Microstructures and Hardness Changes of Au0.1Be Under four Strengthening Methods

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Abstract: With the epidemic of coronavirus pneumonia (COVID-19) worldwide gold price reaches to a new heights, which inevitably increase the costs of gold products especially jewelry industry. The jewelry industry including other industries need harder gold based microalloy to produce more delicate, more light but bigger size gold products. We prepared 3 gold based micro-alloys --Au0.1Li,Au0.1Be and Au0.1B an tested that Be is the most effective element in strengthening fine gold. With the 0.1wt.% Be additions the hardness of fine gold is improved from 30HV to 69HV and the grain sizes of fine gold are significantly refined from the range of 300 -700um to the range of 6-30um. Thereafter, work hardening, Supercooling testing, Heat Treatment and Nitrogen Ion Implantation testing were applied to see how they influence the hardness and microstructures of Au0.1Be.

1. Introduction

Gold is an ancient metal, known as the precious metal among precious metals. The charming yellow color and long history makes it has high aesthetic and cultural values. Gold also has many excellent properties including electrical conductivity, thermal conductivity, chemical stability, weldability[1-2], excellent castability, processability and biocompatibility[3]. Based on the homepage data of World Gold Council, the world demands for gold are divided into four sectors-jewelry, investment, central bank reserves and industrial technology. In terms of specific applications, gold and its alloys are used in jewelry industry[4], financial field, electronic industry (as a connecting material for circuit board[5]). Gold is an ideal material for electronic sensors[6], semiconductor, photoelectron, micro system composition[7], surface protection, electrodeposition molding[8-9], special welding materials[10]and dentistry [11].

However, the low Vickers hardness (30HV), yield strength and Mohs hardness(2.5) of high-purity gold makes it has obvious defects in many industries, such as easy deformation, scratch, wear and more costs[12]. In the specific application, we hope to keep the excellent properties of high-purity gold, such as color, good conductivity, thermal conductivity, weldability, chemical stability, etc, but also hope that the hardness and strength of gold can be substantially improved. Due to Coronavirus disease (COVID-19) pandemic, countries have increased the amount of market capital which pushed up the price of gold to a high level. Jewelry industry which represents the largest source of annual demand for gold and still accounts for around 50% of total demand has the strong desire to develop a
new gold based micro-alloy (especially in eastern jewelry market), which master alloys can not exceed 0.1wt.% but hardness is more than 100HV in order to make less weight bigger size, more delicate and attractive gold jewelry. In the aspect of gold strengthening, Ning Yuantao has done a lot of research [13-15], who summarized the application of gold microalloy in many fields and pointed out that some elements with light atomic weight, such as Li, Na, K, Be, Mg, Ca and Sr, have high solid solution strengthening coefficient (HS) value. Rare earth metals also have high HS value. In rare earth metals, HS (SC, Y, Eu) > HS (light rare earth, from La to Sm) > HS (heavy rare earth, from Gd to Lu)[16-18]. Zhou Xinming and Li Yinglong also analyzed the factors affecting the strengthening of gold. It was pointed out that adding Zr (0.1%), Ba (> 0.01%), Ta (0.3%) or Nb (0.3%) in pure gold can refine gold grain sizes and strengthen gold. In addition, the addition of Bi (> 0.1%) or Pb (> 0.02%) will form low melting point compounds with gold and enrich at grain boundaries, resulting in micro alloy brittleness [19-20]. Xiang Xiongzhi and Li yine pointed out that the rare earth element yttrium has good strengthening effect. Generally, the addition amount of yttrium is controlled within 0.02% - 0.08%, and 0.05% - 0.06% of Zr, Ni and Sn are added at the same time [21-23]. However, on the condition of less than 0.1wt.% additions in gold we haven’t retrieved a kind of gold base micro-alloy which Vickers Hardness as cast is more than 60HV. In order to find harder gold base micro-alloy we chose low atomic number elements Li,Be,B that have high HS and made three gold based gold samples to do deep investigations.

2. Materials and methods
Fine gold (Purui New Materials ,99.99 wt%) and addition elements Li,Be and Be(the purity of all additive elements are more than 99.95 wt.%) were prepared. 3 samples of gold-based micro-alloy shown in table 1 were made one by one in a medium frequency vacuum induction furnace (VIF) in an Al2O3 crucible and cast under an argon atmosphere, respectively. To evaluate the mechanical properties of the 3 samples, Vickers hardness tests by BUEHLER Hardness Tester were conducted on the condition of 100g load under 10s holding time, the results were also shown in Table1. Then sample 2 which has the highest Vickers Hardness compared with the other samples was selected to do more tests to discover its characteristics. The Sample 2 was prepared for micro structural investigation using optical microscopy (OM) and a Nova400Nano Scanning Electron Microscope (SEM) with an energy dispersive X-ray spectrometer (EDS) for element analysis. In order to disclose the crystal structure of the sample 2, X-ray Diffraction (XRD, model X’Pert PRO DY2198) testing was applied. Sample was milled by Focused Ion Beam(FIB) and transmission electron microscope (TEM) was used to do deeper investigation of the crystal structure. For improving the hardness of gold, the researchers have proposed hardening methods such as microalloying hardened coupled with work hardening, heat treatment hardening, surface hardening[24] and Supercooling hardening to take hardness of gold to new heights.

For work hardening, the sample 2 was cut into a sheet which size is 25(length)*10(width)*2(thickness) mm3 by wire cutting, then the sheet was polished and passed a rolling mill. The deformation rate was 40%, 60% and 70% shown in table 2, and no annealing treatment was carried out. The sample 2 was also prepared for heat treatment on the condition of 560°C for 20minutes in a furnace. Thereafter, the sample was taken out and cooled into water immediately. The sample 2 was also used to do surface treatment – nitrogen ion implantation that was chosen because gold and nitrogen can form intermetallic compounds to strengthen gold. There are two kinds of Au and N compounds, AuN3 and Au2N [25]. The name of the instrument is composite ion implanter(model LZD-800). Testing conditions are that the injection dose 2.4 * 1017/cm-2, the injection time 20 minutes and the accelerating voltage 65kv. For supercooling hardening, sample was prepared and melted in a new Al2O3 crucible by welding gun without gas protection. At the same time, Iron mold was cooled by liquid nitrogen until frost layer appears on the surface of the iron mold. Then the melting sample was poured into the iron mold.
Table 1  3 Samples’ Composition and Vickers Hardness

| Sample number | elements | composition after alloyed | Vickers Hardness |
|---------------|----------|----------------------------|------------------|
| 1             | Au 99.9wt.% | Li 0.1 wt.%                | 63               |
| 2             | Au 99.9 wt.% | Be 0.1 wt.%                | 69               |
| 3             | Au 99.9 wt.% | B 0.1 wt.%                 | 58               |

Table 2 Thickness and Reduction In Area (RA) of sample 2

| RA rate | Original | 40% | 60% | 70% |
|---------|----------|-----|-----|-----|
| thickness | 2.2mm | 1.32mm | 0.88mm | 0.66mm |

3. Results and Discussion

3.1 Microstructure testing

In order to examine why the sample 2 has 69HV compared to 30HV of fine gold, OM and SEM were utilized to observe the sample 2 shown in Fig.1 and Fig.2. We found that the grain sizes of fine gold whose grain sizes range from 300 um to 700um shown in Fig.3 were substantially refined because of trace Be additions. The structure of the sample is typical dendrite. the grain sizes are relatively uniform. The arrangement of the first grade dendrites is not very regular, but most of the secondary grade dendrites are approximately parallel. There are also a few equiaxed crystals which are distributed among the dendrites. The length of main dendrites is larger, some of them can even reach 120um, but the proportion is very low. The secondary grade dendrites are the main part, and the size range is between 6um and 30um.
3.2 XRD and TEM testing

We observed that wide grooves distribute between grain boundaries in the sample 2 shown in Fig.2 because of aqua regia etching. It may be attributed to different solubility in aqua regia between dendrites and phase that was originally located along grain boundaries. To make it clear XRD and TEM testing were conducted. XRD shown in Fig.4 presented that Lattice Parameter (angstrom) of the sample 2 is 4.0743 which indicated only one phase FCC in the sample 2. With the help of Focused Ion Beam (FIB) a flake of the sample 2 was prepared shown in Fig.5 and then was tested by TEM. From the diffraction patterns we were able to identify an FCC solid solution phase along with the Au3Be intermetallic phase shown in Fig.6. Then we can make a conclusion that the sample 2 is made of the dendrite phase (FCC solid solution) and Au3Be intermetallic phase that is distributed along the grain boundaries.
Figure 4 XRD results including one phase: gold solid solution (FCC)

Figure 5 Milling flake by Focused Ion Beam (FIB)
3.3 Work hardening
Deformation changes the microstructure of metals and their alloys, which inevitably leads to the changes of mechanical properties of metals. According to practical experience, the hardness of metal or their alloys will increase after deformation, while the ductility will decrease to some degree. The extent of hardness increase and the degree of ductility decrease vary with different metal materials. In order to disclose the relationship between deformation and mechanical properties sheet of the sample 2 was prepared to be processed by rolling mill. Reduction In Area, thickness, HV value and surface quality are shown in Table 3. The results presented that the sample’s hardness was improved significantly from 69HV to 112HV when the reduction in area rate is 60%. As original area rate reduced to 40% fine fractures were observed on the surface of the sample 2. But the fine fractures did not developed during the course of reduction rate from 40% to 70%. The microstructures of the sample 2 in reduction in area rate 60% were exhibited in Fig.7. It can be seen that the grains are obviously elongated under external rolling pressure, and the grains have certain directional arrangement. “Fine fractures” actually are not real fractures, they are Au3Be phase shown in dark area similar to real fractures. Therefore, the sample 2 has good ductility. OM testing also disclosed the grain elongation along certain directions shown in Fig.8.

| RA rate | Original | 40% | 60% | 70% |
|---------|----------|-----|-----|-----|
| thickness | 2.2mm | 1.32mm | 0.88mm | 0.66mm |
| HV value | 69 | 100 | 112 | 102 |
Surface quality | smooth | fine fracture | fine fracture | fine fracture

Figure 7. SEM image of sample 2 in reduction in area rate 60%

Figure 8. Optical microscope image of sample 2 in reduction in area rate 60%

3.4 Supercooling testing
We took out the cast ingot of the sample 2 when the iron mold cooled by liquid nitrogen was the same with room temperature. Then hardness tester and OM were applied to get the mechanical properties and microstructures. The result showed that the hardness of the sample 2 decreased from 69HV to 33HV. Grain sizes changed from the almost dendrites with average grain size of 20um to grain equiaxed with the size range 150-250um(an average of 200um). That exceeds our expectations. The reason is that the temperature of liquid nitrogen is very low, which causes the occurrence of deep supercooling that promotes the rapid growth of grains.
Figure 9. Optical microscope image of sample 2 after supercooling

3.5 Heat Treatment
Under the condition of 560℃ for 20 minutes in a furnace the hardness and microstructure were tested. The hardness of the sample decreased from 69HV to 35HV. The microstructures almost dendrites transformed into equiaxed crystals which sizes become larger in the range of 30μm-70μm shown in Fig.10.

Figure 10. Optical microscope image of sample 2 after heat treatment

3.6 Nitrogen ion implantation testing
After nitrogen ion implantation the hardness of the sample 2 decreased from 69HV to 38HV. The grain sizes range from 30μm to 60μm and their shapes are neither dendrites nor typical equiaxed crystals but Irregular polygon shown in Fig.11. It can be seen that nitrogen ion implantation does not improve the hardness of the sample 2, on the contrary, it caused hardness decrease. It may have much to do with the temperature 380 ℃ of the working chamber while nitrogen ion implantation, which makes the sample subjected to heat treatment to certain extent.
Figure 11. Optical microscope image of sample 2 after nitrogen ion implantation

4. Conclusions
Due to the industry needs especially in jewelry industry, we made 3 gold-based alloys - Au0.1Li, Au0.1Be and Au0.1B in a medium frequency vacuum induction furnace. After testing the three samples by BUEHLER Hardness Tester we chose the hardest sample 2 to do deeper investigations. Optical Microscope, SEM, XRD, TEM, Work Hardening, Supercooling testing, Heat Treatment and Nitrogen Ion Implantation testing were applied to investigate the microstructure and mechanical properties of the sample 2 systematically. The conclusions are as follows:

(1) The Vickers Hardness of three samples from sample 1 to 3 (Au0.1Li, Au0.1Be and Au0.1B) is as follows: 63, 69 and 58 which state clearly that the sample 2 is the highest one and Be is the most effective. Gold hardness as cast can be improved from 30HV to 69HV by additions of 1.0 wt.% Be, which is the highest hardness by 0.1 wt.% additions in gold being reported.

(2) 0.1 wt.% Be additions can refine gold grain sizes substantially. The main size range is between 6μm and 30μm. There are two phases in the sample 2, one is FCC solid solution, the other is intermetallic compound Au6Be which distribute along the dendrite crystal boundaries. Grain size reduction is the main reason that leads to the hardness improvement.

(3) Work hardening is a very effective method that can improve hardness of the sample 2 from 69HV to 112HV when the reduction in area rate is 60%. Supercooling, Heat Treatment and Nitrogen Ion Implantation can not improve the hardness of the sample 2, on the contrary, they decrease the hardness of the sample 2 from 69HV to 33HV, 35HV and 38HV, respectively. Grain size growths are the main factors which lead to the decrease of the sample 2.

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