chemical stability and good weldability [1]. These special properties make it widely used in the electronics industry [2-3], semiconductor industry [4], jewelry industry [5], materials protection [6], dental industry [7] and so on. As we know, pure gold has low Vickers hardness (30), yield strength and Moh's hardness (2.5), these mechanical properties limit its application in specific industries and make pure gold products easily subjected to deformation, scratch and wear [8]. Micro alloying is the basic method to keep the good properties and avoid the weak aspects of gold [9].

Actually, gold based micro alloys have important significance in many application fields. In electronic industry, micro-gold alloy with 0.1 wt.% copper adding can not only increase gold wire strength but also make stronger binding with the aluminum matrix [10]. In dental industry, the gold micro alloy made by adding indium 0.2wt.% and zinc 0.1wt.% to pure gold has warm color and good filling effect [11]. In jewelry industry, jewelers and jewelry designers attach importance to the hardness of gold because gold with high hardness means precise works and low costs. For choices of the elements to strengthen pure gold there are many suggestions which were already presented [12-16]. Among them, Si and Ce are thought to be effective in strengthening pure gold, which was proved to be very effective [17]. Zr is also a good candidate to strengthen gold [18]. Zr, Si and Ce totally less than 1 wt.% as additives to strengthen pure gold has not been discussed. Our group made Au-Zr-Si-Ce micro-alloy and focus our attention on the aspect to investigate how these additions influence microstructures and mechanical properties of pure gold.

## 2. EXPERIMENTAL PROCEDURES

Before melting the component of each element was prepared, gold content is more than 99.99 wt.%, Zr, Si, Ce are all high pure. Gold was alloyed with Zr, Si, Ce in a medium frequency melter (MFM) in an  $Al_2O_3$  crucible and cast under an inert argon atmosphere. In order to check whether the alloy is successful chemical analysis of the cast alloy was conducted by using inductively coupled plasma mass spectrometry (ICP-MS) and ICP-AES respectively. To evaluate the mechanical properties of the Au-Zr-Si-Ce micro-alloy, Vickers hardness tests by High Quality Hardness Tester were conducted on the condition of 100-g load and a 10-s holding time. Samples were prepared for microstructural investigation using optical microscopy (OM) and a Nov.400 Nano scanning electron microscope (SEM) with an energy dispersive X-ray spectrometer (EDS) for element analysis. The mechanical properties of the micro alloy are closely related to the species and distribution of the internal phases. Samples were milled by Focused Ion Beam (FIB) and transmission electron microscope (TEM) was used to do deep investigation. Differential thermal analysis (DTA) test also applied to the micro-alloy using a Joint Analyzer STA449C-QMS403C. The heating TG-MG Cooling rate was 10 °C/min degrees and, the selected maximum and Temperature was 1100 °C. The heat microscope tests were also conducted with a confocal laser scanning (CLS) heating microscope (model Lasertec 1LM21SVF17SP). The heating and cooling rate was set at 1 °C/s. So the thermal characteristics of the micro-alloy can be revealed statically and dynamically.

## 3. RESULTS

### 3.1 CHEMICAL ANALYSIS

Sometimes, because the difference of elemental vapor pressure chemical composition of each element may have obvious changes before and after melting, this will lead to the failure of micro alloying. In order to make sure that the chemical composition reach to our requirements and, at the same time, have objective components of each elements we use ICP-MS and ICP-AES to do chemical analysis. The results of original composition, testing composition and adjusted composition were shown in Table 1. Because testing results are different when the micro-alloy was tested by ICP-MS and ICP-AES respectively, we adjusted the testing results to have a rational composition. The basis of composition adjustment is which tested results are close to the original chemical composition. The testing results indicate that the alloy was successful.

Table 1 Original composition, Comparison of elements and concentrations detected by AES and ICP-MS, respectively, and adjusted composition

Element	wt. % original composition	wt. % by AES	wt. % by ICP-MS	wt. % adjusted composition
Au	99.05	99.091	99.2828	99.0836
Zr	0.78	0.75	0.63	0.75
Ce	0.06	0.063	0.072	0.063
Si	0.10	0.096	0.0078	0.096
others			0.0074	0.0074

### 3.2 VICKERS HARDNESS TESTING

As it known, The Vickers hardness of pure gold is approximate 30HV. But the Vickers hardness of the Au-Zr-Si-Ce micro alloy is 69HV. The results show that the addition of Zr, Si and Ce (<1 wt.% totally) can increase gold hardness significantly. In addition, three samples were applied deformation, the deformation rates are Reduction In Area (RA) 40%, 60%, 70%, respectively, when deformation rate reaches to RA70% cracks were found. The Vickers hardness are shown in Table 2. We can see from the results that deformation can further increase the Vickers hardness of the sample. The peak hardness 121HV was achieved when the sample was deformed to RA 60%.

Table 2 Reduction In Area (RA) and corresponding HV value of Au-Zr-Ce-Si micro alloy

Original thickness and HV value	RA 40% and HV value	RA 60% and HV value	RA 70% and HV value
1.2 mm	0.72 mm	0.48 mm	0.36 mm
69HV	113HV	121HV	94HV

### 3.3 MICROSTRUCTURE FEATURES

#### 3.3.1 METALLOGRAPHIC CHARACTERISTICS

After finishing etching by aqua regia, the sample was applied to Optical Microscopy testing (OM). Under OM we can see that the crystals are equiaxed, the average grain sizes are 20 μm (Fig. 1(a)). Compared to the Au-Ce-Si micro alloy with an average grain size approximately 150 μm (Fig. 1(b)) the crystal grains of our sample are well refined, which indicates that Zr has further effect in refining grain size.

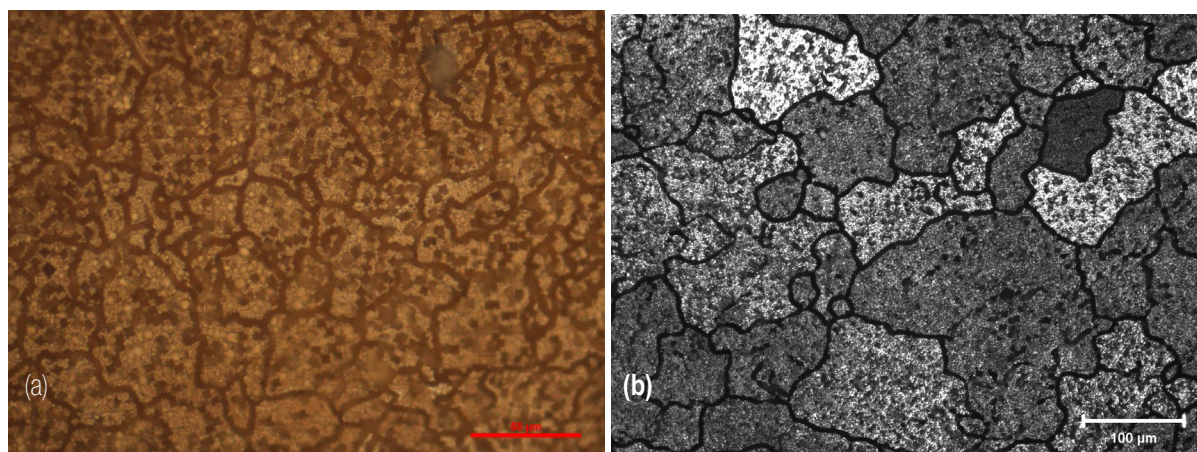


Figure 1. Light Optical microscope image of the Au-Zr-Ce-Si micro-alloy after etching (a) and the Au-Ce-Si micro-alloy after etching (b)

### 3.3.2 SEM Testing

In order to further reveal the distribution of the elements in the sample, SEM was used to do the testing. From Figure 2 we can see chemical composition segregate at the grain boundary and in the grain spaces. Some components were analyzed by using EDS shown in Table 3. Au, Si and Ce all can be detected except Zr, in order to avoid machine problem we did EDS analysis in other two analytic center, there was still no Zr to be found. Because we quench the sample quickly we infer that the distribution of Zr is uniform in the sample. From testing results shown in Fig.2 (a-b) Si contents are 0.26 wt.% and 0.24 wt.% in bright region while Si content are 2.52 wt.%, 2.78 wt.% and 3.11 wt.% shown in Fig.2 (c-e) in the dark region, Si content in bright region are significantly lower than that of the dark domain; Ce content in bright region are .03wt.% and 0.31wt.% shown in Fig. 2(a-b) while Ce content in dark field are 0.02 wt.%, 0.10 wt.% and 3.18 wt.% (Fig.2 (c-e)).

On the average, Ce composition in bright region are also lower than Ce composition in dark region. In order to further discover the microstructures of Au-Zr-Si-Ce micro-alloy by SEM and how the microstructures change after Reduction In Area(RA), we chose Fig. 2(f) before RA and Fig. 2(g) after RA 60% to do some comparison. We can find from Fig. 2(g) that each grain is prolonged to certain direction and tend to be parallel each other as well as the prolonged grain boundaries. It can be seen that not only the grains but also the grain boundaries no cracks appear, which indicates that Au-Zr-Si-Ce micro-alloy can keep its ductility when Reduction In Area(RA) reaches to 60%. On the other hand, deformation increases the dislocation density of the micro-alloy, therefore, give rise to the hardness improvement of the micro-alloy.

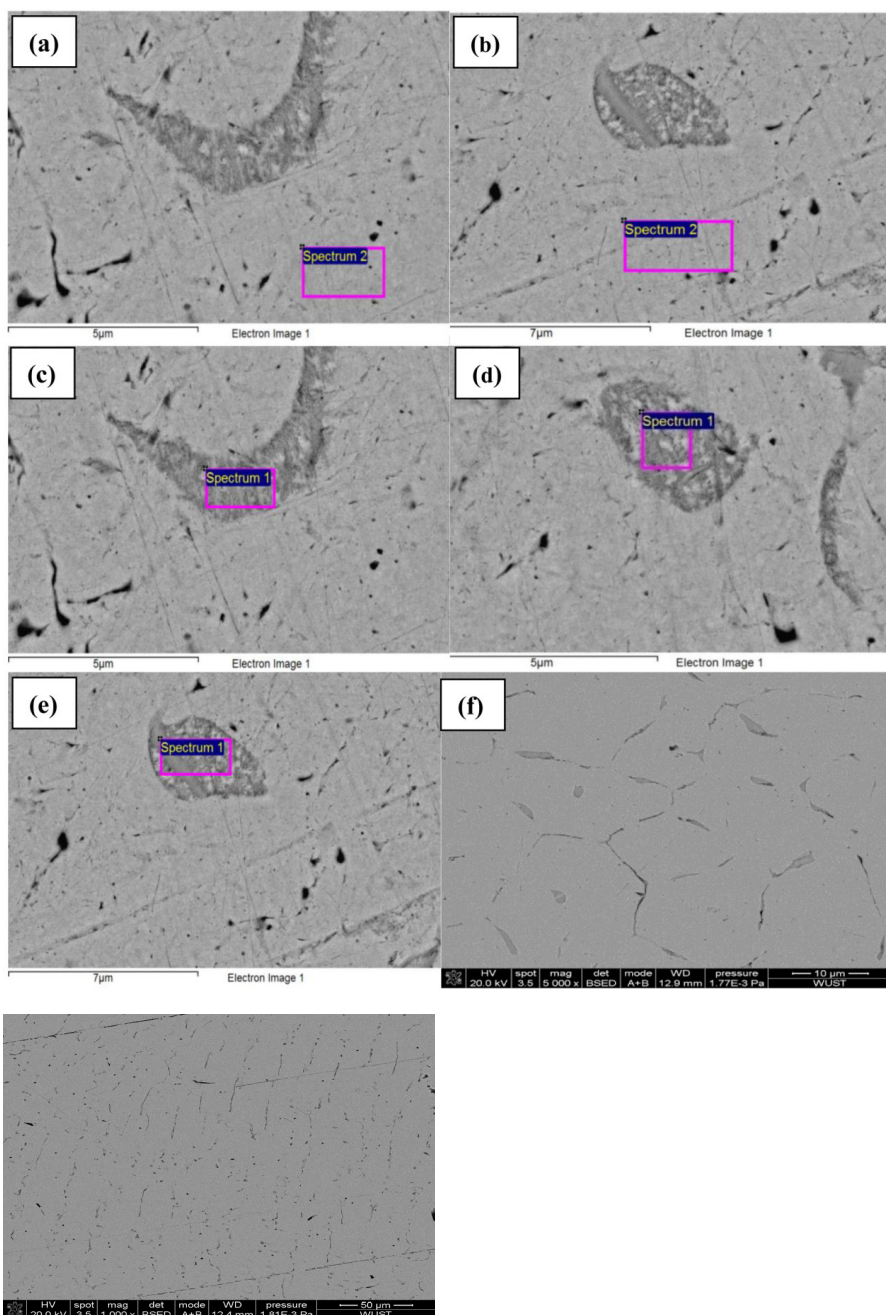


Figure 2(a-g). SEM images of the Au-Zr-Ce-Si micro-alloy

Table3 EDS chemical analysis on the bright and dark phases shown in Fig. 2(a-e)

Elements	Bright Region in Fig.2(a)	Bright Region in Fig.2(b)	Dark Region in Fig.2(c)	Dark Region In Fig.2(d)	Dark Region In Fig.2(e)
Si K	0.26 (wt %)	0.24 (wt %)	2.52 (wt %)	2.78 (wt %)	3.11(wt %)
Ce L	0.03 (wt %)	0.31 (wt %)	0.02 (wt %)	0.10 (wt %)	3.18(wt %)
Au M	99.71 (wt %)	99.45 (wt %)	97.46 (wt %)	97.12 (wt %)	93.71(wt %)
total	100.00	100.00	100.00	100.00	100.00

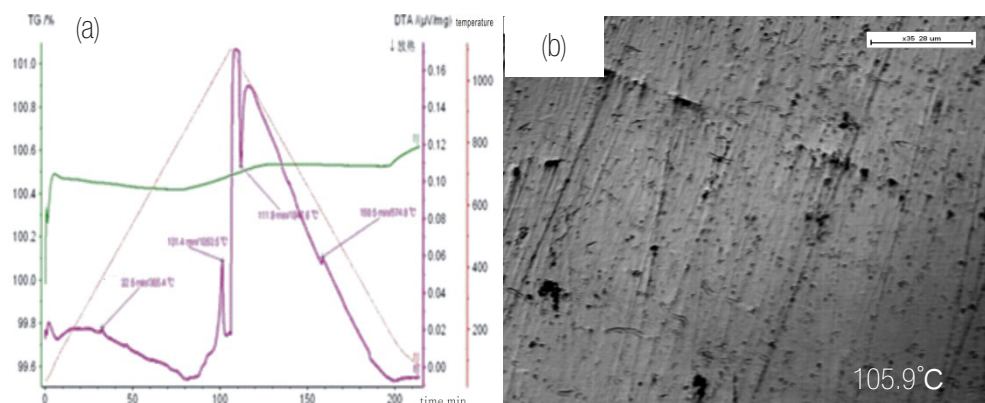
### 3.4 DTA ANALYSIS AND HEATING MICROSCOPE FEATURES

#### 3.4.1 DTA TESTING

DTA is a very useful method to detect thermal characteristics of materials, it was conducted to find what the thermal changes were caused by the trace additives of Zr,Si and Ce. This can further confirm the formation of secondary phase in the Au-Zr-Ce-Si micro-alloy. Fig. 3(a) shows the DTA trace during heating and subsequent cooling. Based on the measurement, melting and solidification temperatures are 1053.5°C and 1042.5°C, respectively, which are little bit lower to the melting point of pure gold (1064°C). However, an additional phase transition occurs upon heating at temperature as low as 365.4 °C.

#### 3.4.2 HEATING MICROSCOPE FEATURES

Using in situ heat microscopy can reveal dynamic changes in the structure, kinetics of phase transformation, and thermal stability more visually compared to DTA. Representative images collected at different temperatures during heating and cooling are shown in Fig. 3. The surface is identical when the alloy is heated to 105.9°C(Fig.3(b)), When the temperatures is at 368.6°C (Fig. 3(c)) several small dots can be observed to emerge, which is an indication of phase transition beginning, the temperature is well consistent with the DTA measurement. Then more dots suddenly disemboque at 398.9°C, With increasing temperature, liquid phase transferred from dots which often pour out from the grain boundaries cover the surface partly at 621.2 °C(Fig. 3(d)) and then the surface melt completely when the alloy is heated 854.7°C (Fig. 3(e)). During the course of cooling recrystallization can be seen until the surface is stable at 271.6°C (Fig. 3(f)). Although the grain sizes grow slightly large when they are subjected to a heating-cooling cycle, it seems that the additions of trace Zr,Si and Ce can restrain growth of crystal grains to some degree. This suggests that the Au-Zr-Ce-Si micro-alloy has excellent thermal stability.



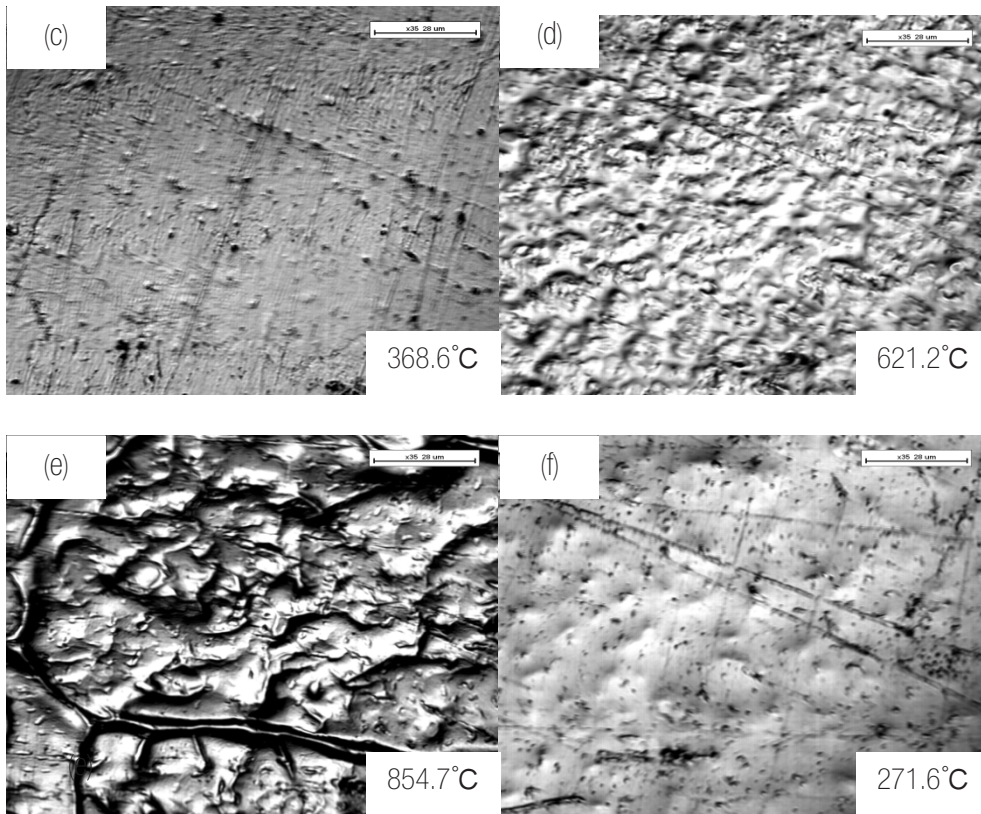


Figure 3. DTA curve of Au-Zr-Ce-Si microalloy(a), and the microstructure change upon heating to (b)105.9°C, (c)398.9°C, (d)621.2°C. and (e) 854.7°C, (f) shows microstructures upon cooling to and 271.6°C, respectively.

### 3.5 TEM ANALYSIS

The mechanical properties have close relationship with its phase types and phase distributions of the Au-Zr-Si-Ce micro-alloy. There is no doubt that TEM analysis can provide scientific data to settle this problem. Our group firstly chose Ion Mill (FEI QUANTA 200 3D) to do sample preparations, when samples were thinned to certain thickness most of them are easy to curl, therefore, Ion Mill is not appropriate to do sample preparations of gold based micro-alloy. Then Focused Ion Beam (FIB) was applied to get small sample slice from sample surface by FIB, then the thickness of the micro-alloy is thinned by FIB to approximate 110 nm, Samples thickness of gold based micro-alloy more than 140nm often incur bad penetrability for TEM testing. TEM testing was used to get phase types, the results are shown in Fig.4. The diffraction patterns in Fig.4(c) and Fig.4(d) are gotten from Fig.4(a) where bright region exists and Fig.4(b) respectively. Fig.4(a) in bright region exhibits  $\langle 001 \rangle$  FCC phase, Fig.4(b) exhibits  $\langle 110 \rangle$  FCC phase. It seems that sample is uniform and consists of a solid solution FCC phase, there may have some problems which have much to do with the small sample slice milled almost inside one crystal grain.

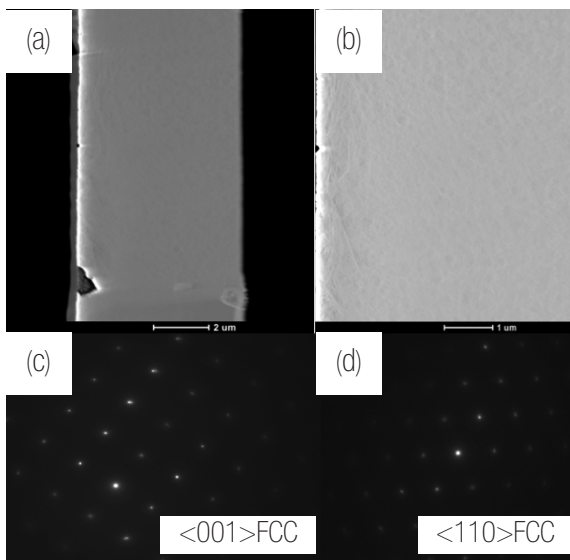


Figure 4. TEM images(a-b) of the Au-Zr-Ce-Si micro-alloy and their diffraction pattern(c-d)

## 4. DISCUSSION

From the literatures we know that whichever of trace Zr, Si or Ce is effective to strengthen fine gold. If we put three elements (<1 wt. %) together as additions to make gold based micro-alloy they should work to improve the hardness of fine gold. The process of micro-alloying is proved successfully because the chemical composition before alloying is almost the same to the chemical composition after alloying which are shown in table 1. The success to make an Au-Zr-Si-Ce micro-alloy is the firm foundation to do deep investigation on how the trace additives influence the microstructures and mechanical properties of fine gold. In order to better understand these influences we should make it clear firstly what the distributions of each element and phases are.

For the distributions of elements, it can be seen in Fig.2 clearly that chemical analysis by EDS indicates that the dark regions are rich both in Ce and Si and bright regions are poor in Ce and Si after Zr, Ce and Si addition. No finding of Zr via EDS seems to be strange and needs to do deep investigation, as for the distributions of Zr in Au-Zr-Si-Ce micro-alloy we infer that it is uniform, this conclusion is supported that Zr solid solubility in Au reaches to 2 wt.% at 800°C [13]. With rapid cooling the even distribution of Zr in sample could be achieved.

As we know, elements often form certain phases to influence many characteristics of materials. Based on the even distribution of Zr in sample and TEM testing results which confirmed the existence of solid solution FCC phase we know FCC phase is consisted of Au as solvent and few Zr as main solute. According to Au-Si [19] and Au-Ce [20] phase diagram, solubility of Si and Ce in Au is nearly zero. Therefore, Si and Ce should have been completely depleted to form secondary phases and segregated to interdendritic spaces and grain boundaries, this results were proved especially by Fig.2(f), the BSE image display dark regions embedded in bright matrix, suggesting the formation of secondary phase. The formation of secondary phase is further confirmed by thermal analysis. Fig. 3(a) shows the DTA trace during heating and subsequent cooling. When the temperature is as low as 365.4 °C additional phase transition occurs. The phase transition temperature 365.4 °C is consistent to the testing results by in situ heat microscopy which indicated phase transition beginning at 368.6 °C (Fig. 3(c)) when several small dots can be observed to emerge. This phase transition temperature of Au-Zr-Si-Ce micro-alloy is almost the same to the Au-Si-Ce micro-alloy whose phase transition temperature is at 366.7 °C [17]. These testing results give firm evidence that Zr addition had no influence on the phase transition initially, they also give support that our inference about even distribution of Zr in sample is rational. On the bases of Ref. [10] and Au-Ce, Au-Si, and Ce-Si phase diagrams, it is highly possible that CeAu<sub>2</sub>Si<sub>2</sub> phase forms at boundaries. This silicide phase has low melting temperature and higher hardness [17].

As shown in Fig.1(a), the Au-Zr-Si-Ce micro-alloy consists of equiaxed grains with an average grain size 20 μm. Compared to the Au-Zr-Si-Ce micro-alloy which has an average grain size approximately 150 μm in Fig.1(b), our sample is further refined significantly because of Zr addition. Based on crystalline law of metallic materials, Zr solute forms many crystalline nuclei which prevent each grain from growing large, which naturally refines the grain size of fine gold. Due to the very low solubility of Si and Ce, they tend to segregate and distribute in the grain space and to grain boundaries even the cooling speed is very high, this was proofed by heat microscopy testing in Fig.3 during the heating and cooling circle. The segregation of Si and Ce likely form many barrier layers to impede growth of crystal grains. Therefore, 20 μm grain size of the Au-Zr-Si-Ce micro-alloy is attributed to the effectiveness of Zr, Si and Ce altogether in refining grain size. By the addition of Zr, Si and Ce the hardness of pure gold is increased from 30HV to 69HV. With subsequent cold rolling to 60% RA, hardness of the gold micro-alloy can be further increased to 121HV. There are no doubt that grain refinement is one of factors which lead to 69HV. According to Hall-Petch relation, smaller grains lead to higher strength, and thus higher hardness [21]. Besides the grain refinement, if we analyze the phase types and their distribution of the gold micro-alloy we can easily draw a conclusion that FCC solid solution and second precipitation are the other factors which contribute to strengthened hardness.

## 5. CONCLUSIONS

We made a gold based micro-alloy by adding trace Zr, Ce and Si which is no more than 1 wt.%. We also did investigation systematically using ICP-MS, ICP-AES, High Quality Hardness Tester, DTA, Heat Microscopy, OM, SEM and TEM. The conclusions are as follows:

- (1) Zr, Si and Ce are all effective to refine pure gold, addition of less than 1 wt.% Zr, Si and Ce can refine grain size of gold to 20 μm.
- (2) The addition of trace Zr to Au-Si-Ce micro-alloy will not change its initial phase transition temperature.
- (3) Gold hardness can be increased from 30HV to 69HV by addition of less than 1 wt.% Zr, Si and Ce. The hardness can be further increased to 121HV by subsequent RA 60% cold rolling.
- (4) Strengthening mechanisms of the Au-Zr-Si-Ce micro-alloy are mainly FCC solid solution Strengthening, second precipitation strengthening and grain refinement strengthening.

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