Mechanical Properties and Thermal Stability of Nanocrystalline Gold Prepared by Gas Deposition Method[†]

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Specimens of nanocrystalline Au with various grain sizes were prepared by the gas deposition method. Results of measurements of (1) Young's modulus by the nanoindentation method, (2) anelasticity, (3) grain size by SEM, STM and X-ray diffraction, (4) Vickers microhardness and (5) elastic limit by bending tests at R.T. and 77 K, and their behaviors during annealing were described. High mechanical strength almost as high as whiskers was found in as-deposited state. Thermal stabilities of the grain size and mechanical strength were found to be higher for specimens with smaller initial grain size. For the specimens with grain size ~ 7 nm, no grain growth was observed up to annealing for 1 h at 770 K and a growth to twice of the initial size, even after 1070 K. Possible origins of this remarkable thermal stability were discussed.

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I. Introduction

Nanocrystals are polycrystals with grain sizes of around 5 to 100 nm. Because of a high density of grain boundaries, characteristic properties of atoms in boundaries which may be different from those of atoms in crystals or amorphous materials would be revealed in nanocrystals. Further the strain field in boundary core regions may extend into the crystallites in both sides and may change their properties. Dislocations and other defects may also change their properties in the small crystallites⁽¹⁾. Therefore with an expectation of finding new properties, nanocrystalline (hereafter, n-) materials draw an intensive attention. In order to extract essential property of nanostructures, here, we shall focus on n-pure metals.

There are various methods to prepare n-pure metals, e.g.: inert gas condensation and compaction method, gas deposition method (GDM), electro-deposition method, ball-milling and ultra heavy deformation. So far, most works have been made on these materials produced by the inert gas condensation and compaction method mainly by the groups in Germany and USA. In these works it can be found that n-pure metals have almost 5 times larger values than ordinary polycrystals (annealed) in hardness and yield stress⁽²⁾. They are, however, thermally very unstable⁽¹⁾, e.g., in high density n-pure metals (n-Cu, Pd and Ag⁽³⁾; n-Cu and Pd⁽⁴⁾), grain growth was reported to occur even at or near room temperature. However, it should also be noted that small fraction of crystals is often observed to remain stable up to near the melting temperatures⁽¹⁾. Similar observations of a high strength and a low thermal stability were made also in n-specimens prepared by the electro-deposition method⁽⁵⁾.

In contrast to this, n-Au prepared by GDM was found

Fig. 1 Schematic drawing of the apparatus for the gas deposition method.

to show a high strength and on certain conditions a high thermal stability as will be described below. GDM is a product of Hayashi Ultra-Fine Particle Project (1981–1986), one of research projects of the Exploratory Research for Advanced Technology in Japan⁽⁶⁾. A schematic drawing of the apparatus we are using now for GDM, is shown in Fig. 1. Briefly, in the evaporation chamber, melt of Au (99.999% pure) is evaporated in ~ 0.1 MPa He gas to obtain nano-sized particles. These particles are transferred by a pressure difference through a fine pipe into the deposition chamber with ~ 0.1 kPa He gas and deposited onto a glass substrate. The impinging speed of particles on the substrate is near a sound velocity. The merit of this method is that it requires no compaction process in contrast to the compaction method and any figures on the substrate can be drawn by moving the substrate. Specimen sizes obtained are typically $\sim 15 \mu\text{m} \times 1 \text{ mm} \times 30 \text{ mm}$ with various grain sizes.

II. Mechanical Properties

1. Young's modulus

Young's modulus E was measured by the nanoindentation method⁽⁷⁾ on n-Au specimens whose grain size D was estimated as ~ 10 nm and porosity, as $\sim 26\%$.

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Young's modulus of these specimens E^* was roughly 70% of that of coarse grained Au, $E(\text{Au})=79$ GPa. Among possible origins of decrease in E : (a) low E of grain boundary region, (b) dislocations in grains and (c) pores (in grain boundaries), contribution of (a) is now known to be negligible. As for (b), one mobile dislocation line in each grain can reduce E by more than 14%. However the above value of E^* is in a reasonable range expected from 26% porosity⁽⁸⁾. Therefore (c) may be considered to be dominant here, with minor contribution of (b).

2. Anelasticity

Figure 2 shows the internal friction Q^{-1} and resonant frequency f of n-Au specimen ($D \approx 30$ nm, and probable porosity $\approx 20\text{--}50\%$)⁽⁹⁾. A small peak in Q^{-1} at 120 K is the Bordoni peak which indicates an existence of some dislocation lines in crystallites. The peaks at 460, 550 and 750 K can be explained as the peaks associated with the motion of dislocations in or around unstable boundary regions, boundary sliding without impurities and that with impurities, respectively. From consideration of the above effect of pores on E (see II-1) and the observation of little effect of irradiation on E ⁽¹⁰⁾, a pronounced recovery of the modulus defects during warm up in 450–800 K (Fig. 2(a)) is probably due mainly to round off or reduction of pores.

3. Hardness

Vickers microhardness of n-Au was found to be $H_v \approx 1\text{--}2$ GPa⁽¹¹⁾⁽¹²⁾. From a general relation between hardness H_v and yield stress σ_y , $\sigma_y \approx H_v/3$, we can estimate $\sigma_y \approx 0.3\text{--}0.7$ GPa.

4. Elastic limit

Deformation behavior of n-Au specimens was studied by bending under an optical microscope equipped with video-camera⁽¹³⁾⁽¹⁴⁾. The specimen was bent by applying a load on the free end with the other end being clamped by a rigid holder. The displacement of the free end δ_m was increased stepwise and kept for 2–3 s before unloading at each step. After each unloading, a residual displacement δ_r was measured. From them, we could estimate the surface residual (or permanent) strain ε_r for each given max. surface strain ε_m . The value of ε_m at which ε_r starts to deviate from zero gives the yield strain (or elastic limit) ε_y . Deformation of the specimen is completely elastic when $\varepsilon_m < \varepsilon_y$. The experiments were conducted at R.T. and in liquid nitrogen (at 77 K), with the results shown in Figs. 3 and 4⁽¹⁴⁾. Figure 3 shows that ε_y decreases with decreasing grain size. It is noted that ε_y is often very sensitive to the preparation conditions of specimens. There are many stress intensifiers such as pores and other flaws in n-Au specimens which should reduce the strength. Therefore it might be argued that ε_y decreased with decreasing grain size because there might have been more these defects in the specimens of smaller grain size. However, since ε_y becomes very large at 77 K (Fig. 4) and decreases with increasing holding time at

Fig. 2 (a) Resonant frequency f and (b) internal friction Q^{-1} vs. temperature observed for a n-Au specimen with grain size ~ 30 nm. Each curve was obtained after heating to successively higher temperatures in numerical order as indicated in the figure. The heating rate is 1 K/min⁽⁹⁾.

Fig. 3

Fig. 4

Fig. 3 Max. surface strain vs. surface residual strain observed in bending test at R.T. for n-Au specimens with various grain sizes⁽¹⁴⁾.

Fig. 4 Max. surface strain vs. surface residual strain observed in bending tests at R.T. and 77 K for n-Au specimens with surfaces mechanically polished by diamond paste⁽¹⁴⁾.

R.T.⁽¹⁵⁾, grain boundary sliding (which is a thermally activated process) is considered to be a major reason for this decrease in ε_y with the decrease in grain size. An example of surface appearances observed by STM is shown in Fig. 5, for a specimen as deposited with $D \approx 12$ nm. No apparent difference except grain sizes was seen for other specimens.

Now, $\varepsilon_y \approx 1\text{--}2\%$ means $\sigma_y \approx E^*/(50\text{--}100)$, then the above value for $E^* \approx 55$ GPa gives $\sigma_y \approx 0.5\text{--}1$ GPa. This is in reasonable agreement with that estimated from hardness (II-3). This remarkable strength of n-Au indicates that grains have no dislocation which can contribute to plastic deformation, and also grain boundaries are very strong. A little smaller σ_y was observed in tensile test of n-Au specimens with $E^*/E(\text{Au}) \approx 90\%$ ⁽¹⁶⁾.

III. Thermal Stability

1. Grain growth during annealing

Specimens of n-Au with various initial grain sizes were prepared by GDM and their grain sizes were measured by STM⁽¹⁷⁾ and X-ray diffraction method⁽¹⁸⁾. The results are shown in Fig. 6⁽¹⁷⁾. Specimens A, B and C were annealed in air and examined by STM. Specimen D was annealed in vacuum and examined both by STM and by X-ray, but in the figure, only the results of X-ray diffraction are

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 5 Surface observed by STM for a specimen of grain size ~ 12 nm. (Scales in nm).

Fig. 6 Grain size vs. annealing temperature for n-Au with various as-deposited grain sizes. Data of Specimens A, B and C were obtained from STM observations, and data of Specimen D were from X-ray diffraction. Vertical lines show very roughly the range of the size observed⁽¹⁷⁾.

Fig. 7 Hardness, grain size and density vs. annealing temperature for n-Au specimen with grain size ~ 20 nm, density $\sim 51\%$. Annealing was made in vacuum of 10^{-4} Pa for 1 min. Heating rate to each annealing temperature (HR) is given in K/min. Specimens 1, 2 and 3, 4 were taken from two different lots, respectively. Results on an ordinary coarse grained Au is shown together for comparison⁽¹²⁾.

Fig. 8 Max. surface strain vs. surface residual strain observed in bending test at R.T. for n-Au specimen annealed at various temperatures indicated⁽¹⁵⁾.

shown because the results of STM and X-ray are almost the same. It is known that no effect of annealing atmosphere on the grain size could be found⁽¹⁸⁾. The figure shows that the larger is the initial grain size (as deposited), the lower is the thermal stability. It is noteworthy that the n-Au specimens with grain size of about 10 nm show no grain growth up to annealing at 770 K for 1 h and a growth to twice of its original size even after 1070 K annealing. By the way, no measurement on porosity was made on these specimens, however, porosity of a specimen prepared similarly as Specimen D was roughly 26%.

2. Thermal stability of hardness⁽¹¹⁾⁽¹²⁾

H_v vs. annealing temperature for n-Au specimens with $D \approx 20$ nm and porosity 49% is shown in Fig. 7. Generally speaking, a high value of H_v and a small grain size were kept up to annealing of ~ 900 K for 1 min, *i.e.* quite stable (the grain sizes were measured here by SEM). Gradual increase in H_v during annealing was probably caused by an increase in E^* due to a decrease in porosity (see II-1) as seen in the above figure. H_v of the specimens with $D \approx 10$ nm and porosity 24% showed a similar behavior. On the other hand, for the specimen with $D \approx 60$ nm and porosity 19%, H_v decreased in the annealing temperatures 600–700 K for 1 min, *i.e.* less stable⁽¹²⁾. The thermal stability of H_v is very similar as in the case of grain size (see III-1), *i.e.* less stable for the larger initial grain size. (On this point, the conclusion of Ref. (12) must be revised.)

3. Thermal stability of elastic limit (or yield stress)

Bending tests as described in the Section II-4 were made on n-Au specimens with initial grain sizes of 7 and 17 nm, and after various annealings⁽¹⁵⁾. In the present case, the bending load was held for ~ 1 s before un-

loading at each step. Annealings were carried out in vacuum of $\sim 10^{-4}$ Pa at various temperatures with interval of 100 K up to 1153 K for 1 h. The heating rate was 100 K/h.

An example of the results on the specimen with $D \approx 7$ nm (tested at R.T.) is shown in Fig. 8. (The result on an ordinary coarse-grained specimen is shown together for comparison.) For this specimen, as deposited and after annealings up to 873 K, deformation was almost completely elastic up to $\epsilon_m \approx 0.6\%$ and even after annealing at 973 K ($0.73 T_m$) was completely elastic up to $\epsilon_m \approx 0.4\%$. In order to show the annealing stage more clearly, in Fig. 9(a), the largest ϵ_m for $\epsilon_r = 0$ (lower curve) and the smallest ϵ_m for $\epsilon_r > 0$ (upper curve) were plotted against annealing temperature. Then yield strain ϵ_y should be in between the two curves. The results for the bending tests at 77 K are shown in Fig. 9(b). In the figures a recovery stage of ϵ_y was clearly seen at around 900–1100 K and appears independent of the test temperature. This recovery stage just coincides with the temperature range where the grain growth starts to occur (see Fig. 6). Similar results on the specimen with $D \approx 17$ nm were observed, but in this case ϵ_y recovery at around 700–800 K, again roughly in coincidence with the grain growth.

It is now clear that in general, ϵ_y after annealings decreases with increasing grain size for both in R.T. tests and in 77 K tests. On the other hand, ϵ_y for the as-deposited specimens appears to increase with an increase in D at least for R.T. tests (see Fig. 3) (for 77 K tests, it is not clear but seems not much different). As for the value of ϵ_y , for example, for the specimen with initial $D \approx 7$ nm, after 1073 K annealing, expected values of D and ϵ_y became roughly 17 nm (see Fig. 6) and 0.2–0.4% (at R.T.) or 0.2–0.4% (at 77 K) (see Fig. 9), respectively. In contrast, for the as-deposited specimen of $D \approx 17$ nm, ϵ_y was 1.0–1.2% (at R.T.) or above 1.2% (at

Fig. 9 (a) Yield strain vs. annealing temperature observed in bending tests at R.T. for n-Au with as-deposited grain size ~ 7 nm. See text for a detail. (b) Similar as (a) but in bending tests at 77 K.

77 K). Since these values seem rather sensitive to preparation conditions which are not well controlled at the present moment, further work should be required to clarify the reason for this discrepancy between two types of specimens, *i.e.*, as-deposited and annealed. This discrepancy seems, however, to indicate a change in the deformation mode in the two types of specimens. It might be possible that in the annealed specimens, some abnormally grown grains now contain dislocations which can contribute to plastic deformation.

Now, a high thermal stability of n-Au prepared by GDM was verified for grain growth and mechanical properties such as hardness and yield strain, when the grain size is below ~ 10 nm.

IV. Origin of High Thermal Stability

In GDM, nano-sized particles with a very high speed are deposited on a substrate and no compaction process is involved during specimen preparation. Even in these specimens, highly stressed regions, *e.g.*, around an indent of Vickers test is found to be very unstable⁽¹¹⁾. On the other hand, specimens prepared by the compaction method are heavily deformed during preparation. Therefore, at first sight, the high thermal stability of specimens prepared by GDM would be caused by the low internal strains. This idea was found improbable because the internal strains appeared to be even a little higher in the specimens prepared by GDM⁽¹⁹⁾.

In principle, the growth rate of grains may be described by (mobility of the grain boundary) $\times$ (driving force). The mobility is controlled by diffusion process and numerous experiments show that it cannot ordinarily be a retarding factor for grain growth in the present high temperatures. However, the driving force may become very small, if a mechanical equilibrium is established. For the 2-dimensional case, regular hexagonal grains can attain mechanical balance between the grain boundary tensions. It is, however, well known that achievement of mechanical equilibrium is not possible within a 3-dimensional arrangement of identical grains (Kelvin tetrakaidecahedron). Large pores on grain junctions (3 and 4 grains) would somewhat relieve this difficulty and work as pinning points. Then for the high thermal stability, a distribution in grain size must be narrow enough

and specimens should contain pores in grain junctions. In such a case, grain growth would be controlled by the shrinkage of pores which may be hindered by He atoms inside the pores and this would be a process to occur at quite a high temperature. In the compaction method, pores contain no He atom. But only He atoms in pores are not enough to attain the high stability observed here. It is of practical importance that in the present method we can obtain the high thermal stability with a little loss of mechanical strength.

V. Conclusions

Specimens of n-Au with various grain sizes were prepared by GDM. Their mechanical properties (Young's modulus, anelasticity, hardness and elastic limit) and grain size, and their annealing behaviors were studied. High mechanical strength almost as high as whiskers was found in as-deposited state. For the specimens with grain size ~ 7 nm, thermal stabilities of the grain size and mechanical strength were found to be remarkably high compared to those prepared by the compaction method. The high thermal stability is considered to be associated with a mechanical equilibrium among the boundary tensions, probably attained by a narrow size distribution and many pores in boundaries containing He atoms.

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